

Multiscale Computational Investigation of the Dielectric Response of Radio-Oxidized Polyethylene

Étude de la réponse diélectrique du polyéthylène par simulations multi-échelle

Thèse de doctorat de l'Université Paris-Saclay

École doctorale n° 564 – Physique en Île-de-France (EDPIF)

Spécialité de doctorat : Physique

Graduate School : Physique. Référent : Faculté des Sciences d'Orsay

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Titre : Étude de la réponse diélectrique du polyéthylène par simulations multi-échelle

Mots clés : polyéthylène; radio-oxydation; réponse diélectrique; théorie de la fonctionnelle de la densité; dynamique moléculaire; isolation nucléaire

Résumé : Le polyéthylène (PE) est un matériau isolant majeur utilisé dans de nombreuses applications, notamment l'isolation des câbles dans les centrales nucléaires, où la radio-oxydation peut modifier ses propriétés diélectriques. Prédire la réponse diélectrique des polymères reste difficile, car des mécanismes électroniques, vibrationnels et dynamiques mésoscopiques agissent à différentes échelles spatiales et temporelles, même à température ambiante. Cette thèse construit des modèles de PE semi-cristallin afin d'étudier, à l'échelle atomique, l'effet des défauts de radio-oxydation sur la réponse diélectrique. L'approche combine des simulations quantiques, pour décrire la réponse électronique et la contribution vibrationnelle, avec la dynamique moléculaire classique, pour suivre les chaînes polymères à tem-

pérature ambiante jusqu'au domaine du GHz. Les calculs quantiques en réponse linéaire relient ces contributions à l'environnement atomique local des défauts. Leur comparaison avec la dynamique moléculaire met en évidence le rôle de la température et du mouvement des chaînes dans la constante diélectrique statique, tandis que l'analyse structurale estime l'effet de chaque défaut sur la cristallinité. Enfin, l'analyse de la fonction de corrélation dipolaire montre que les défauts se couplent différemment entre eux et avec la matrice de PE, augmentant la permittivité et induisant des pics de pertes diélectriques dépendant du défaut. Ainsi, la réponse diélectrique du PE radio-oxydé ne se déduit pas de la seule polarité des défauts, mais résulte de la chimie locale, de la cristallinité et de la dynamique moléculaire.

Title: Multiscale Computational Investigation of the Dielectric Response of Radio-Oxidized Polyethylene

Keywords: polyethylene; radio-oxidation; dielectric response; density functional theory; molecular dynamics; nuclear insulation

Abstract: Polyethylene (PE) is a major insulating material used in many applications, including cable insulation in nuclear power plants, where radio-oxidation can modify its dielectric properties. Predicting the dielectric response of polymers remains challenging because electronic, vibrational, and mesoscale dynamical mechanisms act across different spatial and temporal scales, even at room temperature. This thesis builds semicrystalline PE models to investigate, at the atomistic scale, how radio-oxidation defects affect the dielectric response. The approach combines quantum-level simulations, which describe the electronic response and vibrational contribution, with classical molecular dynamics, which captures polymer-chain dynamics at room temperature

down to the GHz domain. Linear-response quantum calculations relate these contributions to the local atomic environment of the defects. Their comparison with molecular dynamics highlights the role of temperature and chain motion in the static dielectric constant, while structural analysis estimates how each defect affects crystallinity. Finally, analysis of the dipolar correlation function shows that defects couple differently with one another and with the PE matrix, increasing the permittivity and inducing dielectric-loss peaks that depend on defect type. Thus, the dielectric response of radio-oxidized PE cannot be inferred from defect polarity alone; it emerges from local chemistry, crystallinity, and molecular dynamics.

Acknowledgements

Looking back, the path that led to this thesis began during my master's degree at SRM University in India, where I first developed a genuine passion for science and research. My master's project, devoted to a peptide-based biosensor for the detection of biomolecules, gave me my first experience of carrying out an extended research project. I am especially grateful to my master's project supervisor, Dr V. J. Surya, who introduced me to first-principles calculations. Her patient guidance, encouragement, and genuine care played an important role in shaping my interest in computational research. I would also like to thank my friends Sreeram Jayan, Rence P. Reji, and Darin Joseph for their friendship, encouragement, and help throughout my master's studies.

Moving to France was a major step in my life, both personally and professionally. Adapting to a new country and environment would have been much more difficult without the kindness of the people around me. I am particularly grateful to my lab-mate Jasurbek, who helped me settle in France and supported me during those important first months. I also warmly thank Thejus Pius, Luisa, and my other friends for their companionship, practical help, and the sense of familiarity and community they brought to my life in France.

My deepest gratitude goes to Guido Roma, director of this thesis at the CEA. I am sincerely thankful for his understanding, availability, guidance, and constant support throughout this doctoral work. The methods, software, and scientific questions I encountered during the PhD were very different from those of my master's project. Guido helped me become familiar with these new computational techniques, encouraged me to work independently, and guided me through each stage of the research. His patience and confidence made it possible for me to grow both as a researcher and as a person. I am equally grateful to Xavier Colin, co-director of this thesis, for his valuable guidance, careful feedback, and scientific perspective. I would like to express my sincere thanks to all the members of the SRMP team for welcoming me and for creating a stimulating and supportive working environment. I thank the other students in the lab (Elisa, Nicolas, Thomas, Adrien, Antoine, Omou, Rohit, Brice) for the scientific discussions, technical assistance, and everyday moments shared with colleagues during these years. I also thank Jean-Luc Béchade and Clara Desgranges, who led the laboratory during my time there, for their support and for providing the conditions in which this research could be carried out. I am honored that Petru Notingher, Claire Loison, Claire Lemarchand, Cindy Rountree, and Davide Fabiani agreed to serve on my thesis jury. I sincerely thank them for the time devoted to reading and evaluating this work, for sharing their expertise, and for participating in my defense.

Finally, my warmest thanks go to my parents, Rosily and Shaju, whose love, sacrifices, and unwavering belief in me have supported every stage of my journey. I also thank my dear friends Arunima, Eby, Jelwin, and Danya, as well as all those who encouraged me from near and far. Their patience, confidence, friendship, and support carried me through the difficult moments and made the completion of this thesis possible. To everyone who has been part of this journey, in ways both large and small, I offer my heartfelt gratitude.

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Résumé étendu en français

Le polyéthylène (PE) est largement employé comme isolant électrique en raison de sa faible permittivité, de ses faibles pertes diélectriques, de sa bonne tenue mécanique et de sa facilité de mise en œuvre. Sous forme réticulée, il constitue notamment l'isolation de nombreux câbles d'instrumentation, de contrôle et de puissance dans les centrales nucléaires. Ces câbles doivent conserver leur fonction pendant plusieurs décennies, y compris après un vieillissement prolongé et lors de situations accidentelles. Ils sont pourtant soumis, à des degrés variables, à la température, au rayonnement ionisant, à l'oxygène et aux contraintes mécaniques. Leur remplacement étant difficile et coûteux, comprendre et prévoir l'évolution de leurs propriétés est un enjeu important pour la sûreté et la prolongation de la durée d'exploitation des installations [1-3].

L'une des conséquences majeures de ce vieillissement est la radio-thermo-oxydation. L'irradiation ou l'activation thermique crée des macroradicaux sur la chaîne de PE. En présence d'oxygène, ceux-ci alimentent une succession de réactions produisant notamment des groupes alcool, aldéhyde, cétone, ester, acide carboxylique, ainsi que des insaturations de type vinyène ou énone. Ces modifications peuvent s'accompagner de coupures de chaîne, de réticulation et de chimicristallisation. Sur le plan électrique, elles introduisent des liaisons polaires dans une matrice initialement presque apolaire et modifient à la fois la permittivité et les pertes. Des expériences menées sur des PE irradiés ou thermiquement oxydés montrent effectivement une augmentation de la permittivité et de la dissipation diélectrique corrélée à la formation de produits d'oxydation [4-6]. Cependant, une mesure macroscopique ne permet pas d'attribuer cette évolution à une espèce chimique donnée ni de séparer les mécanismes microscopiques qui la produisent.

La difficulté vient aussi de la nature semi-cristalline du PE. Le matériau réel associe des lamelles cristallines, des zones amorphes et des interfaces où le compactage, l'orientation des chaînes et la mobilité moléculaire diffèrent. L'oxygène diffuse principalement dans les zones les moins denses, de sorte que les défauts ne sont ni distribués uniformément ni placés dans des environnements équivalents [7]. Une même fonction chimique peut donc avoir une réponse différente selon sa position, son orientation et son voisinage. En outre, la permittivité observée résulte de mécanismes agissant sur des échelles de temps distinctes : déplacement du nuage électronique, vibrations ioniques et réorientation de dipôles permanents. Une description uniquement fondée sur le moment dipolaire isolé d'un groupe fonctionnel ne suffit donc pas.

L'objectif de cette thèse est de relier, à l'échelle atomique, la nature des produits de radio-oxydation, la morphologie semi-cristalline et les différentes composantes de la réponse diélectrique. L'approche adoptée est multi-échelle. Les contributions électronique et ionique sont calculées par théorie de la fonctionnelle de la densité (DFT) et théorie de la perturbation de la fonctionnelle de la densité (DFPT), tandis que la contribution orientable et sa dynamique sont obtenues par dynamique moléculaire classique. Cette combinaison permet d'analyser successivement la polarisation intrinsèque du solide, sa distribution spatiale et les fluctuations collectives des dipôles sur des trajectoires de plusieurs dizaines à centaines de nanosecondes.

Le modèle quantique principal est une cellule lamellaire semi-cristalline de 151 atomes et de densité moyenne $0,88 \text{ g cm}^{-3}$, issue d'un modèle précédemment développé pour représenter explicitement les régions cristalline, interfaciale et amorphe [8]. Sept défauts sont étudiés séparément à 2 et 4 mol % : alcool, aldéhyde, acide carboxylique, énone, ester, cétone et vinyène. Les calculs sont réalisés avec *Quantum Espresso* [9]. La DFPT fournit la permittivité électronique ε_∞ , les charges effectives de Born, les modes vibrationnels actifs en infrarouge et la permittivité statique harmonique ε_0 [10]. Des champs électriques finis de signes opposés sont également appliqués selon la normale aux lamelles afin de reconstruire un profil local $\varepsilon(z)$ à partir de la densité de charge induite et de la polarisation macroscopiquement moyennée [11, 12].

Dans cette notation, ε_∞ représente la réponse rapide des électrons à noyaux fixes, tandis que $\varepsilon_0 - \varepsilon_\infty$ mesure la polarisation ionique obtenue dans l'approximation harmonique. Cette dernière décrit les déplacements collectifs autour d'un minimum d'énergie, mais non la rotation lente et anhar-

monique des dipôles permanents à température finie. La dynamique moléculaire vise précisément ce troisième mécanisme. Les deux approches ne sont donc pas redondantes : elles séparent des fenêtres de fréquence et des phénomènes physiques différents. Pour construire les estimations statiques issues de la dynamique, l'incrément orientable est ajouté à ε_∞ ; la contribution vibrationnelle quantique n'est pas ajoutée une seconde fois.

La première étape consiste à quantifier l'effet de la morphologie du PE vierge. Le cristal idéal donne $\varepsilon_\infty = 2,70$ et $\varepsilon_0 = 2,73$, avec une anisotropie associée à l'alignement des chaînes. Le modèle amorphe donne respectivement 2,38 et 2,44 et devient presque isotrope. Le modèle lamellaire semi-cristallin conduit à 2,23 et 2,26, avec une anisotropie d'environ 1 % seulement. Sa valeur statique est proche des valeurs expérimentales publiées pour le PE, ce qui justifie son emploi comme référence. Cette comparaison montre surtout qu'une structure entièrement cristalline surestime la réponse d'un matériau réel et que la morphologie doit être explicitement prise en compte avant d'évaluer l'effet chimique des défauts.

Dans les cellules oxydées, ε_∞ reste comprise dans une plage étroite, approximativement entre 2,20 et 2,26. L'ajout d'oxygène ne provoque donc pas nécessairement une forte augmentation de la polarisation électronique : le signe de la faible variation dépend du groupe chimique et de son environnement. La contribution ionique est beaucoup plus discriminante. À 4 mol %, l'aldéhyde présente la plus grande permittivité statique harmonique, $\varepsilon_0 = 2,431$, suivi de l'alcool (2,414), de l'acide carboxylique (2,381), de l'énone (2,377), de la cétone (2,374), de l'ester (2,330) et du vinylène (2,270), contre 2,258 pour le PE vierge. L'incrément ionique atteint 0,228 pour l'aldéhyde, alors qu'il n'est que de 0,034 pour le vinylène.

Les charges effectives de Born confirment la forte polarité dynamique des liaisons contenant de l'oxygène, en particulier des carbonyles, mais leur module ne suffit pas à prédire la permittivité. Une contribution importante apparaît seulement si ces charges dynamiques se couplent à des modes collectifs actifs en infrarouge, de basse fréquence et de géométrie appropriée. L'aldéhyde illustre ce mécanisme : sans posséder systématiquement la charge de Born la plus élevée, il concentre une part importante du poids diélectrique dans les modes inférieurs à $100\text{--}200\text{ cm}^{-1}$. À l'inverse, malgré la forte polarité de sa liaison carbonyle, l'ester produit une contribution ionique plus faible à la permittivité. Le classement des défauts ne peut donc pas être déduit d'un unique descripteur local ; il résulte du couplage entre chimie, vibrations et structure hôte.

Les calculs positionnels renforcent cette conclusion. Du cœur cristallin à la région amorphe, la dispersion de ε_∞ reste très faible pour les sept familles (0,006–0,018), confirmant que la réponse électronique moyenne dépend surtout de la chimie locale. En revanche, ε_0 varie davantage avec le compactage et le spectre vibrationnel. La position qui la maximise dépend du défaut : l'aldéhyde et la cétone atteignent leurs valeurs les plus élevées dans certaines configurations cristallines, tandis que l'acide carboxylique, l'énone et l'ester sont renforcés dans des environnements interfaciaux ou amorphes. La morphologie agit donc par des modifications propres à chaque défaut plutôt que selon une tendance unique du cristal vers l'amorphe. Le vinylène demeure presque insensible à la position.

Le profil $\varepsilon(z)$ apporte une information inaccessible à partir de la seule moyenne de cellule. L'énone et le vinylène produisent des déplacements positifs lorsque leur liaison insaturée se projette efficacement selon le champ. L'aldéhyde et l'acide carboxylique génèrent plutôt des lobes locaux positifs et négatifs dont la compensation réduit la variation moyenne malgré une forte perturbation microscopique. Deux effets structuraux sont ainsi séparés : à chimie fixée, la projection de la liaison polaire ou insaturée détermine principalement l'amplitude et la forme de la réponse locale ; la position dans la lamelle détermine ensuite si ses parties positives et négatives se renforcent ou se compensent dans la moyenne interne. Deux configurations de permittivité moyenne voisine peuvent donc présenter des paysages diélectriques locaux très différents.

La procédure est d'abord vérifiée sur une chaîne finie de PE entourée de vide : les densités induites s'annulent dans la région vide, où $\varepsilon(z)$ revient à 1, tandis que $\varepsilon(z)$ converge vers une valeur quasi constante dans la région polymère. L'application aux lamelles pliées montre ensuite que cette

valeur moyenne signée et l'amplitude quadratique de la perturbation locale répondent à des questions distinctes. Une faible variation moyenne peut correspondre soit à un défaut peu actif, soit à une forte redistribution dont les contributions se compensent. Cette distinction est pertinente pour le vieillissement électrique, car une hétérogénéité locale peut influencer le champ microscopique ou le piégeage des charges sans modifier fortement la permittivité moyenne mesurée.

La dynamique moléculaire complète cette description statique en donnant accès à la polarisation orientable. Les systèmes contiennent chacun 2000 unités méthylène et des défauts alcool, aldéhyde, ester ou cétone introduits séparément à 2 et 4 mol %. Ils sont construits avec *Moltemplate*, décrits par le champ de force tout-atome OPLS et simulés avec *LAMMPS* [13-15]. Après fusion à 600 K, refroidissement, relaxation et production, les fluctuations du moment dipolaire total fournissent l'incrément orientable $\Delta\epsilon$ selon la relation de Neumann [16]. L'autocorrélation dipolaire, ses ajustements de Kohlrausch-Williams-Watts et sa transformation fréquentielle donnent en parallèle les temps de relaxation et les spectres de pertes.

Les analyses utilisent des fenêtres temporelles appariées de 100 ns afin de comparer les 24 états de température, de chimie et de concentration sur une base identique. Les composantes cartésiennes permettent de contrôler l'anisotropie résiduelle, et une analyse par blocs fournit l'erreur statistique sur $\Delta\epsilon$. Le moment total est également séparé entre atomes appartenant aux fonctions oxydées et atomes de la matrice. Cette partition donne trois termes exactement additifs : l'auto-corrélation des défauts, celle de la matrice et leur covariance croisée. Elle offre un diagnostic plus riche que la seule valeur de permittivité, car elle indique si la matrice suit le mouvement des groupes polaires ou s'y oppose.

À 300 K, la cétone possède la contribution orientable la plus élevée : $\Delta\epsilon = 0,323$ à 2 mol % et 0,883 à 4 mol %. Elle est suivie par l'aldéhyde (0,286 et 0,570), l'ester (0,119 et 0,217), puis l'alcool (0,108 et 0,130). En ajoutant la contribution électronique issue de la DFPT, les permittivités statiques estimées à 4 mol % sont respectivement 3,126, 2,773, 2,416 et 2,387. Le rapport entre la réponse orientable de la cétone et celle de l'alcool atteint environ 6,8. L'effet de la concentration est presque linéaire pour l'aldéhyde, superlinéaire pour la cétone et sous-linéaire pour l'alcool. Le taux de cristallinité mesuré dans les cellules ne reproduit pas ce classement, ce qui exclut une interprétation fondée sur la seule morphologie globale.

La décomposition des fluctuations explique une partie de ces différences. La contribution propre des défauts fixe l'échelle principale, mais la covariance entre les dipôles des défauts et ceux de la matrice peut amplifier ou réduire la réponse. À 4 mol %, le terme croisé représente environ +20 % pour la cétone, +14 % pour l'ester, +9 % pour l'aldéhyde et -7 % pour l'alcool. La cétone combine donc de fortes fluctuations propres et un couplage collectif constructif avec son environnement. Dans l'ester, une anticorrélation interne entre les contributions carbonyle et éther limite la polarisation totale. L'alcool conserve la plus forte fraction de dipôle rémanent et présente une covariance négative avec la matrice, signes d'une réorientation plus contrainte. Un réseau de liaisons hydrogène constitue une explication plausible, mais il n'est pas directement démontré par les cellules et le champ de force employés ; cette interprétation doit donc rester prudente.

Les simulations à 280, 300 et 320 K confirment un résultat robuste : la cétone et l'aldéhyde restent les défauts les plus polarisants, tandis que l'ester et l'alcool donnent des réponses plus faibles ; la cétone produit également le pic de pertes le plus intense dans l'ensemble des états étudiés. En revanche, les positions des pics et les temps de relaxation ne suivent pas une évolution monotone universelle avec la température. Seules deux des huit séries présentent une diminution monotone du temps moyen. Ces résultats dynamiques doivent être considérés comme des tendances comparatives plutôt que comme des prédictions spectroscopiques absolues.

Enfin, une série exploratoire où les défauts sont ajoutés progressivement de 1 à 4 mol % reproduit l'augmentation de la permittivité et le classement général cétone/aldéhyde au-dessus d'ester/alcool. Elle retrouve aussi le signe du couplage défaut-matrice à 4 mol % : environ -15 % pour l'alcool, +8 % pour l'aldéhyde, +17 % pour l'ester et +20 % pour la cétone. Cette concordance montre que le mé-

canisme de couplage est reproductible dans le protocole choisi. Elle ne constitue toutefois ni une simulation du vieillissement chimique réel ni un échantillonnage statistique complet, car une seule séquence d'insertion et une seule trajectoire par chimie ont été considérées.

La comparaison directe des valeurs quantiques et classiques exige de la prudence, car les cellules, la représentation des charges et les échelles temporelles diffèrent. Les deux méthodes évaluent aussi des mécanismes distincts. En DFPT, l'aldéhyde possède la plus forte contribution ionique grâce au couplage de ses charges dynamiques avec des modes vibrationnels de basse fréquence. À 300 K, la dynamique moléculaire attribue la plus forte contribution orientable à la cétone, dont les fluctuations dipolaires et la covariance positive avec la matrice sont plus élevées. Ce contraste montre que la fonction dominante dépend du mécanisme de polarisation et donc de la fréquence et de la température de mesure.

Plus généralement, les modèles représentent un PE chimiquement contrôlé plutôt qu'un câble industriel complet. Ils n'incluent pas simultanément la réticulation, les antioxydants, les charges, l'humidité, les sous-produits mobiles, les gradients d'oxygène ni les mélanges de fonctions créés au cours du vieillissement. Le champ de force classique emploie des charges fixes et la série en température est simulée à volume constant. Il serait donc excessif d'associer une valeur calculée à un âge de câble ou à une dose précise. En revanche, la séparation des mécanismes fournit des hypothèses testables : l'aldéhyde devrait se distinguer par son activité vibrationnelle, la cétone par une forte réponse orientable et de fortes pertes, tandis qu'une population d'alcools peut rester polaire mais peu mobile. La confrontation de ces signatures avec la spectroscopie infrarouge et la spectroscopie diélectrique large bande pourrait améliorer l'interprétation des indicateurs de vieillissement.

Cette thèse établit ainsi qu'il n'existe pas de classement universel des défauts d'oxydation indépendant du mécanisme observé. L'aldéhyde domine la polarisation ionique harmonique, tandis que la cétone domine les fluctuations orientables à température finie. La valeur macroscopique dépend conjointement de la fonction chimique, de sa concentration, de sa position dans la morphologie lamellaire, de son orientation et des corrélations collectives avec la matrice. Cette lecture multi-échelle permet de relier plus rigoureusement les signatures moléculaires de l'oxydation aux mesures diélectriques utilisées pour diagnostiquer les câbles. Les prolongements prioritaires sont l'étude de mélanges réalistes de défauts, un traitement explicite des liaisons hydrogène et de la polarisabilité, des cellules et trajectoires plus grandes, ainsi que le couplage de la réponse diélectrique au piégeage et au transport des charges, puis au claquage électrique.

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1 – Introduction

1.1. Polyethylene: Structure and Morphology

Polyethylene (PE) is the polymer with the simplest chemical structure among polyolefins, composed of repeating $-\text{CH}_2-\text{CH}_2$ methylene units. A single ethylene (C_2H_4) monomer polymerizes to form long chains. Its properties vary depending on chain branching density, molecular weight, and degree of crystallinity. Thus, PE can be produced in several architectures, including high-density polyethylene (HDPE, $\rho \approx 0.94\text{--}0.97 \text{ g cm}^{-3}$), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE, $\rho \approx 0.91\text{--}0.93 \text{ g cm}^{-3}$), ultra-high-molecular-weight polyethylene (UHMWPE), and cross-linked polyethylene (XLPE) [1, 2]. A key feature of polyethylene is that it is semicrystalline in nature [3]. Figure 1.1 illustrates semicrystalline polyethylene across multiple length scales, beginning from bulk morphology and progressing toward molecular crystal structure. A spherulite is the basic superstructure of polyethylene, where a bulk semicrystalline sample larger than 1 mm contains multiple spherulitic domains. Each spherulite is a roughly spherical structure that grows outward from a nucleation point during crystallization and can be 10–50 μm in size. On further magnification to the nanometer scale, the lamellar stack structure consists of alternating crystalline lamellae (10–20 nm) and amorphous layers between them. The crystalline lamellae contain ordered chains that fold back on themselves at upper and lower lamellar surfaces, whereas the amorphous layers contain disordered chain segments with loops, folds, and tie molecules located between adjacent lamellae [4]. At the molecular level, the PE chains are packed with each other in a crystal lattice with periodicity in three dimensions, where the PE crystal structure is arranged in an orthorhombic unit cell. At this level, sp^3 hybridization of carbon atoms dictates the fundamental geometry of the polymer chain. Each sp^3 hybrid orbital possesses 25% s -character and 75% p -character, resulting in a characteristic tetrahedral geometry with bond angles of 109.5° and giving rise to polyethylene's characteristic planar zig-zag conformation when the polymer chain adopts an all-*trans* configuration in the crystalline state [5].

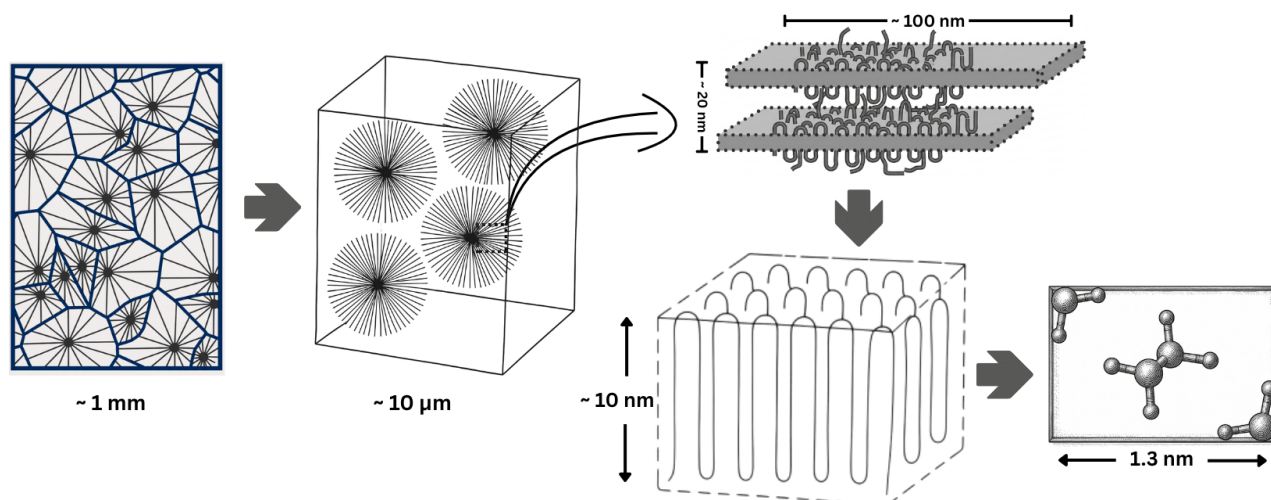


Figure 1.1: Multiscale structural hierarchy of semicrystalline polyethylene. From left to right: bulk spherulitic morphology ($\sim 1 \text{ mm}$), individual spherulite ($\sim 10 \mu\text{m}$), lamellar stack with alternating crystalline and amorphous layers ($\sim 100 \text{ nm}$), a single crystalline lamella showing chain-folded architecture ($\sim 10 \text{ nm}$), and the orthorhombic unit cell of crystalline PE ($\sim 1.3 \text{ nm}$).

1.2. Polyethylene as Cable Insulation in Nuclear Power Plants

Polyethylene is the most widely produced synthetic polymer on the global market because of its large production volume, low cost, and chemical simplicity. The annual PE production exceeds more than 100 million tonnes, accounting for approximately 34% of the total plastics market [6, 7]. The non-polar and semicrystalline nature of PE gives rise to low dielectric loss, with a loss tangent ($\tan \delta$) below 10^{-3} in the appropriate high-frequency measurement range. PE-based materials also offer mechanical resistance, low water absorption, flexibility, and ease of processing, which explains their extensive use as insulation for signal and power cables from low-voltage to high-voltage applications [8]. In nuclear power plants (NPPs), PE-based insulation is used because it must maintain electrical isolation under combined thermal, radiation, and environmental stressors. The cable network in a single NPP can be very large, with a total cable length of approximately 1000–2000 km per plant [9]. Within nuclear power plants, cables are deployed across power transmission, thermocouple, instrumentation and control (I&C) systems. These cables support reactor operations, continuous safety monitoring, automated control, and accident mitigation functions. In power cables, the insulation separates the metallic core from neighboring conductors, shields, jackets, and the ground. The cables must continue to fulfill their intended function despite aging stressors such as temperature, radiation, moisture and vibration. Cross-linked polyethylene (XLPE) is the most commonly used type of PE because of its internal network of covalent bonds, which improves the thermal and mechanical stability. NRC data for U.S. NPP cable insulation show that XLPE and ethylene-propylene rubber (EPR) are the two dominant insulation materials used, with XLPE at about 37%, EPR at about 36%, and PE at only 4% [10]. Figure 1.2 lists the various polymeric insulation materials used in NPP cables.

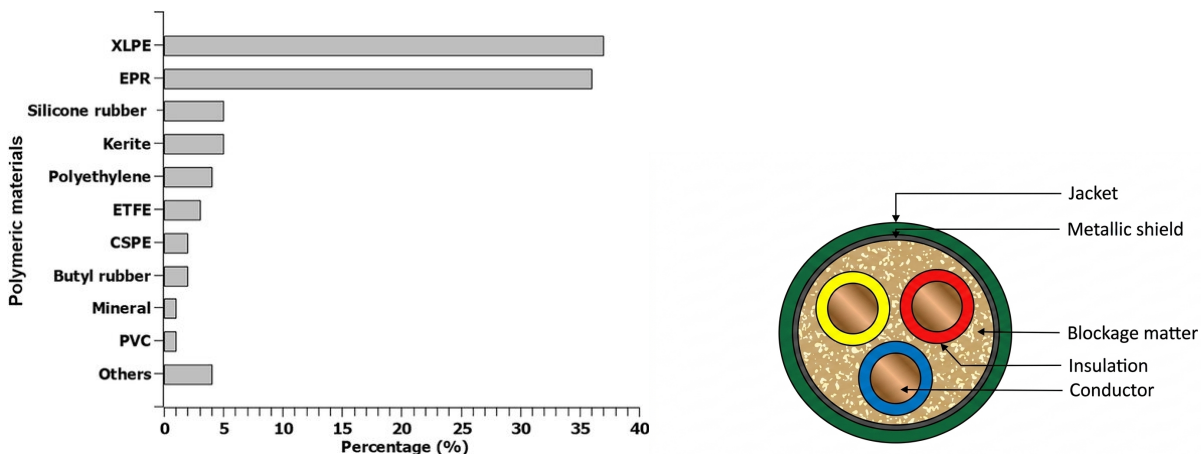


Figure 1.2: (Left) Distribution of polymeric insulation materials used in nuclear power plant cables taken from [11], after the NRC survey of [10]. (Right) Schematic cross-section of a typical multi-core NPP power cable, illustrating the conductor, insulation layer, metallic shield, and outer jacket.

1.3. Aging of Polyethylene under Nuclear Service Conditions

In nuclear power plants, polymeric cable insulation is exposed to ionizing radiation, elevated temperature, and in some installations mechanical stress and chemical contamination [12, 13]. Under these combined stresses, the polymer undergoes a progressive aging process that alters its molecular structure, mechanical properties, and dielectric response. Under typical operating conditions, XLPE cable insulation is exposed to service temperatures on the order of 50°C , with accumulated doses reaching approximately 10^4 Gy over a 40-year service period [9, 14]. In localized hot-spot regions, temperatures can approach 100°C , and gamma dose rates can reach levels between 0.1 and 0.7 Gy h^{-1} [9, 14]. A hot spot held continuously at 0.1 Gy h^{-1} would accumulate about 35 kGy over 40 years, several times the plant-average figure above, so the accumulated dose varies strongly with

location. Furthermore, cables must remain functional during emergency scenarios such as Design-Basis Accidents (DBA) or Loss-of-Coolant Accidents (LOCA). In these scenarios, radiation levels can increase dramatically, exposing the insulation to cumulative doses of several hundred kGy that must be withstood to ensure safety functions. Consequently, safety-related cables must retain their required functions after long-term operational aging and during or after the simulated accident environment. Thus, monitoring aging mechanisms of cables is a critical factor for the life extension and long-term operation of NPPs, since installed cable networks are generally difficult and costly to replace. The original design life of most NPPs was 40 years but the potential lifetime of NPPs can be extended to 60–80 years only if the performance of all components, including cables, can be guaranteed [9].

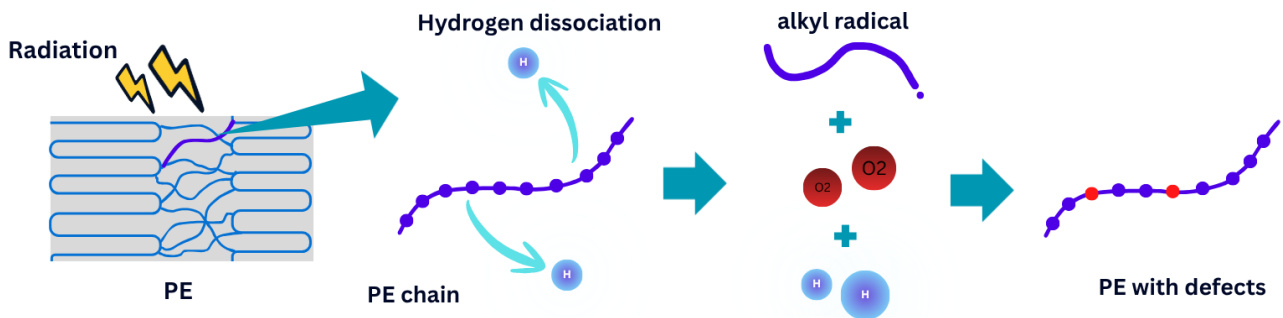


Figure 1.3: Schematic representation of radiation-induced degradation of polyethylene. Ionising radiation causes hydrogen dissociation from the PE backbone, generating alkyl radicals that react with molecular oxygen to form oxygen-containing polar defects along the polymer chain.

Oxidation is the most critical mechanism that causes the aging of PE. The irradiation of PE in the presence of oxygen results in the formation of a series of polar oxygenated functional groups grafted onto the otherwise non-polar polyethylene backbone. In NPP cables, radical formation is mainly caused by ionizing radiation and by thermally activated reactions; mechanical damage, additives, impurities and metallic species from the conductor may further influence the reaction pathway [17, 18]. At the molecular scale, the radio-oxidation of polyethylene is generally described as a radical chain process. As shown in Figure 1.3, ionizing radiation and thermal activation generate alkyl macro-radicals on the PE backbone, mainly through C–H bond cleavage and related excited-state processes. In the presence of oxygen, these alkyl radicals react rapidly with O_2 to form peroxy radicals, which can further abstract hydrogen from neighboring chains to produce hydroperoxides and regenerate new alkyl radicals. The subsequent decomposition of hydroperoxides, together with reactions involving peroxy, alkoxy and hydroxyl radicals, gives rise to the main oxidation defects in PE, including alcohols, ketones, aldehydes, carboxylic acids, esters and peroxide species. These reactions also determine the balance between chain scission and crosslinking, and therefore control the evolution of both the mechanical and dielectric properties of aged PE [17, 19, 20].

The conventional radio-thermo-oxidation degradation mechanism of PE is summarized in Fig. 1.4. The oxidative degradation of PE can be conceptualized in three stages: (1) initiation of alkyl radicals, (2) propagation through the autoxidation cycle, and (3) branching and termination reactions that generate the principal oxidized defect species. Ionizing radiation (gamma rays, electron beams), thermal energy, UV light, or mechanical stress initiates the process by extracting a hydrogen atom from the polymer backbone ($PH \rightarrow P^\bullet + H^\bullet$). These alkyl radicals react spontaneously and without energy barrier with dissolved molecular oxygen to form peroxy radicals ($P^\bullet + O_2 \rightarrow PO_2^\bullet$). From this point, the scheme in Fig. 1.4 branches into two kinetically distinct pathways whose relative importance depends critically on the irradiation dose rate.

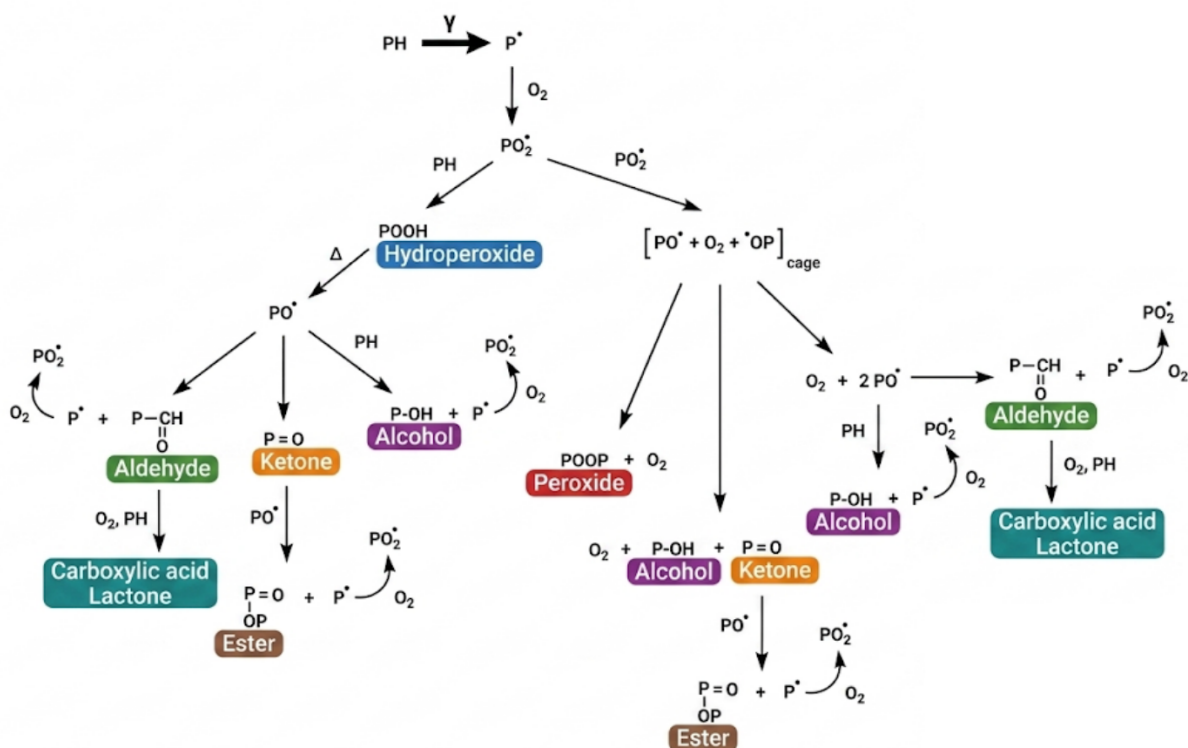


Figure 1.4: Detailed radio-thermo-oxidation mechanism of polyethylene. The scheme shows the initiation of alkyl radicals by γ -irradiation, their reaction with O_2 to form peroxy radicals and hydroperoxides, and the subsequent branching reactions that produce the principal polar defect species: aldehyde, ketone, alcohol, carboxylic acid/lactone, ester, and peroxide. Adapted from [15, 16].

In the conventional left-hand path—the basic autoxidation scheme (BAS) of Bolland and Gee—the peroxy radical abstracts a hydrogen atom from a neighboring PE chain to form a hydroperoxide ($PO_2^\bullet + PH \rightarrow POOH + P^\bullet$), which subsequently undergoes homolytic O–O bond cleavage to regenerate alkoxy and hydroxyl radicals ($POOH \rightarrow PO^\bullet + \bullet OH$), driving the chain-branching reactions that produce aldehydes, ketones, alcohols, carboxylic acids, esters, and lactones. However, density functional theory (DFT) calculations have shown that this pathway faces substantial kinetic obstacles: unimolecular PO–OH bond dissociation carries an activation energy of approximately 2.09 eV in a molecular model and 2.05 eV at the crystalline lamella surface, while the bimolecular disproportionation ($2 POOH \rightarrow POO^\bullet + PO^\bullet + H_2O$) requires 1.54 eV in the crystal interior and 0.91 eV at the lamella surface [19, 20]—barriers high enough to question the actual prevalence of the hydroperoxide decomposition route under the temperatures and dose rates relevant to NPP cable aging. There exists an alternative route that describes a competing pathway that bypasses hydroperoxide formation altogether with two adjacent peroxy radicals undergoing a bimolecular cage reaction to produce alkoxy radicals directly ($2 PO_2^\bullet \rightarrow 2 PO^\bullet + O_2$). DFT calculations show that this reaction is essentially without barrier at the surface of crystalline lamellae, so that once a sufficient steady-state concentration of peroxy radicals is maintained—a condition met when the irradiation dose rate is sufficiently high—alkoxy radicals form readily without the need to pass through the hydroperoxide bottleneck. These alkoxy radicals then trigger the same cascade of terminal products as the left-hand path where β -scission of the C–C bond adjacent to the oxygen site yields an aldehyde chain-end and a new alkyl radical ($PO^\bullet \rightarrow P-CHO + P^\bullet$), which can be further oxidized to carboxylic acid ($P-COOH$) or react with alcohols to form esters; hydrogen abstraction from the backbone by an alkoxy radical, rather than β -scission, produces an alcohol ($PO^\bullet + PH \rightarrow P-OH + P^\bullet$), subsequently oxidized to a ketone ($P-OH + O_2/PO_2^\bullet \rightarrow P=O + \bullet OH/POOH$); and hydrogen abstraction in the absence of oxygen creates vinylene unsaturations ($-CH=CH-$), which upon further oxidation yield enone groups

($-\text{CH}=\text{CH}-\text{CO}-$).

The dose-rate dependence of the dominant pathway is therefore a critical consideration. At low dose rates, where the population of peroxy radicals remains dilute and bimolecular encounters are rare, degradation is expected to proceed mainly through thermally activated hydroperoxide-related routes. At higher radical concentrations, the bimolecular peroxy–peroxy route can become competitive because it bypasses the energetically costly hydroperoxide-decomposition step. However, the threshold dose rate at which this route becomes dominant at room temperature is not established by the present work. The relative importance of the two routes depends on radical generation rate, oxygen availability, radical mobility, local morphology, and temperature [20].

1.4. Dielectric Properties of Pristine and Oxidized Polyethylene

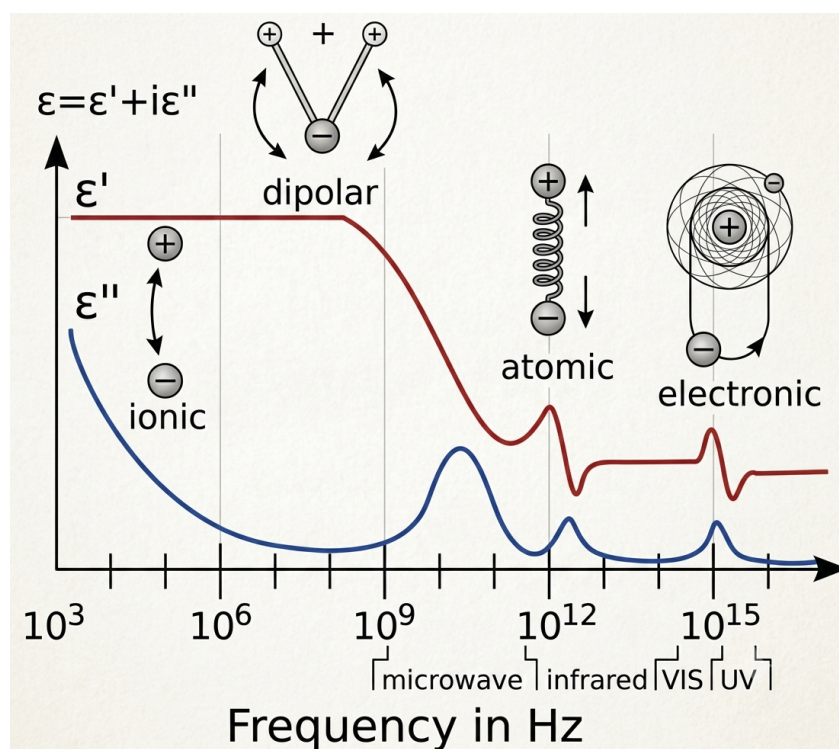


Figure 1.5: Frequency dependence of the relative permittivity $\epsilon'(\omega)$ (red) and dielectric loss $\epsilon''(\omega)$ (blue) in polymers. The figure illustrates the three principal polarization mechanisms. Adapted from [21].

The complex dielectric permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ of a dielectric material is a function of frequency ω , temperature, and the chemical and morphological nature of the material. Elucidating the role of frequency dependence is fundamental to both the experimental diagnosis of the cable condition and the computational prediction of the dielectric spectra. The macroscopic polarization of a dielectric material is the sum of three microscopic mechanisms, each characterized by a relaxation time [22, 23]. (i) Electronic polarization arises from the displacement of valence electron clouds relative to the atomic nuclei; it responds instantaneously to the applied field and contributes to the high-frequency dielectric constant ϵ_∞ . (ii) Ionic (vibrational) polarization arises from the distortion of atoms or molecular segments under the field and is governed by IR-active phonon modes. (iii) Dipolar (orientational) polarization arises from the reorientation of permanent electric dipoles, molecular segments, or chain segments carrying a net dipole moment; this mechanism operates at radio and microwave frequencies and is responsible for the dielectric loss peaks observed in aged PE.

Polyethylene is non-polar and carries no permanent dipoles. At optical and very high frequencies, its dielectric response is dominated by electronic polarization due to distortion of the valence electron clouds on the C–C and C–H bonds. At lower measurement frequencies, such as 1 kHz, the

measured relative permittivity is instead a low-frequency value that can include any slow polarization processes active in the material. For pristine HDPE, reported room-temperature values at 1 kHz are $\epsilon_r = 2.26\text{--}2.35$, with LDPE showing slightly lower values ($\epsilon_r = 2.20\text{--}2.28$) under comparable low-frequency conditions [24, 25].

Upon the introduction of polar functional groups, such as carbonyl groups (dipole moment $\mu \approx 2.3\text{--}2.7$ D) or hydroxyl groups ($\mu \approx 1.7$ D), the bulk polarization and dielectric behavior of PE can change significantly. Boukezzi *et al.* [26] studied thermally aged cross-linked polyethylene (XLPE) cable insulation and observed that ϵ_r increased from 2.30 (pristine) to 2.55 after 2000 hours of aging at 135°C, a 10.9% increase. Similarly, Colin *et al.* [27] reported that ϵ_r of HDPE increased from 2.28 to 2.48 (8.8% increase) after gamma irradiation to 500 kGy in air at 60°C, correlating with carbonyl index (CI) growth from 0 to 0.45. Oxidative degradation is also reflected in the increase of dielectric loss tangent, which is associated with dissipative polarization processes. Zaharescu *et al.* [28] studied gamma-irradiated LDPE (50–300 kGy in air) and observed $\tan \delta$ (1 kHz, 25°C) increasing from 3.2×10^{-4} (pristine) to 1.8×10^{-3} (300 kGy). Hoàng and Lowe [29] studied oxidized HDPE pipes and found $\tan \delta$ (1 MHz, 25°C) increasing from 4×10^{-4} to 2.5×10^{-3} in severely oxidized surface layers (CI > 0.6). The increase in dielectric loss depends on frequency and temperature, reflecting the activation of different loss mechanisms. Oxidation can therefore create new relaxation processes or enhance existing ones. Suljovrujic studied the post-irradiation dielectric response of LDPE, LLDPE, and HDPE from 1 kHz to 1 MHz over 25–325 K and related the enhanced relaxation strength to carbonyl groups introduced by irradiation and subsequent oxidation [30]. Earlier measurements likewise showed that polar groups, including hydroxyl- and carbonyl-containing species, increase the dielectric loss of polyethylene [31].

Table 1.1: Experimental data on dielectric property changes of polyethylene with oxidative aging. ϵ_r : relative permittivity at 1 kHz; $\tan \delta$: dielectric loss tangent at 1 kHz; CI: carbonyl index from FTIR.

Material & Treatment	ϵ_r (1 kHz)	$\tan \delta$ (1 kHz)	CI	Ref.
HDPE (pristine)	2.28	3×10^{-4}	0	[27]
HDPE (γ -irrad., 500 kGy, air, 60°C)	2.48	1.5×10^{-3}	0.45	[27]
LDPE (pristine)	2.24	3.2×10^{-4}	0	[28]
LDPE (γ -irrad., 300 kGy, air)	2.42	1.8×10^{-3}	0.38	[28]
XLPE (pristine)	2.30	2.5×10^{-4}	0	[26]
XLPE (thermal aging, 135°C, 2000 h)	2.55	1.2×10^{-3}	0.52	[26]

1.5. Open Issues Addressed by this Thesis

Recent years have led to significant progress in understanding the degradation of polyethylene at the atomic scale. Oxidation products in PE can be characterized by several experimental techniques, including FTIR spectroscopy for functional-group identification, solid-state NMR for oxidized carbon and oxygen environments, EPR spectroscopy for radical intermediates, and UV-Vis absorption for selected electronic signatures. Earlier FTIR-based studies had already shown that the broad carbonyl region formed during PE oxidation contains multiple chemical contributions. Sugimoto *et al.*, for example, resolved the carbonyl region of aged XLPE cable insulation into carboxylic acid, ester, and anhydride components and observed that carboxylic acid is a primary oxidation product, while esters and anhydrides are secondary products whose relative yields increase with aging temperature [32]. Ferry *et al.* built on this result by combining FTIR spectroscopy with theoretical infrared spectrum calculations, which allowed the decomposition and assignment of overlapping radio-oxidation bands in LLDPE and XLPE [33].

The chemical products identified by spectroscopy are directly relevant to dielectric behavior because they introduce permanent dipoles into an otherwise non-polar polymer. Other cable-aging studies show that degradation chemistry depends strongly on dose rate, temperature, and morphology. Liu, Fifield, and Bowler demonstrated with industry-grade filled XLPE that gamma radiation disrupts the crystalline phase, produces smaller and less perfect crystals, and alters the balance between chain scission and crosslinking depending on aging temperature [14]. Hettal et al. reported that oxidation of LDPE and XLPE can increase the dielectric constant from approximately 2.3 ± 0.3 to values above 4.5, while volume resistivity can drop by several orders of magnitude as oxygenated groups are incorporated into the polymer [34]. In silane-crosslinked polyethylene (Si-XLPE), they further confirmed that radio-thermal aging changes both physicochemical and electrical properties. This interpretation is consistent with the broadband dielectric spectroscopy results of Fabiani and Suraci on nuclear-grade low-voltage cables, where both real and imaginary permittivity increased with aging time; the real permittivity changed by about 20%, while the imaginary permittivity at 0.1 Hz and 100 kHz changed by approximately one order of magnitude [35].

However, the literature identifies several unresolved difficulties in investigating the influence of aging on the dielectric behavior of PE. First, diffusion-limited oxidation can make aging spatially non-uniform, especially at high dose rate and temperature, so the measured dielectric response is an average over differently aged regions rather than a property of one homogeneous material [35]. Second, the chemical interpretation of dielectric spectra remains indirect. Hettal et al. explicitly state that, because of the wide variety of oxidation products and limited structure-property relationships, it is not currently possible to experimentally determine the electrical impact of each oxidation product individually [34]. Therefore, although experiments clearly establish that irradiation and oxidation generate polar defects in PE and that these defects modify dielectric behavior, they do not yet provide a defect-resolved explanation. Several factors must be studied to understand the parameters influencing the measured dielectric response, including defect chemistry, concentration, crystalline/amorphous morphology, oxygen diffusion gradients, space-charge accumulation, different polarization mechanisms, and post-irradiation reactions.

First-principles studies have clarified key steps of the oxidation chemistry in PE, especially the formation and decomposition of hydroperoxides. Kinetic models for PE radio-thermal oxidation have tracked the time evolution of radical and hydroperoxide concentrations and predicted the formation of carbonyl and hydroxyl products [34, 36, 37]. The DFT study by Ahn et al. [19] extended this analysis to the atomic scale by computing reaction energetics and transition states of oxidation pathways using a lamellar PE slab model. Their results showed that the local environment, including crystalline or non-crystalline surroundings and inter-chain spacing, can influence both activation barriers and reaction products. Significant progress has also been made in the computational prediction of polymer dielectric properties. DFPT provides a first-principles framework for calculating response properties such as dielectric tensors and Born effective charges [38]. For PE-based systems, DFT/DFPT calculations have been used to estimate dielectric constants with reasonable agreement to experiment and to provide a baseline for modeling dielectric response [39–41].

Classical molecular dynamics does not build on DFPT; instead, it complements first-principles methods by providing access to dynamical aspects on time scales inaccessible to first-principles simulations. Molecular-dynamics modeling of polyethylene was established through early simulations of crystalline and polyethylene-like systems by Noid, Sumpter, and Wunderlich, followed by atomistic bulk-PE simulations by Pant, Han, Smith, and conformational-dynamics studies by Boyd and co-workers [42–46]. These works showed that PE relaxation is governed by local torsional transitions, conformational defects, and temperature-dependent chain mobility, providing the microscopic basis for later MD studies of dielectric relaxation in polar or oxidized polyolefins. The calculation of dielectric response from MD is commonly based on the Neumann fluctuation formula, in which the static orientational contribution to the dielectric constant is obtained from fluctuations of the total dipole moment of the simulation cell [47]. This approach has been widely used for polar liq-

uids and polymers; for example, Borodin, Bedrov, and Smith applied MD to dielectric relaxation in aqueous poly(ethylene oxide) systems, while the OPLS-AA force field developed by Jorgensen et al. provides a standard all-atom framework for modeling organic molecules and polymer segments [48, 49]. More recently, Misra and co-workers applied related MD-based dielectric analysis to polyolefin systems, showing that morphology can strongly influence the dielectric constant of semicrystalline polyolefins [41]. Since oxygen diffusion is severely restricted in crystalline lamellae [36], defects in real cable insulation are expected to be distributed predominantly in amorphous and interfacial regions rather than uniformly throughout the material. The positional dependence of the dielectric increment on defect location within the lamellar stack has not yet been quantified computationally. The present work therefore investigates PE radio-oxidation defects in a three-phase lamellar geometry, where crystalline, interfacial, and amorphous regions are represented together with the chemical specificity of the defect.

Taken together, this thesis combines DFPT and MD within a consistent computational framework to separate electronic, ionic, and orientational dielectric contributions for chemical species formed during PE radio-oxidation under nuclear service conditions, with comparison to experimental broadband dielectric spectra of real cable insulation.

1.6. Survey of Previous Studies

Early quantum-chemical investigations of PE focused on establishing its electronic structure and examining how intrinsic electronic states, surfaces, and chemical impurities introduce localized states relevant to charge transport and dielectric degradation. Before the later Ramprasad studies on chemical defects, the Trieste group led by Tosatti and co-workers studied interchain electronic states, surface states, electron and hole self-trapping, and exciton self-trapping in crystalline PE [50–54]. These works established that the electronic structure of PE is sensitive to chain packing, surfaces, local conformational distortions, and chemical defects. Meunier, Quirke, and Aslanides then calculated chemical traps in polymer insulators using density-functional calculations, defining the trap energy in terms of the molecular electron affinity. Their work showed that chemical defects including ketones (C=O), alcohols (C–OH), and alkenes (C=C) can generate much deeper electron traps, often exceeding 1 eV, which can contribute to long-lived space-charge accumulation in cable insulation [55]. Building on these electronic-structure studies, Ramprasad and colleagues used DFT to study the influence of carbonyl and other common chemical defects on the electronic structure of PE. The study found that carbonyl (C=O), vinyl, and conjugated double bonds create deep traps and shallow hopping sites in the PE band gap [56, 57]. Later studies by Chen, Huan, and Ramprasad [58] performed a comprehensive mapping of the electronic structure of PE, examining chemical, morphological, and interfacial complexity. They showed that kink defects, chain ends, and oxygen-containing functional groups (aldehyde, ketone, alcohol, ester) each produce distinct spectral signatures in the electronic density of states, with characteristic trap depths ranging from 0.5 eV (chain ends) to 2.8 eV (carbonyl groups). The work emphasized that semicrystalline morphology introduces additional electronic heterogeneity where the crystalline-amorphous interface creates a band offset of approximately 0.3–0.5 eV. This finding motivates the present thesis to treat PE in its semicrystalline morphology.

Bealing and Ramprasad proposed an atomistic mechanism to explain how chemical defects form and cause degradation of crystalline PE. Using spin-polarized DFT and *ab initio* molecular dynamics, they showed that an injected triplet exciton can localize in a distorted region of PE, weaken nearby C–H bonds, and promote C–H bond scission, leaving reactive radical sites ($-\text{CH}^\bullet-$) on the chain. This study links electronic excitation, bond rupture, and radical formation as the initial step toward defect formation in PE [59]. Chen, Tran, and Ramprasad later extended this study with a more complete set of oxidation-induced defect formation mechanisms in PE using DFT and reactive-force-field molecular dynamics. They described seven reaction pathways, beginning with the formation of PE radicals and leading to vinyl, carbonyl, aldehyde, and hydroxyl defects in PE chains [60]. Similarly, Ahn, Roma, and

Colin used first-principles calculations to examine the atomic-scale mechanisms of radio-oxidation kinetics in PE, establishing the energetics and transition states of the principal oxidation pathways, including alkoxy radical decomposition and peroxy radical rearrangements. This study provides the chemical basis for selecting radio-oxidation defects for the present thesis [19, 20]. Ferry *et al.* [33] presented a theoretical model of a semicrystalline lamellar PE with crystalline and amorphous layers separated by explicit interfacial regions for first-principles calculations. This morphologically realistic model represents a significant step beyond the pure-crystalline or amorphous approximations that have dominated computational studies. IR frequencies and intensities of carbonyl-containing oxidation products were calculated using DFPT to support the deconvolution of the experimental carbonyl region. The same PE model is adopted for this thesis.

The investigation of dielectric properties in chemically modified PE systems was notably advanced by Wang and Ramprasad, who applied DFPT to analyze Si-substituted polyethylene organosilicon structures [61]. They showed that replacing carbon atoms in PE by silicon increases both the electronic and ionic contributions to the dielectric constant, due to enhanced polarizability and more intense vibrational modes involving Si-containing bonds. Pilia et al. extended this study by screening Group IV chemical motifs replacing CH₂ units in PE to improve the dielectric permittivity of PE-like chains [62]. Fukushima et al. provided one of the earliest analyses of the effect of chemical defects on the dielectric response of crystalline PE using DFPT [63]. The study showed that, in a crystalline model of PE, the dielectric constants are strongly anisotropic and sensitive to defect type. Specifically, iodine defects increase the high-frequency dielectric constant, while hydroxyl (–OH) and carboxyl (–COOH) groups cause anisotropic changes in the static dielectric constant. Misra *et al.* compared DFT/DFPT and MD predictions of the dielectric constant for PE functionalized with six polar side groups (–CH₃, –NH₂, –NO₂, –COOH, –OH, –SH) at 4.2 mol % concentration [41]. They computed ϵ_∞ and ϵ^0 for crystalline PE configurations and compared them to the responses of semicrystalline morphologies using MD simulations. They found that the static dielectric constant computed for the semicrystalline model of PE in MD can be up to an order of magnitude larger than that obtained from pure-crystalline models using DFPT-only calculations because MD simulations of semicrystalline morphologies reveal much larger orientational contributions from amorphous regions. These results suggest that an accurate representation of semicrystalline morphology is important for reliable dielectric-constant calculations. However, microstructure is only one of the differences between the two approaches; DFPT and MD also differ in the polarization mechanisms, time scales, and length scales that they can describe. These findings motivate the combined use of DFPT, MD, and a semicrystalline PE model in the present work.

Molecular dynamics allows access to dielectric contributions that DFT/DFPT models cannot capture, such as dipole relaxation, segmental motion, and frequency-dependent dielectric loss. Several MD studies have developed the methodology for computing dielectric constants and dielectric losses from dipole fluctuations [64–66]. Jämsbeck, Unge, and Laihonon used MD to compute dielectric permittivity and losses in polymer systems containing additives, using the total dipole moment for the static dielectric constant and its autocorrelation function for the dielectric loss spectrum [67]. Related work on polypropylene–additive compounds showed that atomistic MD could reproduce dielectric constants and estimate loss in quantitative agreement with broadband dielectric spectroscopy measurements [68]. The study by Misra and co-workers investigated the correlation between chemical modification, morphology, and dielectric performance of hydroxyl-functionalized polyethylene to understand the mechanisms by which polar groups modulate the dielectric response of polyolefins [69]. Their findings revealed that even low concentrations of –OH groups can increase static relative permittivity and also reduce overall crystallinity. These changes are a consequence of the intrinsic dipole moment of the hydroxyl group and also the local polymer morphology and hydrogen-bonding environment. Umari and Pasquarello [70] used *ab initio* molecular dynamics (Car–Parrinello MD) to compute dielectric properties of organic and inorganic materials from first principles, including finite-temperature effects. The method was validated for bulk MgO (achieving $\epsilon_s = 9.8$ vs. experimental 9.7) and silica ($\epsilon_s = 3.8$ vs. experimental 3.8), demonstrating quantitative accuracy. However, the compu-

tational burden strongly limits the size of atomic models and the accessible simulation times. Giustino, Umari, and Pasquarello [71] extended the *ab initio* MD framework to calculate position-dependent (local) dielectric permittivity profiles in nanoscale systems including Si/SiO₂ interfaces and oxide slabs. By analyzing the spatial variation of induced polarization under an applied field, they demonstrated that the local dielectric constant can be computed. These methods show why first-principles and local-dielectric approaches are useful for identifying the influence of individual defects, while also explaining why the present thesis combines them with larger-scale MD models for semicrystalline PE.

Taken together, previous studies show that chemical defects in PE introduce localized trap states and can strongly alter the electronic structure. Studies based on first-principles calculations and on MD with reactive force-field potentials have identified feasible atomistic pathways for the formation of vinyl, hydroperoxide, carbonyl, aldehyde, hydroxyl, and carboxyl oxidation products. Furthermore, finite-field and DFPT studies have shown that polar defects can modify the dielectric response of PE, while MD studies have shown that morphology and dipolar relaxation can strongly affect the orientational contribution to permittivity and dielectric loss. Building upon these collective insights, the present thesis combines DFT/DFPT and MD to study realistic PE radio-oxidation defects, their spatial distribution across crystalline, interfacial, and amorphous regions in a semicrystalline lamellar morphology, and their discrete electronic, ionic, and orientational contributions to the dielectric response.

1.7. Motivations for this Thesis

Polyethylene-based materials are widely used as insulation in low- and medium-voltage cables, including safety-relevant cable systems in nuclear power plants. These cables require demonstration that the dielectric properties of the insulation remain within acceptable limits for the extended service period. In this context, the progressive degradation of cable insulation by heat, irradiation, oxygen, and moisture is not only a materials problem but also a reliability and safety issue, because insulation failure can compromise the performance of power, instrumentation, and control systems. Since dielectric behavior is one of the core functional properties of cable insulation, understanding how aging-induced chemical changes modify the dielectric response of polyethylene is directly relevant to the assessment of cable health in nuclear environments.

From a scientific point of view, polyethylene remains a model material for studying the coupling between polymer chemistry, semicrystalline morphology, and electrical performance. At the fundamental level, a small concentration of polar functional groups modifies the dielectric response of an otherwise non-polar, semicrystalline polymer. Studies have shown that chemical defects, morphological disorder, and interfacial complexity can strongly alter the electronic structure of polyethylene and cause dielectric degradation. Experimental dielectric spectroscopy on aged XLPE cables has shown that dielectric observables correlate with oxidation and mechanical degradation, confirming that dielectric response is a sensitive marker of aging. The present work aims at providing a unified picture that directly connects specific polar oxidation defects, their location in a semicrystalline polyethylene environment, and their contribution to both static and frequency-dependent dielectric properties. This thesis is therefore motivated by the need to bridge polymer aging chemistry and dielectric response at the atomistic scale.

The methodological motivation of this thesis arises from the fact that no single computational technique can, by itself, describe all relevant contributions to the dielectric behavior of aged polyethylene. Density functional theory and density functional perturbation theory are well suited to treating the electronic structure of defected systems and to computing the electronic and ionic contributions to permittivity, but they remain limited to relatively small periodic models and cannot capture the slower orientational dynamics associated with polymer-chain motion. Classical molecular dynamics, by contrast, provides access to dipole-moment fluctuations over longer times and larger length scales, making it possible to calculate static and frequency-dependent dielectric response associated with molecular and segmental relaxation. The combination of these approaches is therefore methodolog-

Table 1.2: Summary of computational studies on dielectric properties of polyethylene-based polymers.

Reference	System	Method	Contributions
Wang and Ramprasad [61]	Si-substituted PE-like organosilicon chains	DFT/DFPT	Electronic and ionic dielectric constants
Pilania et al. [62]	Group-IV-substituted PE-chains	DFT/DFPT	PE-motifs to improve dielectric permittivity
Wang, Pilania and Ramprasad [72]	C-, Si- and Ge-based polymer backbones	First-principles DFT/DFPT	Electronic, ionic, and total dielectric response
Misra et al. [69]	Hydroxyl-functionalized PE and PP	MD and dielectric measurements	Static permittivity and dielectric loss
Misra et al. [41]	Functionalized semicrystalline polyolefins	DFT/DFPT and classical MD	Orientational dielectric contribution as a function of morphology
Misra and Kumar [73]	Functionalized PE copolymers	MD, time-temperature superposition	Frequency-dependent dielectric loss over different temperature ranges
Cheng et al. [74]	Amorphous PE with chemical defects	Classical MD	Complex dielectric constants of defective PE
Jambeck, Unge and Laihonon [67]	PE/polyolefin with molecular additives	Classical MD	Dielectric permittivity and loss from total dipole-moment fluctuations
Fukushima et al. [63]	Crystalline PE with I, OH, COOH defects	Finite-field DFT	Anisotropic dielectric constants.
Mishra et al. [75]	Amorphous polymer dielectrics	Polarizable reactive MD	Static and frequency-dependent permittivity
Tang et al. [40]	PE, PTFE, PS and other polymers	Molecular DFT, Clausius-Mossotti	Static dielectric constants from molecular polarizability

ically justified: first-principles calculations provide chemically resolved dielectric information, while molecular dynamics captures the dynamic and collective contributions that emerge in semicrystalline morphologies. By combining DFT/DFPT with classical MD, and by decomposing the dielectric response into self and cross contributions, the thesis aims at building a multiscale framework capable of relating defect chemistry to measurable dielectric observables in a way that neither approach could achieve alone.

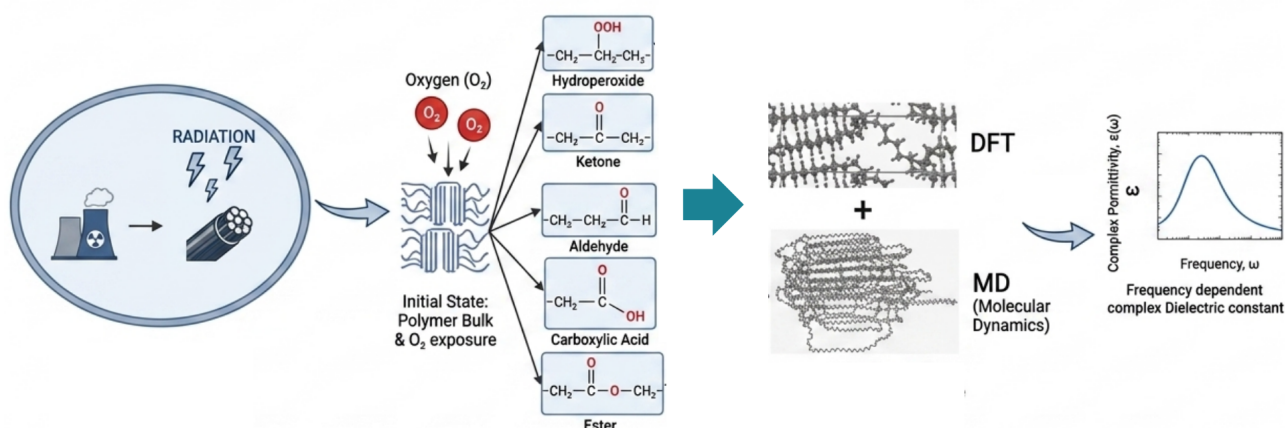


Figure 1.6: Schematic summary of the multiscale approach used to investigate the influence of irradiation on the dielectric properties of polyethylene, both as a model polymer and as an industrially relevant cable-insulation material.

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2 – Methodology

This chapter describes the computational methodology adopted in this thesis. The thesis employs a multiscale computational strategy to study chemical defects in semicrystalline polyethylene (PE) and its dielectric response over several frequency ranges and time scales. The dielectric response of a material characterizes how its internal charge distribution polarizes under an applied external electric field. Under low-frequency fields, all polarization mechanisms contribute to the total permittivity. Conversely, at high frequencies, only the fastest electronic responses will react to the field. For this reason, the dielectric permittivity is frequency dependent in nature and is written as a complex quantity,

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega), \quad (2.1)$$

where $\varepsilon'(\omega)$ is the real part and $\varepsilon''(\omega)$ is the imaginary part. The real part represents the ability of the material to store electrostatic energy, whereas the imaginary part represents the energy dissipation arising from dielectric relaxation. The central methodological problem is that no single simulation method can capture all relevant polarization mechanisms that contribute to the dielectric response. The electronic response and the vibrational lattice contribution require a first-principles description, while the slow orientational response of polar defects and the evolution of semicrystalline morphology require atomistic molecular dynamics over nanosecond time scales. For this reason, the work combines density functional theory (DFT), density functional perturbation theory (DFPT), finite-field position-dependent dielectric calculations, and classical molecular dynamics (MD).

The polyethylene backbone is chemically non-polar, so pristine PE does not possess strong permanent dipoles along the chain. As a result, the dielectric response of ideal polyethylene is dominated by the electronic contribution at high frequencies, together with a comparatively small vibrational contribution at much lower frequencies. Radio-oxidative degradation of polyethylene forms polar oxygenated groups (alcohols, ketones, aldehydes, esters, and carboxylic acids), creating localized permanent dipoles. These dipoles can reorient under an electric field and, therefore, give rise to a measurable relaxation process in a broad frequency range. The strength and timescale of this relaxation depend not only on the dipole moment of the defect itself but also on the local mobility of the polymer chain, the degree of crystallinity, and the coupling between the defect and the surrounding matrix. In such polar polymeric materials, dielectric relaxation is often discussed in terms of different frequency regimes. At very high frequencies, typically in the optical range, only electronic polarization can follow the field, and the dielectric constant approaches the high-frequency limit ε_∞ . At somewhat lower frequencies, in the infrared and terahertz regime, vibrational and lattice-related responses contribute to the permittivity. At low frequencies, dipolar reorientation can become active. These frequency windows are not separated by sharp boundaries, and their exact position depends on temperature, morphology, and molecular dynamics. For semicrystalline polyethylene, the amorphous and crystalline regions also respond differently, so the observed dielectric spectrum reflects both local chemistry and structure. For polyethylene-based systems containing polar oxidation defects, the total dielectric response can therefore be understood as the sum of several contributions acting on different timescales. The high-frequency limit is governed mainly by electronic polarization, which is well described by first-principles calculations. The lower-frequency enhancement arises from the slower reorientation of permanent dipoles associated with defect groups and from their coupling to chain dynamics. In addition, semicrystalline morphology can introduce interfacial effects and dynamic heterogeneity, which broaden the relaxation spectrum and shift the characteristic times. The analysis of dielectric relaxation in this work is therefore based on the combined interpretation of the static permittivity, the dipole autocorrelation function, the characteristic relaxation time, and the frequency-dependent dielectric loss spectrum.

The dielectric properties of polyethylene are therefore studied in two stages to explore the ef-

fects of aging across different frequency ranges. In the first stage of this multiscale approach, density functional theory (DFT) and density functional perturbation theory (DFPT) are used to compute the ground-state electronic structure, the high-frequency (electronic) dielectric tensor ε^∞ , and the static dielectric tensor ε^0 , including ionic contributions. In the second stage, classical molecular dynamics (MD) is used to capture finite-temperature morphological evolution and orientational polarization dynamics over nanosecond time scales that are inaccessible within the DFPT framework. By combining these two methods, the electronic, ionic, and orientational polarization mechanisms contributing to the frequency-dependent complex permittivity, $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, are investigated within one multiscale framework. All DFT and DFPT calculations were performed using the open-source Quantum ESPRESSO (QE) package [1, 2], version 7.2. QE implements the self-consistent plane-wave pseudopotential method within periodic boundary conditions and provides seamlessly integrated modules for ground-state calculations (pw.x), phonon and linear-response calculations (ph.x), and post-processing (dynmat.x, pp.x), while classical MD simulations were carried out with LAMMPS [3]. Initial MD configurations were generated using Moltemplate [4]. The theoretical foundations and practical implementation of each method are explained in the following sections.

2.1. First-Principles Methodology

The first-principles part of this multiscale study combines density functional theory (DFT) with its linear-response extension, density functional perturbation theory (DFPT). DFT offers the quantum-mechanical ground-state electronic structure, including geometry, total energy, and electron density, from which the structural characteristics are studied. Building on these results, DFPT calculates the second-order response of the system to atomic displacements and homogeneous electric fields, resulting in phonon frequencies, Born effective charges, and the static dielectric tensor.

Density functional theory (DFT) is a quantum-mechanical framework that describes the many-electron system in terms of electron density $n(\mathbf{r})$ [5, 6]. The Kohn-Sham equation is used to describe these fictitious non-interacting electrons with the same electron density as the real interacting electron system. The Kohn-Sham (KS) equations read as follows

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}[n](\mathbf{r}) + V_{\text{xc}}[n](\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \quad (2.2)$$

where V_{ext} is the external potential from the ion cores, V_{H} is the Hartree potential, and V_{xc} is the exchange-correlation (XC) potential. The ground-state electron density is calculated from the self-consistent solution of these equations from which forces, stresses, and structural relaxations are computed. Because the precise exchange-correlation functional is unknown, the accuracy of DFT computations depends on the choice of approximation for $V_{\text{xc}}[n]$. The optB86b-vdW van der Waals density functional was used [7, 8] to describe the semicrystalline polyethylene model, in which the XC energy is written as:

$$E_{\text{xc}} = E_{\text{x}}^{\text{GGA}} + E_{\text{c}}^{\text{LDA}} + E_{\text{c}}^{\text{nl}}. \quad (2.3)$$

where the non-local correlation energy term E_{c}^{nl} captures the long-range dispersion self-consistently. The optB86b functional has been validated against experimental structural parameters and provides a better description of lattice constants and intermolecular distances in layered and molecular systems [7], making it well suited for PE, where dispersion governs the cohesion between all-trans chains. The plane-wave method is used for these calculations, where the core electrons of C, H, and O are represented by norm-conserving pseudopotentials generated with the optB86b functional. In a periodic plane-wave calculation the KS orbitals are expanded in a basis of plane waves $e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}$, truncated at a maximum kinetic energy

$$\frac{\hbar^2}{2m_e} |\mathbf{k} + \mathbf{G}|^2 \leq E_{\text{cut}}. \quad (2.4)$$

A charge-density cutoff $E_\rho = 4 E_{\text{cut}}$ (standard for norm-conserving pseudopotentials) controls the Fourier representation of the charge density and local potentials. The converged parameters adopted throughout this work are 80 Ry for E_{cut} and 320 Ry for the E_ρ parameter. The Brillouin zone is sampled using a Γ -centered Monkhorst–Pack [9] $\mathbf{k}$ -point mesh of dimensions $2 \times 3 \times 2$, reflecting the orthorhombic shape and relative dimensions of the simulation cell.

Each structure was fully relaxed by optimizing the ionic positions until the convergence criteria were satisfied. The self-consistent field (SCF) cycle was considered converged when the difference in energy between two successive iterations was smaller than 1.0×10^{-14} Ry. The total energy was taken as converged when the change between successive ionic steps fell below 1.0×10^{-4} Ry. The structure was regarded as optimized once all residual Hellmann–Feynman forces were less than 1.0×10^{-4} Ry/Bohr. The Davidson iterative diagonalisation algorithm [10] was used to solve the KS equations at each SCF step. All structural modifications to introduce chemical defects—alcohol ($-\text{OH}$), aldehyde ($-\text{CHO}$), ketone ($\text{C}=\text{O}$), carboxylic acid ($-\text{COOH}$), enone, ester ($-\text{COO}-$), and vinylene ($-\text{CH}=\text{CH}-$)—were followed by a full geometry relaxation under these criteria prior to any dielectric analysis.

2.1.1. Density Functional Perturbation Theory

Density Functional Perturbation Theory [11, 12] extends DFT to the linear-response regime by describing how the ground-state energy, electron density, and wave functions change in response to a small external perturbation. Under a finite external electric field the system is subjected to a small perturbation (λ), and the total energy can then be expanded to second order around the unperturbed ground state as:

$$E(\lambda) = E^{(0)} + \lambda E^{(1)} + \frac{1}{2} \lambda^2 E^{(2)} + \mathcal{O}(\lambda^3). \quad (2.5)$$

The zeroth-order term is the ground-state energy, the first-order term gives the linear response, and the second-order term contains the harmonic response of the system. The second-order term $E^{(2)}$ contains the information needed to construct the interatomic force constants, the dielectric susceptibility, and the Born effective charges. The first-order changes in the wave functions, $\delta\psi_i^{(1)}$, induced by the perturbation, are obtained by solving the Sternheimer equations, which are the linearized form of the Kohn–Sham equations:

$$(\hat{H}_{\text{KS}} - \varepsilon_i) |\delta\psi_i^{(1)}\rangle = -\hat{P}_c \delta\hat{V}^{(1)} |\psi_i^{(0)}\rangle, \quad (2.6)$$

where $\hat{P}_c$ projects onto the conduction-band manifold and $\delta\hat{V}^{(1)}$ is the first-order change in the self-consistent potential. All relevant second-order derivatives of the total energy needed for lattice-dynamical and dielectric properties are derived from this. The dynamical matrix, which encodes the lattice response to atomic displacements in the wave vector is:

$$D_{\kappa\alpha, \kappa'\alpha'}(\mathbf{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \frac{\partial^2 E}{\partial u_{\kappa\alpha}(\mathbf{q}) \partial u_{\kappa'\alpha'}^*(\mathbf{q})}, \quad (2.7)$$

where κ, κ' label the atoms in the unit cell, α, α' are Cartesian directions, and M_κ is the atomic mass. The diagonalization of $D(\mathbf{q})$ gives the phonon frequencies $\omega_m(\mathbf{q})$ and the corresponding eigenvectors, which describe the vibration pattern of each normal mode. From this, the Born effective charge tensor that describes the change in macroscopic polarization is calculated using:

$$Z_{\kappa, \alpha\beta}^* = \Omega_0 \left. \frac{\partial P_\beta}{\partial u_{\kappa\alpha}} \right|_{\mathbf{E}=0} = \left. \frac{\partial F_{\kappa, \alpha}}{\partial \mathcal{E}_\beta} \right|_{\mathbf{u}=0}, \quad (2.8)$$

where Ω_0 is the unit-cell volume. The Born effective charge is a dynamical quantity that measures the coupling between atomic motion and polarization and governs IR activity, dielectric screening, and LO–TO splitting. Born effective charges must satisfy the acoustic sum rule (ASR), $\sum_\kappa Z_{\kappa, \alpha\beta}^* = 0$,

which follows from translational invariance. In practice, numerical incompleteness of the basis and the finite k -point sampling leave small residual violations of this rule. These deviations are corrected in post-processing using `dynamat.x`, so that the physically required translational invariance is restored before analyzing the phonons and dielectric properties.

2.1.2. Dielectric Tensors: Electronic and Ionic Contributions

DFPT provides two key dielectric quantities. The first is the *high-frequency* dielectric tensor $\varepsilon_{\alpha\beta}^{\infty}$ which captures the response of the electrons to an external electric field with the ions fixed. The second quantity is the *static* dielectric tensor, which includes both the electronic response and the ionic contribution coming from infrared-active lattice vibrations at the zone center. In a mode-resolved form, it is written as

$$\varepsilon_{\alpha\beta}^0 = \varepsilon_{\alpha\beta}^{\infty} + \frac{4\pi}{\Omega_0} \sum_m \frac{S_{m,\alpha\beta}}{\omega_m^2}, \quad (2.9)$$

where ω_m is the frequency of the m -th IR-active phonon mode and $S_{m,\alpha\beta}$ is the corresponding oscillator-strength tensor, which depends on the mode-effective Born charge:

$$S_{m,\alpha\beta} = \left(\sum_{\kappa\gamma} Z_{\kappa,\alpha\gamma}^* e_{m,\kappa\gamma} \right) \left(\sum_{\kappa'\gamma'} Z_{\kappa',\beta\gamma'}^* e_{m,\kappa'\gamma'} \right), \quad (2.10)$$

with $e_{m,\kappa\gamma}$ the normalized phonon eigenvector. This expression shows clearly that the static dielectric response is determined not only by the electronic cloud but also by the ease with which the polar phonon modes can be excited. The scalar dielectric constants reported in this work are obtained from the orientational average of the diagonal tensor elements:

$$\bar{\varepsilon} = \frac{\varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}}{3}. \quad (2.11)$$

This average is useful when comparing systems using a single representative dielectric value. In polar materials, long-wavelength longitudinal optical (LO) phonons generate a macroscopic electric field that is absent for transverse optical (TO) phonons. As a result, the LO and TO frequencies become different near $\mathbf{q} \rightarrow 0$, leading to the LO-TO splitting [11]. Within DFPT, this effect is described by a non-analytic correction to the dynamical matrix at the zone center:

$$D_{\kappa\alpha,\kappa'\alpha'}^{\text{NA}}(\mathbf{q} \rightarrow 0) = \frac{4\pi e^2}{\Omega_0} \frac{(\sum_{\beta} \hat{q}_{\beta} Z_{\kappa,\alpha\beta}^*) (\sum_{\beta'} \hat{q}_{\beta'} Z_{\kappa',\alpha'\beta'}^*)}{\sum_{\beta\beta'} \hat{q}_{\beta} \varepsilon_{\beta\beta'}^{\infty} \hat{q}_{\beta'}}, \quad (2.12)$$

where $\hat{\mathbf{q}}$ is the direction of approach to Γ . This term shows that the LO-TO splitting is controlled by the Born effective charges and the electronic dielectric tensor. Therefore, LO-TO splitting is a direct manifestation of the coupling between lattice dynamics and long-range electrostatics in polar materials. The infrared activity of each phonon mode is related to the square of its mode-effective charge. In practical calculations, the `dynamat.x` post-processing tool provides mode frequencies, effective charges, IR activities, and dielectric contributions for each mode. These quantities enable a detailed mode-by-mode decomposition of the ionic contribution to the static dielectric constant and direct comparison with experimental IR spectra.

2.2. Simulation Cell and Structural Model

Semicrystalline polyethylene is characterized by ordered crystalline lamellae separated by amorphous inter-lamellar layers. The structural model employed here is a lamellar slab model derived from previous studies by Ahn *et al.*[13] and Ferry *et al.*[14]. An orthorhombic simulation cell ($9.72 \times 6.95 \times 19.95 \text{ \AA}^3$) contains crystalline lamellae composed of all-trans chains with two free surfaces connected across a vacuum region by alkyl chains that mimic the amorphous phase. The pristine cell

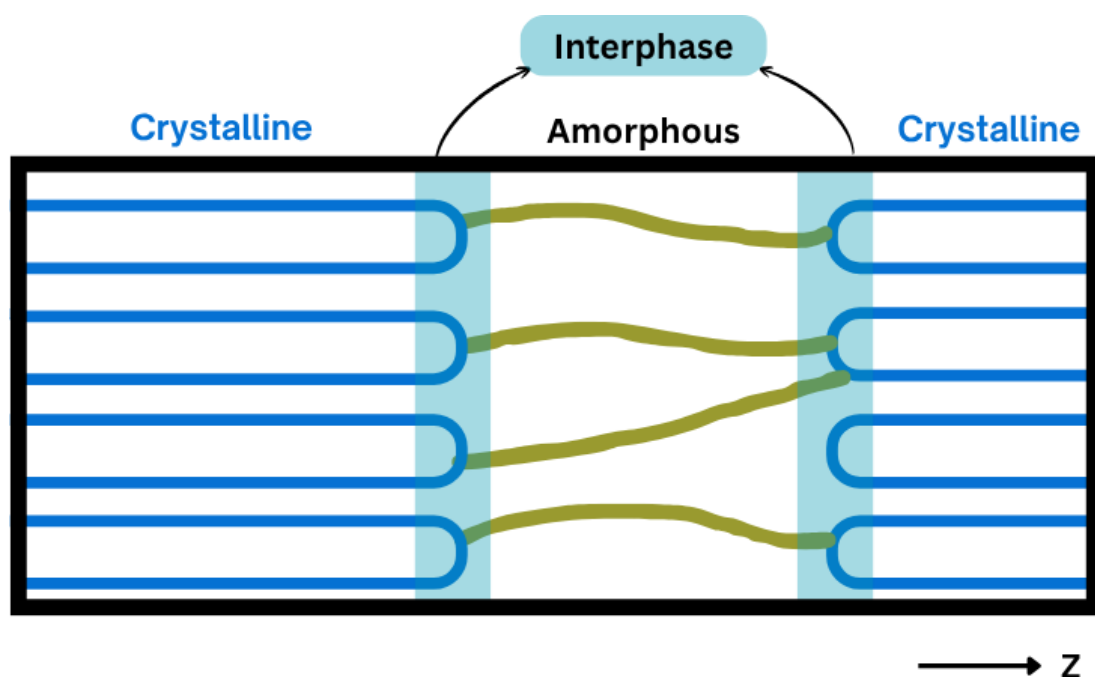


Figure 2.1: Schematic of the semicrystalline polyethylene morphology studied in this work. Ordered crystalline lamellae (blue, horizontal chains) alternate with an amorphous inter-lamellar region (green, disordered chains) through interphase transition zones.

contains 151 atoms and has a density of 0.88 g cm^{-3} , in reasonable agreement with experiment [15]. This three-region slab model (crystalline core, interfacial surfaces, and amorphous bridges) effectively captures the morphological complexity of semicrystalline PE and allows defect placement at sites representative of the different local environments. Chemical defects—alcohol ($-\text{OH}$), aldehyde ($-\text{CHO}$), ketone ($\text{C}=\text{O}$), carboxylic acid ($-\text{COOH}$), enone, ester ($-\text{COO}-$), and vinylene ($\text{C}=\text{C}$)—were introduced at two concentrations, 2 mol % and 4 mol %, by replacing one or two CH_2 units in the simulation cell. At 4 mol %, one defect was fixed at the crystalline–amorphous interface while the second was placed at varying positions (crystalline, interfacial, and amorphous regions) to probe the influence of the local morphological environment and potential defect–defect interactions. All defect-containing structures were fully relaxed using the same criteria as for pristine PE. The energetics of hydroxyl insertion into this cell, and the way they depend on where along the lamellar normal the oxygen is placed, are reported in Appendix A.

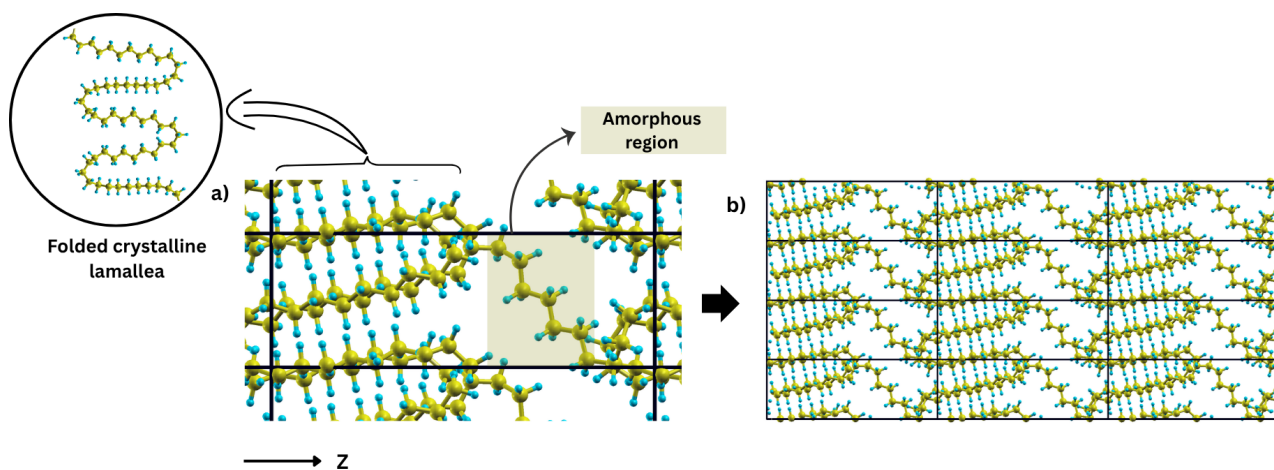


Figure 2.2: (a) Simulation cell for semicrystalline polyethylene with close-up of the folded crystalline lamellar model (yellow: C, cyan: H); (b) Full periodic supercell extended in all directions.

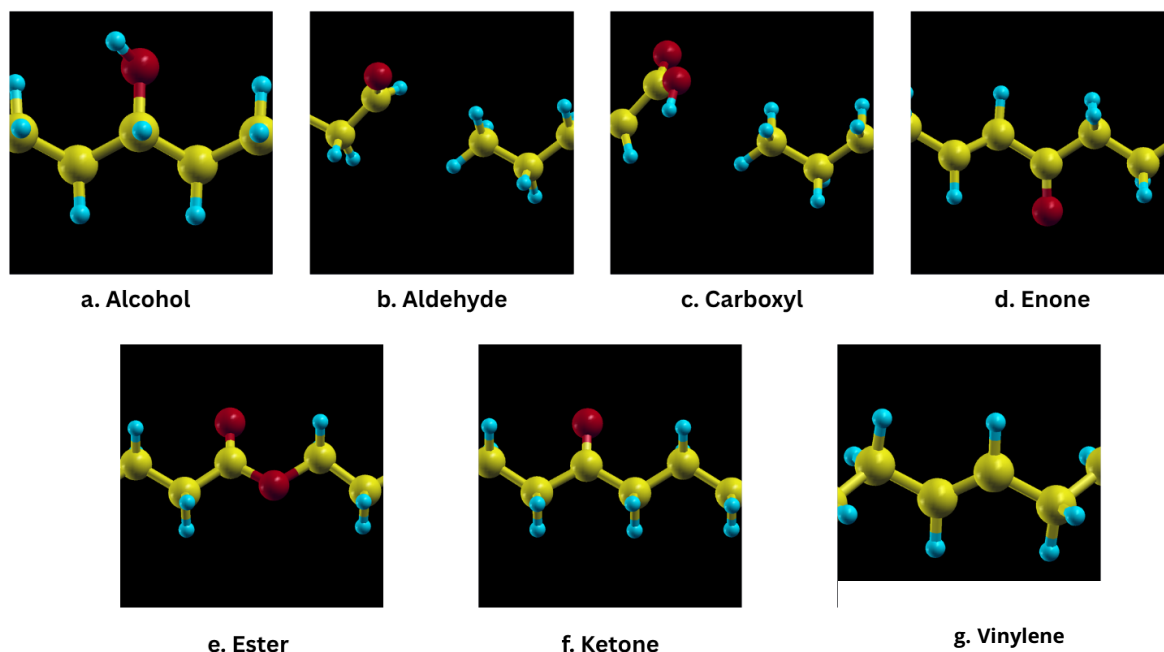


Figure 2.3: Representations of the seven defects introduced into the polyethylene backbone: (a) alcohol ($-\text{OH}$), (b) aldehyde ($-\text{CHO}$), (c) carboxylic acid ($-\text{COOH}$), (d) enone, (e) ester ($-\text{COO}-$), (f) ketone ($\text{C}=\text{O}$), and (g) vinylene ($\text{C}=\text{C}$). Colour code: yellow—C, cyan—H, red—O.

2.2.1. Position-Dependent Dielectric Profiles

The dielectric tensors obtained from DFPT describe the response of the simulation cell as a whole. They are therefore well suited for comparing the overall electronic and static permittivity of a molecular system. To resolve how dielectric response changes across the PE slab, a position-dependent dielectric profile $\varepsilon(z)$ was reconstructed from finite-field charge density differences. The method follows the microscopic polarization framework introduced by Giustino *et al.* [16] for slab and interface systems and later applied to polymer dielectric profiles by Shi and Ramprasad [17] and Yu *et al.* [18]. This analysis was used to resolve the changes in the electronic response from the vacuum region to the folded surface and into the crystalline interior and to determine how a chemical defect perturbs the local dielectric response when it is placed at different positions in the lamella. Figure 2.4 shows the PE structure used for this calculation. The folded slab is periodic in the two in-plane directions and contains vacuum on both sides along z , so that a saw-tooth electric field can be applied along the lamellar normal.

2.2.1.1 Finite-Field Charge-Density Difference

For each relaxed structure, two self-consistent field calculations were carried out with finite electric fields of equal magnitude and opposite sign along the z direction. The finite electric field was introduced in Quantum ESPRESSO through the saw-tooth potential method implemented in `pw.x` module. In this setup, an external electric field is applied with a dipole correction to reduce the artificial interaction between periodically repeated slab images. The direction of the field was set along the z axis, normal to the folded PE slab. The position and width of the discontinuity region of the saw-tooth potential is placed inside the vacuum part of the cell rather than inside the polymer slab. This choice ensures that a uniform electric field is applied along the PE lamella while the potential jump required by periodic boundary conditions is confined to the vacuum region. The production field amplitude was set to $E = 0.0015$ a.u., corresponding to approximately $0.077 \text{ V \AA}^{-1}$.

The electronic charge density from each finite-field calculation was extracted and the induced

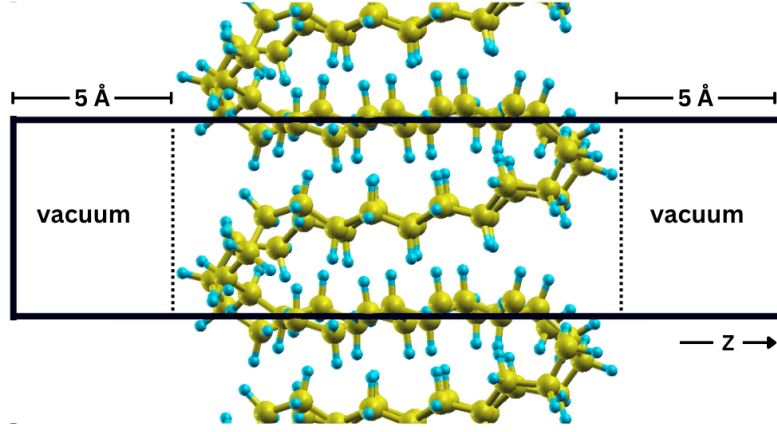


Figure 2.4: Folded semicrystalline polyethylene slab used for the position-dependent relative permittivity calculations. The finite electric field is applied along the slab-normal z direction.

planar-averaged charge density was then obtained with `average.x` from the weighted difference of the positive- and negative-field charge densities,

$$\bar{\rho}_{\text{ind}}(z) = \frac{1}{2} [\bar{\rho}_{+E}(z) - \bar{\rho}_{-E}(z)]. \quad (2.13)$$

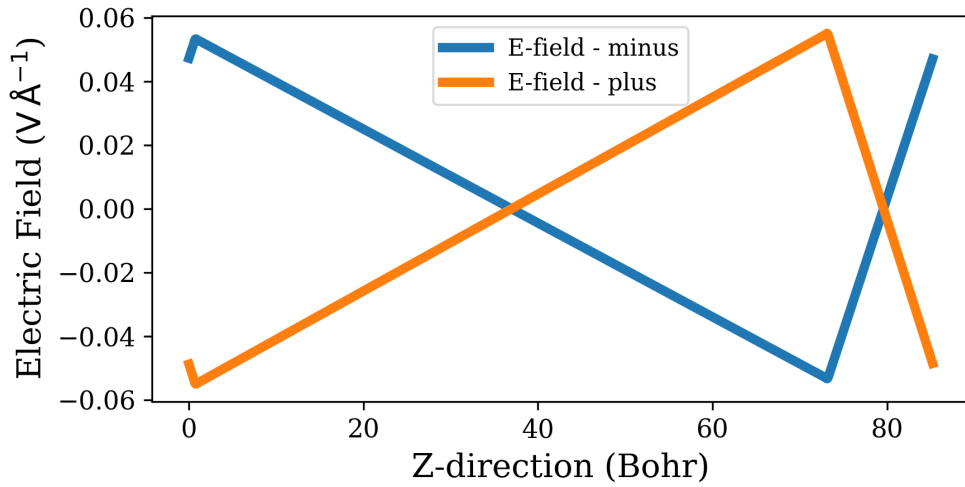


Figure 2.5: Positive and negative finite electric fields applied along the slab-normal direction for the reconstruction of the induced charge-density response.

2.2.1.2 Microscopic Polarization Theory

At the atomistic scale, the position-dependent polarization $\bar{p}(z)$ along the applied field direction is derived from the induced charge density $\bar{\rho}_{\text{ind}}(z)$ via Gauss's law.

$$\frac{d\bar{p}(z)}{dz} = -\bar{\rho}_{\text{ind}}(z), \quad (2.14)$$

where $\bar{\rho}_{\text{ind}}(z)$ is the planar-averaged induced charge density, obtained as the difference of total DFT charge densities computed under applied fields of $+E_{\text{ext}}$ and $-E_{\text{ext}}$ along the slab-normal direction:

$$\bar{\rho}_{\text{ind}}(z) = \frac{1}{2} [\bar{\rho}(z)|_{+E_{\text{ext}}} - \bar{\rho}(z)|_{-E_{\text{ext}}}] . \quad (2.15)$$

Integrating Eq. (2.14) from the vacuum region, where $\bar{p} = 0$ by construction, gives the polarization profile across the slab:

$$\bar{p}(z) = - \int_{-\infty}^z \bar{\rho}_{\text{ind}}(z') dz'. \quad (2.16)$$

The position-dependent relative permittivity can then be computed from the polarization profile [16, 17]:

$$\varepsilon(z) = \frac{\varepsilon_{\text{vac}} E_{\text{ext}}}{\varepsilon_{\text{vac}} E_{\text{ext}} - \bar{p}(z)}. \quad (2.17)$$

where ε_{vac} denotes the vacuum permittivity, written with a distinct subscript to avoid confusion with the static dielectric constant ε_0 of Eq. (2.9). In the vacuum regions $\bar{p}(z) = 0$ and $\varepsilon(z) = 1$, as required, providing a self-consistent boundary condition.

The calculated planar-averaged charge density contains microscopic oscillations from individual C–C and C–H bonds of PE. A macroscopic average was therefore applied along the field direction before reconstructing $\varepsilon(z)$. For the folded PE dielectric profiles, the macroscopic averaging length was set to 4.34 bohr (2.30 Å). This value was selected because it suppresses residual atomic-scale oscillations in the crystalline plateau while keeping the vacuum region close to $\varepsilon = 1$ and avoiding excessive broadening of the slab surfaces. Both parts of this convention were verified explicitly before use: the induced density was checked to scale linearly with the applied field amplitude, and the averaging length was selected by a stated rule rather than by inspection. Those consistency checks are described in Appendix B. The macroscopic polarization profile, $P_{\text{macro}}(z)$, reaches its largest and flattest values inside the polymer slab, where the material acts like a bulk dielectric. Therefore, the bulk dielectric constant was defined as the average of $\varepsilon(z)$ over the region where $P_{\text{macro}}(z)$ exceeds 70% of its maximum value. This threshold excludes points where the polarization is small at positions that lie in vacuum or near a surface transition. For each defect profile, the spatial perturbation relative to pristine PE was defined as

$$\Delta\varepsilon(z) = \varepsilon_{\text{defect}}(z) - \varepsilon_{\text{pristine}}(z), \quad (2.18)$$

and the corresponding bulk shift was

$$\Delta\varepsilon_{\text{bulk}} = \varepsilon_{\text{bulk,defect}} - \varepsilon_{\text{bulk,pristine}}. \quad (2.19)$$

The bulk shift measures whether a defect increases or decreases the plateau-averaged dielectric constant. Because the positive and negative lobes in $\Delta\varepsilon(z)$ can cancel in this scalar average, the full-profile root-mean-square perturbation over the slab was also calculated.

The finite electric field is applied along z , and thus the orientation of each defect relative to the field direction is a relevant descriptor for the local dielectric profile. The defect vectors were extracted from each relaxed structure. For carbonyl-containing defects, the C=O vector was used as the primary bond descriptor. For alcohol, both the C–O and O–H vectors were considered. For vinylene and the unsaturated part of enone, the C=C vector was used. The alignment between a defect vector and the applied field was then measured using the absolute value of its projection onto the z direction:

$$A_z = |\hat{\mathbf{u}} \cdot \hat{\mathbf{z}}|, \quad (2.20)$$

where $\hat{\mathbf{u}}$ is the unit vector along the selected bond or defect group, and $\hat{\mathbf{z}}$ is the unit vector along the applied field. With this definition, $A_z = 1$ means that the defect vector is parallel to the electric field, while $A_z = 0$ means that it is perpendicular to the field. Intermediate values describe partially aligned orientations.

2.3. Molecular Dynamics Simulations

2.3.1. Simulation Framework

Classical molecular dynamics (MD) was used to follow the time evolution of the polyethylene systems at the atomic scale. In this method, the motion of each atom is obtained by solving Newton's

equations of motion. The force acting on each atom comes from the gradient of the total potential energy, so the atomic trajectories are fully determined once the force field and the initial conditions are defined.

$$m_i \ddot{\mathbf{r}}_i(t) = \mathbf{F}_i(t) = -\nabla_{\mathbf{r}_i} U(\{\mathbf{r}\}), \quad i = 1, \dots, N, \quad (2.21)$$

where m_i and $\mathbf{r}_i$ are the mass and position of atom i , $\mathbf{F}_i$ is the force acting on that atom, and $U(\{\mathbf{r}\})$ is the total potential energy of the system. By integrating these equations over time, one obtains the atomic trajectories, from which structural, dynamical, and dielectric properties can be calculated as time averages over the simulation.

The equations of motion were integrated using the velocity-Verlet algorithm [19, 20], which is time-reversible, symplectic (preserving the phase-space volume), and provides second-order accuracy in the time step Δt . It updates the atomic positions first and then uses the new forces to update the velocities:

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t) \Delta t + \frac{1}{2} \frac{\mathbf{F}_i(t)}{m_i} \Delta t^2, \quad (2.22)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{\Delta t}{2m_i} [\mathbf{F}_i(t) + \mathbf{F}_i(t + \Delta t)]. \quad (2.23)$$

In this way, positions and velocities remain synchronized during the simulation, which is important for both thermodynamic and dynamical analyses.

2.3.2. Force-Field Description

2.3.2.1 OPLS-AA Force Field

The atomic interactions were described using the OPLS-AA (Optimized Potentials for Liquid Simulations—All Atom) force field [21]. This is a fixed-charge, all-atom force field that is widely used for organic molecules and polymers. In this model, the total potential energy is written as the sum of bonded and non-bonded contributions:

$$U = U_{\text{bond}} + U_{\text{angle}} + U_{\text{dihedral}} + U_{\text{improper}} + U_{\text{vdW}} + U_{\text{elec}}. \quad (2.24)$$

Bonded interactions. The bonded part of the force field describes bond stretching, angle bending, torsional rotation, and out-of-plane distortions. The bond-stretching and angle-bending terms were represented by harmonic functions:

$$U_{\text{bond}} = \sum_{\text{bonds}} K_r (r - r_0)^2, \quad (2.25)$$

$$U_{\text{angle}} = \sum_{\text{angles}} K_\theta (\theta - \theta_0)^2, \quad (2.26)$$

where K_r and r_0 are the bond force constant and equilibrium bond distance, and K_θ and θ_0 are the corresponding angle parameters. These terms keep the local molecular geometry close to its preferred bond lengths and bond angles.

Torsional rotations around bonds were described by the OPLS cosine-series form:

$$U_{\text{dihedral}} = \sum_{\text{dihedrals}} \left[\frac{K_1}{2} (1 + \cos \phi) + \frac{K_2}{2} (1 - \cos 2\phi) + \frac{K_3}{2} (1 + \cos 3\phi) + \frac{K_4}{2} (1 - \cos 4\phi) \right]. \quad (2.27)$$

which allows the force field to describe rotational barriers and preferred chain conformations. Improper dihedral terms were included where needed to preserve the planarity of sp^2 centers:

$$U_{\text{improper}} = K_\chi [1 + d \cos(n\chi)], \quad (2.28)$$

where K_χ is the force constant, $d = \pm 1$ sets the sign of the term, and n is its multiplicity.

Non-bonded interactions. The non-bonded interactions consist of van der Waals and electrostatic terms. The van der Waals contribution was modeled using a 12–6 Lennard-Jones potential:

$$U_{\text{vdW}}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \times S(r_{ij}), \quad (2.29)$$

where ϵ_{ij} and σ_{ij} are the mixed Lennard-Jones parameters for atom pair i – j , and $S(r_{ij})$ is the switching function used in the LAMMPS implementation to reduce the interaction smoothly to zero between 9.0 and 11.0 Å. Cross-interaction parameters were generated using geometric combining rules. The 1–2 and 1–3 non-bonded interactions were excluded, and the 1–4 Lennard-Jones and Coulomb interactions were scaled by a factor of 0.5, consistent with the OPLS-AA convention.

Electrostatic Coulomb interactions are long-ranged and decay at a rate of $1/r$ and therefore cannot be treated accurately by a simple short cutoff in a periodic system. For this reason, the long-range Coulomb interaction was handled using the particle–particle particle–mesh (PPPM) method [22], which is an efficient mesh-based implementation of Ewald summation [23]. In this method, the Coulomb interaction is divided into a short-range real-space contribution and a long-range reciprocal-space contribution. The long-range part is evaluated on a mesh using fast Fourier transforms, which greatly reduces the computational cost for large systems. A value of 10^{-5} was used, which controls the relative RMS error in the per-atom forces from the long-range solver.

2.3.2.2 Partial Charges and Cell Dipole Moment

OPLS-AA is a non-polarizable force field, and the dielectric response captured by the MD simulations therefore comes from the reorientation of permanent partial charges rather than from explicit electronic polarization. The partial charges assigned to the polyethylene backbone and to the defect groups are listed in Table 2.1. These charges were taken from the OPLS-AA parameter set and chosen so that each local chemical group remains charge neutral.

Table 2.1: Partial atomic charges (in units of e) assigned to the polyethylene backbone and polar defect groups in the OPLS-AA force field.

Group/Defect	Atomic site	Charge (e)
Backbone	C(CH ₃)	−0.180
	H(CH ₃)	+0.060
	C(CH ₂)	−0.120
	H(CH ₂)	+0.060
Alcohol	C(CHOH)	+0.205
	H(CHOH)	+0.060
	O(OH)	−0.683
	H(OH)	+0.418
Aldehyde	C(CHO)	+0.450
	H(CHO)	+0.000
	O(CHO)	−0.450
Ketone	C(CH ₂ –α)	−0.120
	C(CO)	+0.470
	O(CO)	−0.470
Ester	C(CH ₂ –α)	+0.190
	C(C=O)	+0.490
	O(C=O)	−0.410
	O(–OR)	−0.330

The total dipole moment of the simulation cell at time t was computed as

$$\mathbf{M}(t) = \sum_i q_i \mathbf{r}_i(t), \quad (2.30)$$

where q_i is the partial charge of atom i and $\mathbf{r}_i(t)$ is its position vector. In practice, the dipole moment is evaluated using unwrapped atomic positions, so that the result remained continuous when atoms crossed periodic boundaries. The bonded topology becomes more complex when polar defects are introduced into the polyethylene chain. For pristine polyethylene, the model requires 2 bond types (C–C and C–H), 3 angle types (C–C–C, C–C–H, and H–C–H), and 3 dihedral types. The alcohol defect adds the C–O and O–H bond types together with additional angle and dihedral terms, giving a total of 4 bond types, 6 angle types, and 7 dihedral types. The aldehyde defect introduces the terminal carbonyl group and requires an additional improper term to keep the carbonyl carbon planar. The ketone defect similarly introduces an in-chain carbonyl with 4 bond types, 7 angle types, and 9 dihedral types in total. The ester defect is the most complex of the four cases because the –COO– linkage introduces the largest number of new bonded interactions, requiring 6 bond types, 11 angle types, and 15 dihedral types, and 1 improper type.

2.3.3. Model Construction and Simulation Protocol

Initial atomistic models were generated using Moltemplate [4], which was used to build the molecular topology and assign the OPLS-AA force-field parameters. Each system consisted of a single linear polyethylene chain containing 2000 repeat units (CH_2). The desired defect groups were then inserted into the chain at concentrations of 2 or 4 mol %.

A multi-stage melt-quench procedure was used to generate semicrystalline morphologies from the initial extended-chain structures [24]:

1. **Energy minimization.** The initial structure was first relaxed using the conjugate-gradient method in order to remove close contacts and large residual forces.
2. **Melt equilibration at 600 K (NVT).** The system was heated to 600 K, which is above the experimental melting point of polyethylene, and equilibrated in the NVT ensemble so that the chain lost memory of the initial ordered configuration.
3. **Controlled cooling from 600 to 300 K (NPT).** The molten system was cooled to 300 K at a rate of 12 K / ns under the NPT ensemble at 1 atm using isotropic pressure coupling. This cooling rate is commonly used in atomistic polymer simulations to obtain realistic semicrystalline morphologies within accessible simulation times [24].
4. **NPT equilibration at 300 K.** After cooling, the system was equilibrated for 50 ns in the NPT ensemble to allow the density, box size, and lamellar packing to stabilize.
5. **Final NVT equilibration at 300 K.** A final 5 ns equilibration in the NVT ensemble was then carried out to fix the cell volume before the production simulations.

Production simulations were carried out for 100–200 ns depending on the defect type. Longer simulations were used for systems that showed slower relaxation, especially the alcohol defect systems. Thermodynamic quantities such as temperature, kinetic energy, potential energy, pressure, density, and volume were monitored throughout the simulations. The total dipole moment and its decomposition into subgroups were written every 100 fs using the `compute` and `fix ave/time` command framework in LAMMPS. Different statistical ensembles were used at different stages of the simulations. At the beginning of each run, atomic velocities were assigned from a Maxwell–Boltzmann distribution at the target temperature, and the net linear and angular momenta were removed.

The NVE ensemble keeps the number of particles, the volume, and the total energy constant. It was used for short validation checks and for monitoring the quality of the numerical integration.

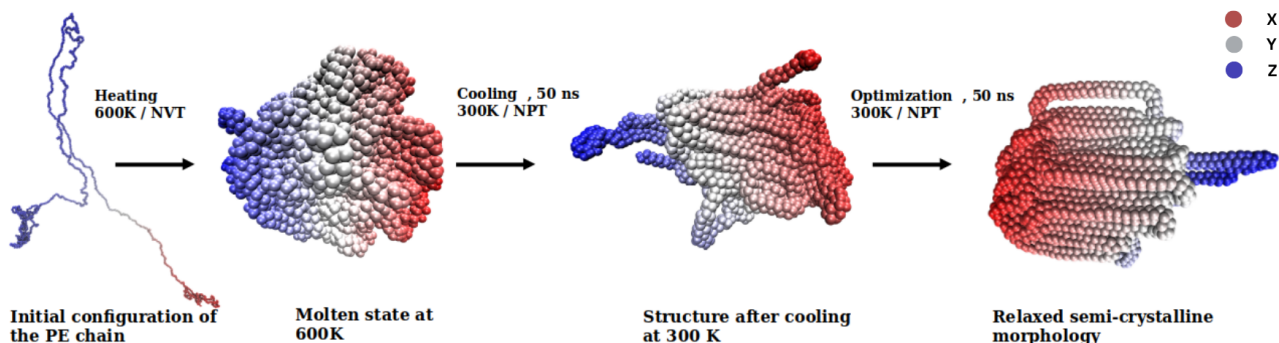
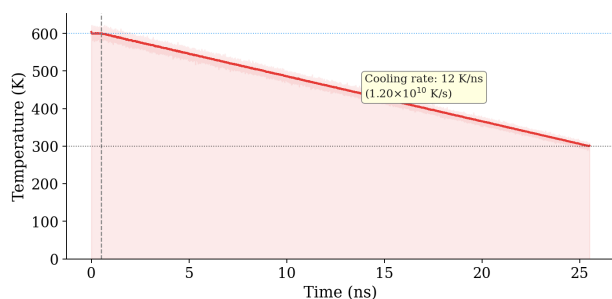
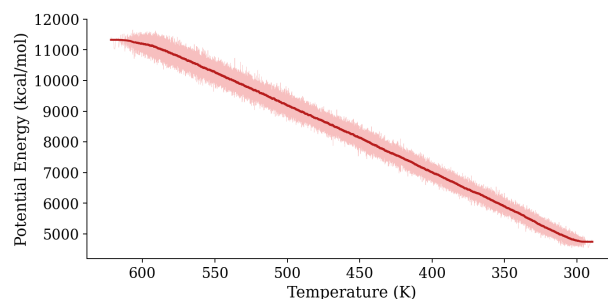


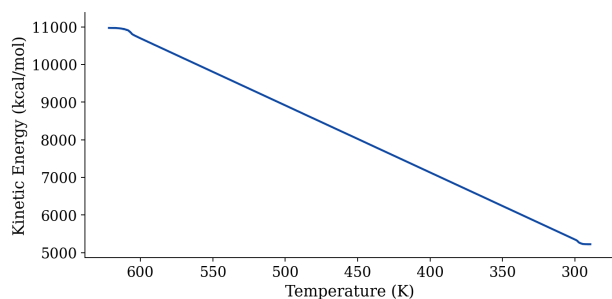
Figure 2.6: Illustration of the melt-quench protocol for generating a semicrystalline PE morphology. Starting from a single extended chain, the system is heated to 600 K (NVT) to produce a fully molten, disordered state, then cooled to 300 K at 12 K ns^{-1} under the NPT ensemble, and finally equilibrated for 50 ns (NPT) to obtain a well-ordered semicrystalline morphology. Chain segments colored red, gray, and blue denote orientation along the x , y , and z directions, respectively.



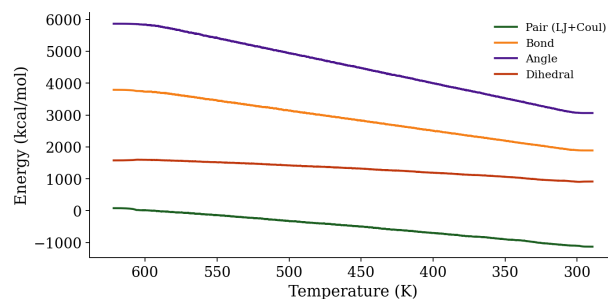
(a) Temperature vs. time during the controlled cooling stage.



(b) Potential energy as a function of temperature during cooling.



(c) Kinetic energy as a function of temperature during cooling.



(d) Force-field energy components (pair, bond, angle, dihedral) as a function of temperature during cooling.

Figure 2.7: Thermodynamic monitoring during the cooling stage (step 3 of the melt-quench protocol) for pristine PE system cooled from 600 K to 300 K at 12 K ns^{-1} .

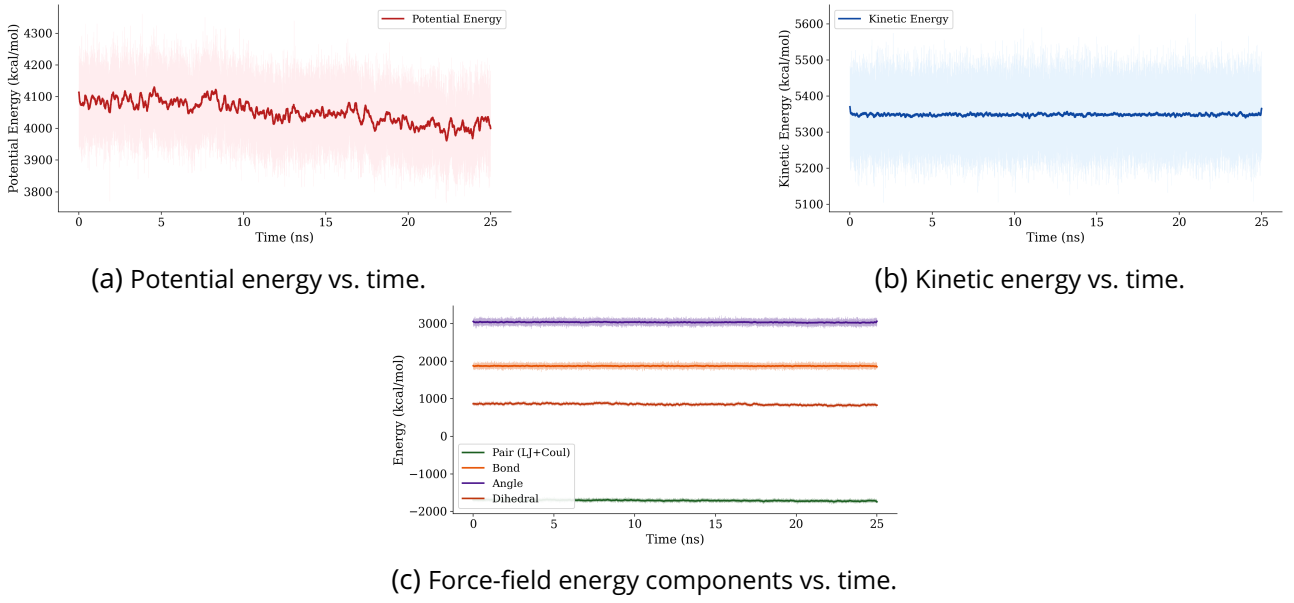


Figure 2.8: Equilibration quality during equilibration at 300 K (NVT ensemble).

The NVT ensemble keeps the number of particles, the volume, and the temperature constant. Temperature control was applied using the Nosé–Hoover thermostat [25, 26] with a damping constant of $\tau_T = 100 \Delta t$. For a time step of 1 fs, this corresponds to a thermostat damping time of 100 fs.

The NPT ensemble keeps the number of particles, the pressure, and the temperature constant. Pressure and temperature were controlled using the Nosé–Hoover thermostat–barostat scheme with damping constants of 100 fs for temperature and 1000 fs for pressure. Isotropic pressure control was used so that the simulation box could expand or contract uniformly in all directions.

2.3.4. Structural Analysis

To estimate the degree of crystallinity, a local bond-orientational order parameter was calculated for the polyethylene backbone [24]. For each backbone carbon atom, a local orientation vector was defined from the midpoints of its two adjacent backbone bonds. The alignment between neighboring orientation vectors was then measured using the second Legendre polynomial:

$$P_2(\cos \theta) = \frac{3 \cos^2 \theta - 1}{2}, \quad (2.31)$$

where θ is the angle between two local orientation vectors. For each carbon atom i , a local orientational order parameter $\bar{P}_{2,i}$ was obtained by averaging P_2 over all neighboring backbone carbons within a cutoff distance of 7 Å. A carbon atom was classified as crystalline when $\bar{P}_{2,i} > 0.6$, and the overall crystallinity was then defined as the fraction of backbone carbon atoms that satisfied this condition.

2.3.5. Dielectric Analysis

2.3.5.1 Static Dielectric Constant from Dipole Fluctuations

The static dielectric constant was obtained from the equilibrium fluctuations of the total dipole moment using the Neumann fluctuation formula [27]:

$$\varepsilon(0) = \varepsilon_\infty + \frac{\langle |\mathbf{M}|^2 \rangle - |\langle \mathbf{M} \rangle|^2}{3 \varepsilon_{\text{vac}} V k_B T}, \quad (2.32)$$

where V is the simulation-cell volume, T is the temperature, ε_{vac} is the vacuum permittivity, and ε_∞ is the high-frequency dielectric constant taken from the DFPT calculations. In this way, the electronic

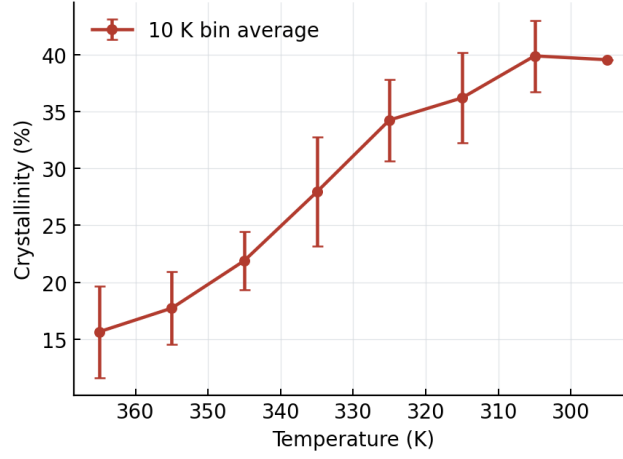


Figure 2.9: Crystallinity of pristine polyethylene during cooling from 600 K to 300 K, calculated from the local backbone orientational order parameter.

contribution from the first-principles calculations was combined with the orientational contribution sampled in the MD simulations. Because the second moment of the total dipole converges slowly, the running cumulative average of $\varepsilon(0)$ was monitored as a function of time. In all systems, this quantity reached a plateau within 40–80 ns.

2.3.5.2 Dipole Autocorrelation Function

To characterize dipolar relaxation, the normalized autocorrelation function of the fluctuating total dipole moment was computed as

$$\phi(t) = \frac{\langle \delta \mathbf{M}(0) \cdot \delta \mathbf{M}(t) \rangle}{\langle |\delta \mathbf{M}(0)|^2 \rangle}, \quad (2.33)$$

where $\delta \mathbf{M}(t) = \mathbf{M}(t) - \langle \mathbf{M} \rangle$. This function describes how quickly the system loses memory of its initial dipolar orientation. The decay of $\phi(t)$ was fitted using a Kohlrausch–Williams–Watts (KWW) stretched-exponential function [28, 29]:

$$\phi(t) = A \exp \left[- \left(\frac{t}{\tau_{\text{KWW}}} \right)^\beta \right], \quad (2.34)$$

where τ_{KWW} is the characteristic relaxation time, β ($0 < \beta \leq 1$) describes the breadth of the relaxation-time distribution, and A accounts for any unresolved short-time decay or imperfect normalization at the first time points. The corresponding mean relaxation time of the fitted function is

$$\langle \tau \rangle = \frac{A \tau_{\text{KWW}}}{\beta} \Gamma \left(\frac{1}{\beta} \right), \quad (2.35)$$

where Γ is the gamma function.

2.3.5.3 Dipole Decomposition into Defect, Matrix, and Cross Terms

To separate the contribution of the defect dipoles from that of the polyethylene matrix, the total dipole moment was decomposed as $\mathbf{M}_{\text{tot}} = \mathbf{M}_{\text{def}} + \mathbf{M}_{\text{mat}}$. The corresponding unnormalized dipole autocorrelation function was then written as

$$C_{\text{tot}}(t) = C_{\text{self,def}}(t) + C_{\text{self,mat}}(t) + C_{\text{cross}}(t), \quad (2.36)$$

where the cross term contains the defect–matrix correlation contribution. Each component was normalized separately and weighted by its zero-time contribution, $w_i = C_i(0)/C_{\text{tot}}(0)$, which is equivalent

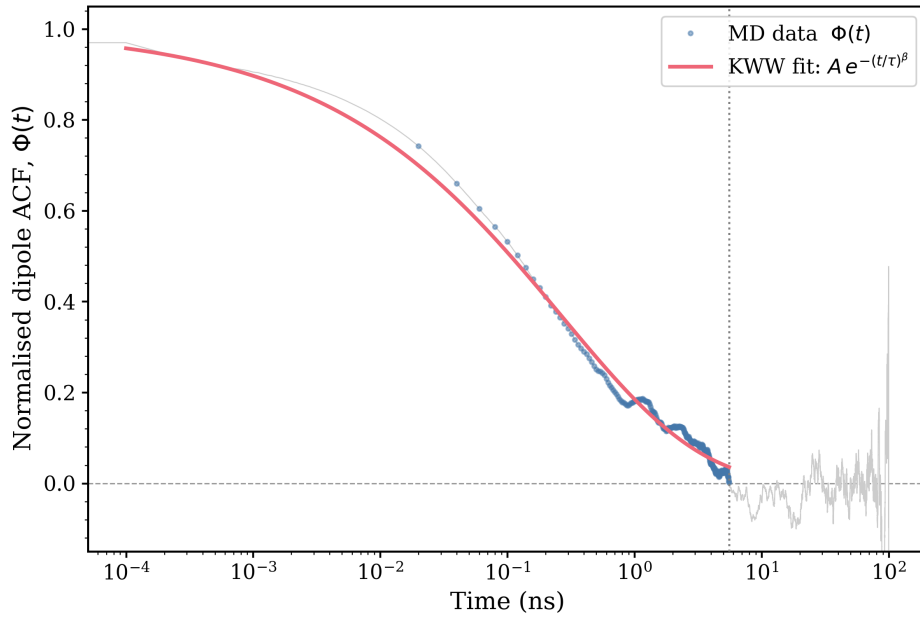


Figure 2.10: Normalised dipole autocorrelation function $\phi(t)$ for a PE system with 2 mol % ketone. The vertical dotted line marks the characteristic relaxation time τ_{KWW} ; the ACF noise beyond this point (gray shading) reflects finite-simulation-time statistical uncertainty.

to $w_i = \Delta\varepsilon_i / \Delta\varepsilon_{\text{total}}$. The total normalized autocorrelation function is then recovered as

$$\phi_{\text{tot}}(t) = w_{\text{def}} \phi_{\text{def}}(t) + w_{\text{mat}} \phi_{\text{mat}}(t) + w_{\text{cross}} \phi_{\text{cross}}(t). \quad (2.37)$$

The weight factors satisfy $w_{\text{def}} + w_{\text{mat}} + w_{\text{cross}} = 1$. The cross term can be negative when the defect and matrix dipoles tend to reorient in opposite directions, which indicates anti-correlated dipolar motion [30, 31].

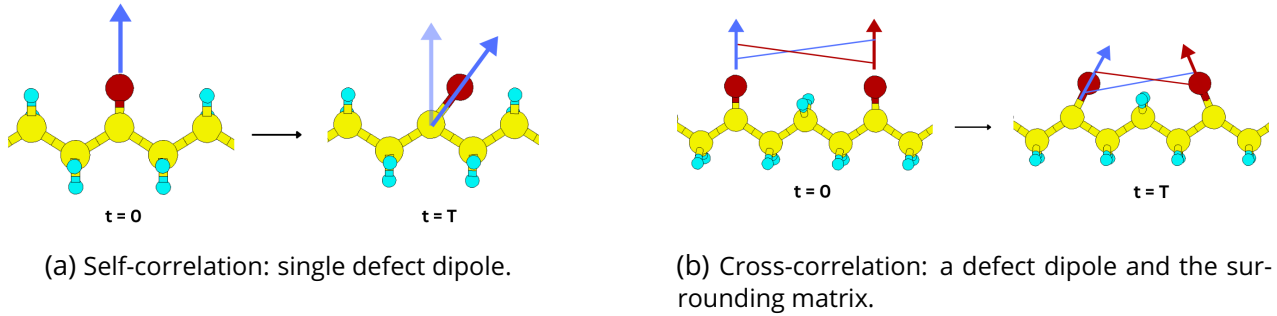


Figure 2.11: Schematic illustration of the dipole-moment decomposition. (a) The self-correlation term captures the reorientation of a single defect dipole (blue arrow) from $t = 0$ to $t = T$; the original direction is shown in light blue for reference. (b) The cross-correlation term captures the relative change in orientation between two distinct defect dipoles (blue and red) from $t = 0$ to $t = T$. A negative cross-term indicates that the two dipoles tend to reorient in opposite directions (anti-correlated motion). Yellow: C, cyan: H, red: O.

2.3.5.4 Frequency-Dependent Dielectric Response

The complex dielectric permittivity was obtained from the Fourier-Laplace transform of the fitted dipole autocorrelation function. Using the convention $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, the frequency-dependent dielectric response is written as

$$\varepsilon^*(\omega) - \varepsilon_\infty = [\varepsilon(0) - \varepsilon_\infty] \int_0^\infty \left(-\frac{d\phi}{dt} \right) e^{-i\omega t} dt. \quad (2.38)$$

The dielectric loss spectrum is then

$$\varepsilon''(\omega) = [\varepsilon(0) - \varepsilon_\infty] \omega \int_0^\infty \phi(t) \cos(\omega t) dt. \quad (2.39)$$

This representation makes it possible to connect the time-domain dipolar relaxation observed in the MD simulations with the frequency-domain dielectric response. The dielectric loss spectrum was further decomposed into defect-self, matrix-self, and cross contributions using the same weights and component autocorrelation functions introduced in Eq. (2.37) [30].

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3 – Dielectric Response of Polyethylene from DFT/DFPT

This chapter describes the application of the DFT, DFPT, and finite-field dielectric-profile methods to polyethylene (PE) models subjected to radio-oxidative aging. This study tries to examine how oxidation-induced defects modify the electronic and ionic contributions to the dielectric response, and how this response changes when the same type of defect is placed in different local environments of a folded lamellar morphology. The chapter is organized in three steps. First, the dielectric response of pristine PE is examined using crystalline, amorphous, and semicrystalline structural models. Second, seven defect chemistries are compared at 2 and 4 mol % using DFPT dielectric tensors, Born effective charges, and mode-resolved phonon analysis. Finally, position-dependent dielectric profiles are calculated for folded-PE slabs to evaluate local dielectric redistribution.

3.1. Morphology-Dependent Dielectric Response of Pristine PE

The morphology of polyethylene strongly affects its structural, electronic, and dielectric properties, so the choice of atomistic model must be treated carefully for reliable dielectric calculations. Semicrystalline PE contains ordered crystalline lamellae, disordered amorphous regions, and interfacial folded-chain regions. Previous studies show that these environments differ in chain packing, electronic structure, and local dielectric response [1–4]. Therefore, the finite DFT models used here should be interpreted as controlled local representations of PE morphology, not as complete experimental samples. Unge et al. [1] studied crystalline, amorphous, and folded-interface PE models using DFT and showed that the crystal-amorphous interface can have a smaller gap than the fully amorphous and crystalline PE model structures. Moyassari et al. [2] reached a similar conclusion for explicit semicrystalline PE, reporting a band gap of 5.82 eV, below the amorphous and crystalline values. Chen, Huan, and Ramprasad further showed that chemical defects, morphology, and interfaces can modify the electronic structure of PE [3]. Misra et al. [4] demonstrated that morphology is also critical for dielectric response, because idealized ordered models alone do not fully capture the ionic contribution expected in semicrystalline polyolefins.

To isolate the role of morphology in the dielectric response, three pristine PE models were compared. A fully crystalline model containing four parallel chains in orthorhombic packing with a density of 1.08 g cm^{-3} . The amorphous model contains 42 methylene units with disordered chain orientations. The semicrystalline lamellar model contains 50 CH_2 units and combines an ordered lamellar region, folded-chain interfacial environments, and a more disordered amorphous-like segment, giving a global average density of 0.88 g cm^{-3} . The calculated dielectric constants are summarized in Table 3.1. The crystalline model gives the largest values, with $\epsilon_\infty = 2.70$ and $\epsilon_0 = 2.73$. The dielectric tensor is anisotropic: the component along the chain direction is larger than the transverse components, with $\epsilon_\infty, z = 2.90$ compared with ϵ_∞, x and ϵ_∞, y near 2.56. The same pattern, which is expected because the PE chains are oriented along z , is also found for ϵ_0 . The amorphous model gives $\epsilon_\infty = 2.38$ and $\epsilon_0 = 2.44$ and is nearly isotropic because the random chain orientations average out the single-chain anisotropy. The semicrystalline lamellar model gives $\epsilon_\infty = 2.23$ and $\epsilon_0 = 2.26$, with tensor components that differ by about 1% or less.

Experimental measurements place the real dielectric constant of polyethylene close to the value obtained for the semicrystalline DFPT model. Conklin et al. [5] measured highly crystalline Marlex 6050 polyethylene at 55.2 GHz and reported $\epsilon' = 2.39$ at room temperature. Ashcraft and Boyd measured oxidized and chlorinated polyethylene over 10 Hz–10 kHz, extended to 100 kHz for chlorinated samples, and their linear PE dielectric-constant curves lie around $\epsilon' = 2.36$ – 2.39 [6]. Chao et al. measured commercial PE plastics by a microwave resonant-cavity method and reported bulk values of

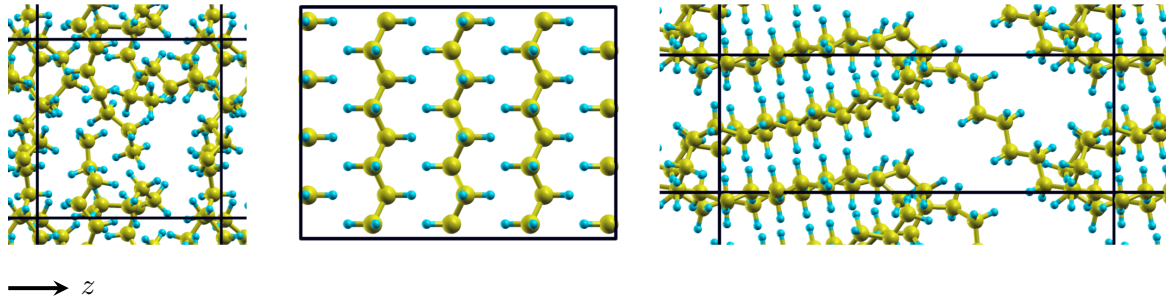


Figure 3.1: Snapshots of the equilibrated PE models used to compare morphology-dependent dielectric response. From left to right: amorphous PE with disordered chain orientation, crystalline PE with ordered orthorhombic packing, and a semicrystalline folded-chain interphase model. Yellow spheres represent carbon atoms and blue spheres represent hydrogen atoms.

2.29 for HDPE, 2.09 for LLDPE, and 2.30 for LDPE [7]. The semicrystalline model value, $\epsilon_0 = 2.26$, falls within this experimental PE range and therefore provides a suitable reference morphology for the following defect calculations.

Table 3.1: DFPT-computed dielectric constants of pristine polyethylene for three models. The anisotropy ratio $\epsilon_z/\epsilon_{x,y}$ quantifies the directional contrast along vs. perpendicular to the chain axis.

Morphology	ϵ_∞	ϵ_0	$\Delta\epsilon$	$\epsilon_z/\epsilon_{x,y}$
Crystalline	2.70	2.73	0.03	~ 1.13
Amorphous	2.38	2.44	0.06	~ 1.00
Semicrystalline	2.23	2.26	0.03	~ 1.01

These findings highlight the advantage of the semicrystalline model in capturing the dielectric response of real polyethylene, as it provides a more realistic representation of the dielectric behavior of practical PE systems than either the fully amorphous or fully crystalline limit. While crystalline domains exhibit pronounced anisotropic polarization at the local scale, their coexistence with amorphous regions leads to an overall response that is effectively isotropic at the macroscopic level. Accordingly, all subsequent DFPT calculations reported in this work are based on the semicrystalline slab model, ensuring that both the baseline dielectric response and the defect-induced variations are assessed in a structurally representative PE environment.

3.2. DFPT Defect Results

3.2.1. High-Frequency Dielectric Constant

The high-frequency dielectric constant, ϵ_∞ , measures the electronic response of the system to an electric perturbation while the ions remain fixed. In the DFPT results below, scalar values are reported as isotropic averages of the diagonal tensor components, $(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})/3$. This quantity isolates how a defect changes the electronic polarizability of the PE cell before any lattice relaxation or IR-active phonon response is included [8–10]. The pristine semicrystalline PE model gives ϵ_∞ of 2.23, which is used as the reference to evaluate the PE models with defects. The defective systems are then compared at concentrations of 2 and 4 mol%, in order to determine how the electronic response changes with defect chemistry.

Figure 3.2a presents the DFPT-computed high-frequency dielectric constant as a function of the type and concentration of the defect, compared to the pristine PE value. In the high-frequency regime, defect-induced changes in ϵ_∞ directly provide an analysis of how each functional group modifies the

electronic polarizability of the PE matrix [10, 11]. This change occurs over a narrow range, with all defective cells remaining between approximately 2.20 and 2.26. The magnitude and sign of the shift in ϵ_∞ are specific to the chemical nature of the defect. The calculated trends are separated into two groups. Enone, alcohol, ketone and vinylene increase ϵ_∞ relative to pristine PE, whereas aldehyde, ester, and carboxylic-acid defects reduce it. Alcohol and enone give the clearest enhancement of the electronic response, increasing ϵ_∞ from the pristine value to 2.244–2.245 at 2 mol % and 2.254–2.257 at 4 mol %. Ketone also produces a smaller positive shift, reaching $\epsilon_\infty = 2.243$ at 4 mol %. Vinylene is nearly neutral: its value remains close to pristine PE at 2 mol % and increases only slightly at 4 mol %, to about 2.236. In contrast, aldehyde, ester, and carboxylic-acid defects reduce the ϵ_∞ relative to pristine PE, particularly at 4 mol %. Ester and aldehyde show the largest reductions, reaching $\epsilon_\infty = 2.199$ and 2.203, respectively, while carboxylic acid remains intermediate at about 2.22. These decreases show that the introduction of a polar oxygen-containing group does not necessarily translate into an increase in the net electronic polarizability of the complete PE matrix. The sign of the response reflects the combined effect of local chemical polarizability, structural relaxation, density redistribution, and defect-modified electronic structure.

This distinction is important for interpreting the later static dielectric results. The high-frequency data establish that the electronic contribution changes by only a few percent across the defect series, whereas the static dielectric constant changes much more strongly once IR-active lattice modes are included.

3.2.2. Static Dielectric Constant

The static dielectric constant, ϵ_0 , is the zero-frequency harmonic response from DFPT. Unlike ϵ_∞ , ϵ_0 includes both the electronic contribution and the lattice contribution from zone-center IR-active phonon modes. The mode-resolved expression introduced in the methodology chapter shows that the lattice term depends on the oscillator strength of each polar phonon and is weighted by the inverse square of the phonon frequency. Thus, a defect can raise ϵ_0 strongly only when its dynamical charges couple to sufficiently low-frequency IR-active motions [8, 9].

Figure 3.2b presents the DFPT-computed ϵ_0 values as a function of defect type and concentration, referenced against the pristine PE value of 2.258. The error bars represent the configurational spread arising from different defect placements in the supercell, while the connecting lines are guides to the eye for the two concentration points. All seven defect groups raise ϵ_0 relative to pristine PE at both concentrations, in clear contrast to the mixed behavior observed for ϵ_∞ . At 2 mol %, most defect-induced changes are small and overlap within the configurational scatter. The calculated trends are summarized in Table 3.2. At 4 mol % concentration, aldehyde gives the largest static dielectric constant, $\epsilon_0 = 2.431$, followed by alcohol (2.414), carboxyl (2.381), enone (2.377), ketone (2.374), ester (2.330), and vinylene (2.270). Compared to the pristine value, these correspond to increases of approximately 7.7%, 6.9%, 5.4%, 5.2%, 5.1%, 3.2%, and 0.5%, respectively. Thus, except for vinylene, which remains very close to pristine PE, oxidative defects produce a measurable enhancement of the intrinsic harmonic static response. This indicates that each defect introduces additional polarization channels, even when its effect on the purely electronic contribution is weak or negative.

The sensitivity of ϵ_0 is seen directly from the ionic increment ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$). At 4 mol %, aldehyde has the largest increment, $\Delta\epsilon = 0.228$, whereas vinylene remains close to the pristine case, increasing only to $\Delta\epsilon = 0.034$. Alcohol also shows an increase, $\Delta\epsilon = 0.158$, while carboxyl, ketone, ester, and enone form an intermediate group with $\Delta\epsilon$ values of approximately 0.12–0.16. The trends in Figure 3.2b and Table 3.2 also show that the ranking of ϵ_0 cannot be evaluated from ϵ_∞ alone. Aldehyde and ester illustrate this point clearly. Aldehyde lowers ϵ_∞ relative to pristine PE but gives the largest ϵ_0 , indicating that its static enhancement is driven by IR-active lattice modes. Ester, in contrast, has large carbonyl-related Born effective charges but produces only a moderate ionic increment. This difference is consistent with the mode-resolved DFPT expression in Chapter 2, Eq. (2.9): large atomic dynamical charges increase the possibility of a strong lattice response, but the final contribution de-

depends on how those charges project onto phonon eigenvectors and on the inverse square weighting by phonon frequency. A large static dielectric contribution therefore requires a strongly polar normal mode at sufficiently low frequency, not merely a polar functional group.

The resulting 4 mol % ranking can therefore be interpreted as follows. Aldehyde is the most effective defect for enhancing the intrinsic harmonic static dielectric response because its polar lattice modes are strongly weighted at low frequency. Alcohol also couples efficiently with IR-active vibrations, although its enhancement is distributed differently over the phonon spectrum. Carboxyl, ketone, enone, and ester produce intermediate static responses, reflecting a balance between dynamical charge and mode stiffness. Vinylene is the weakest contributor because the C = C unit introduces little polar lattice activity in the PE matrix. Overall, the static DFPT results show that chemical defects modify the PE permittivity primarily by creating new or stronger vibrational polarization channels, while the electronic contribution remains comparatively weakly perturbed.

Aldehyde, despite having the smallest carbonyl-related Born effective charges among the oxygen-containing carbonyl defects considered, exhibits the largest ionic increment. This indicates that the large increase in ϵ_0 cannot be attributed to Born effective charge magnitude alone and is instead consistent with a particularly strong contribution from low-frequency IR-active modes through the $1/\omega_m^2$ weighting in the mode-resolved DFPT expression in Chapter 2, Eq. (2.9). Ester provides the complementary case: although it carries the largest carbonyl-related Born effective charges, its ionic increment is more moderate ($\Delta\epsilon = 0.131$), consistent with a smaller contribution from low-frequency polar modes.

Carboxyl, ketone, and enone form an intermediate group at 4 mol %, with ϵ_0 values between 2.374 and 2.381 and ionic increments of approximately 0.123–0.159. Alcohol belongs to the more strongly enhancing class, suggesting that hydroxyl-containing defects can also couple efficiently to IR-active lattice modes. Vinylene stands apart from all other defects: its static dielectric constant remains only slightly above that of pristine PE, and its ionic increment is the smallest in the series. This weak response is consistent with the near-symmetric nature of the C = C unit, which carries only small dynamical charges and therefore contributes little to the IR-active lattice polarization. Overall, the static DFPT results show that oxygenated defects modify PE permittivity mainly by opening additional vibrational polarization channels.

Table 3.2: DFPT-computed isotropic-average dielectric constants for pristine and defected PE. ϵ_∞ is the electronic high-frequency dielectric constant, ϵ_0 is the static dielectric constant, and $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ is the ionic/lattice increment. Defects are ordered by decreasing ϵ_0 at 4 mol %.

Defect	2 mol %			4 mol %		
	ϵ_∞	ϵ_0	$\Delta\epsilon$	ϵ_∞	ϵ_0	$\Delta\epsilon$
Pristine PE	2.232	2.258	0.026	–	–	–
Aldehyde	2.220	2.333	0.114	2.203	2.431	0.228
Alcohol	2.244	2.327	0.083	2.257	2.414	0.157
Carboxyl	2.227	2.309	0.082	2.222	2.381	0.159
Enone	2.245	2.327	0.082	2.254	2.377	0.123
Ketone	2.236	2.317	0.080	2.243	2.374	0.131
Ester	2.216	2.293	0.077	2.199	2.330	0.131
Vinylene	2.234	2.265	0.031	2.236	2.270	0.034

3.2.3. Born Effective Charges

Born effective charges provide the link between chemical bonding and lattice polarization. In DFPT, the Born effective charge tensor of atom κ , $\mathbf{Z}_\kappa^*$, measures the change in macroscopic polariza-

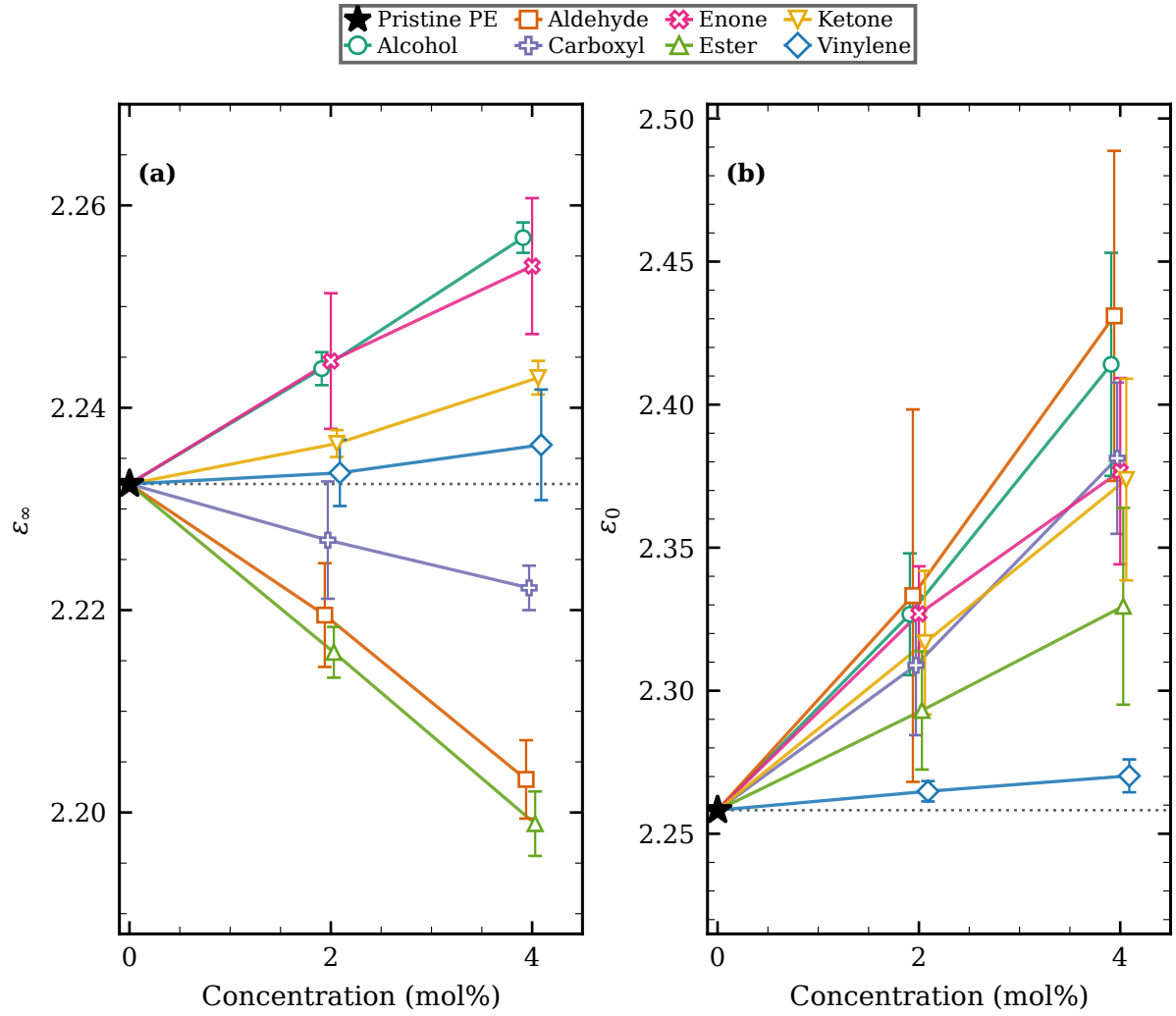


Figure 3.2: DFPT-computed dielectric constants as a function of defect concentration. Panel (a) compares the high-frequency dielectric constant ϵ_∞ for different defects, and panel (b) compares the static dielectric constant ϵ_0 against the pristine PE reference. Error bars represent configurational standard deviations over different defect placements in the supercell.

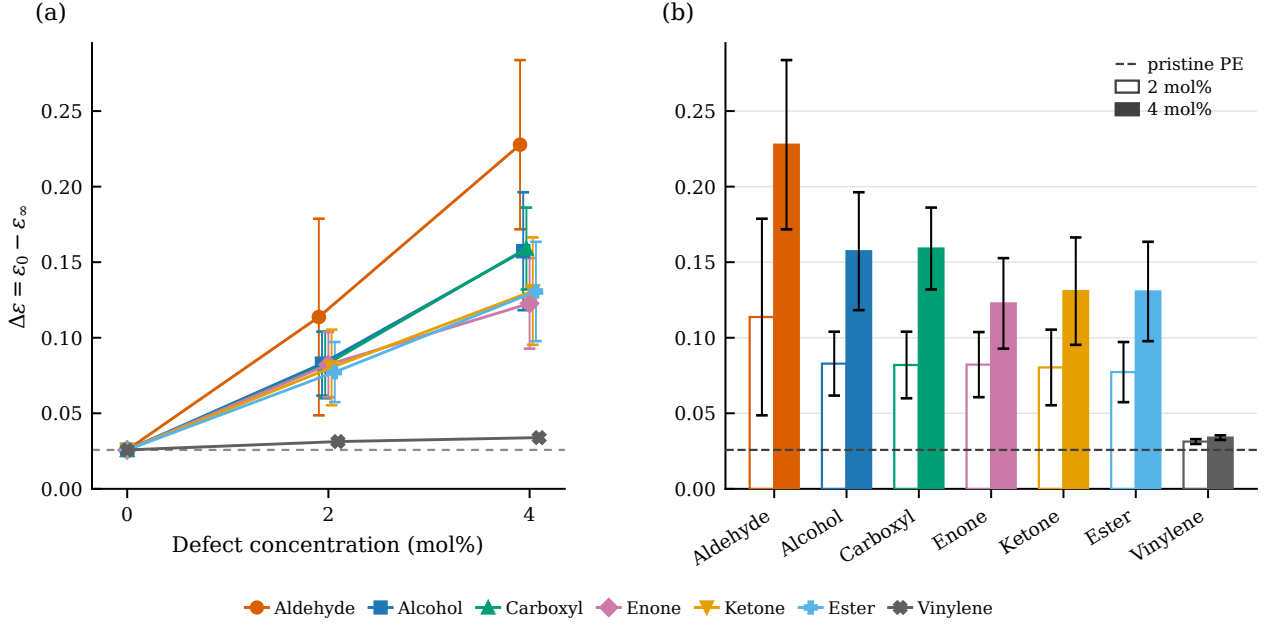


Figure 3.3: Ionic/lattice increment, $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$, for the defect series at 2 and 4 mol %. This figure isolates the contribution that differentiates the static dielectric response from the high-frequency electronic response.

tion caused by an atomic displacement, or equivalently the force induced on that atom by an electric field [8, 9]. Table 3.3 reports isotropic averages, $Z^* = \text{Tr}(\mathbf{Z}^*)/3$, for chemically active atoms in the 4 mol % defective systems after applying the acoustic sum rule. The reported values are averaged across multiple defect configurations, with standard deviations reflecting the underlying configurational variance.

Pristine PE has only small dynamical charges, $Z_C^* = +0.101 \pm 0.028$ and $Z_H^* = -0.052 \pm 0.016$, consistent with the weak polarity of the $-\text{CH}_2-$ repeat unit. Oxidized defects introduce much larger dynamical charges. For carbonyl-containing defects, the carbonyl carbon is strongly positive and follows the order aldehyde (+0.95), ketone (+1.04), enone (+1.22), carboxyl (+1.37), and ester (+1.41). The corresponding carbonyl oxygen atoms carry large negative values between -0.88 and -1.08 . These values identify the $\text{C}=\text{O}$ unit as a major local source of dynamical polarity in oxygenated PE defects. The stretching or bending motions of $\text{C}=\text{O}$ can generate an oscillating dipole and can therefore contribute to the lattice dielectric response. The alcohol system shows large dynamical charges on oxygen and polar hydrogen atoms of the $\text{O}-\text{H}$ group, with $Z^*(\text{O}_{\text{OH}}) = -0.84$ and $Z^*(\text{H}_{\text{pol}}) = +0.33$. Carboxyl ($-\text{COOH}$) also contains an $\text{O}-\text{H}$ group with $Z^*(\text{O}_{\text{OH}}) = -0.91$ and $Z^*(\text{H}_{\text{pol}}) = +0.38$. In enone, dynamical charge is distributed across the conjugated $\text{C}=\text{C}-\text{C}=\text{O}$ unit, with the adjacent sp^2 carbon carrying $Z^*(\text{C}_{\text{sp}^2}) = +1.13 \pm 0.07$. Vinylene, by contrast, has a small isotropic average on the two carbon atoms forming the $\text{C}=\text{C}$ bond, -0.08 ± 0.03 , close to the pristine backbone scale.

Comparison of Tables 3.3 and 3.2 shows that Born effective charges identify atoms that can participate in lattice polarization, but do not by themselves determine the final ranking of $\Delta\epsilon$. Ester has the largest carbonyl-related Born-charge isotropic averages in the series, yet its ionic increment is moderate. Aldehyde has smaller carbonyl-related isotropic averages than ester or carboxyl, but gives the largest $\Delta\epsilon$. The static lattice response is therefore controlled not only by local dynamical charge magnitude, but also by how these charges project onto low-frequency IR-active phonon modes.

3.2.4. Mode-Resolved Phonon Analysis

Born effective charges show which atoms can generate polarization under displacement, but they do not show whether the relevant displacements occur in modes that strongly affect ϵ_0 . For this rea-

Table 3.3: Isotropic Born effective charge averages, $Z^* = \text{Tr}(\mathbf{Z}^*)/3$, for chemically active atoms in the 4 mol % defective PE systems. Values are mean $\pm$ standard deviation over available configurations. O_{br} denotes the single-bonded bridging oxygen in ester. A dash indicates that the chemical role is absent for that defect.

Defect	Carbon		Oxygen			Hydrogen
	$Z^*(\text{C}_{\text{C=O}})$	$Z^*(\text{C}_{\text{sp}^2})$	$Z^*(\text{O}_{\text{C=O}})$	$Z^*(\text{O}_{\text{br}})$	$Z^*(\text{O}_{\text{OH}})$	$Z^*(\text{H}_{\text{pol}})$
Alcohol	-	-	-	-	-0.84 ± 0.03	$+0.33 \pm 0.02$
Aldehyde	$+0.95 \pm 0.02$	-	-0.88 ± 0.02	-	-	$+0.05 \pm 0.01$
Ketone	$+1.04 \pm 0.06$	-	-0.91 ± 0.03	-	-	-
Ester	$+1.41 \pm 0.06$	-	-1.08 ± 0.09	-0.99 ± 0.09	-	-
Carboxyl	$+1.37 \pm 0.03$	-	-0.95 ± 0.06	-	-0.91 ± 0.06	$+0.38 \pm 0.02$
Enone	$+1.22 \pm 0.06$	$+1.13 \pm 0.07$	-0.96 ± 0.04	-	-	-
Vinylene	-	-0.08 ± 0.03	-	-	-	-

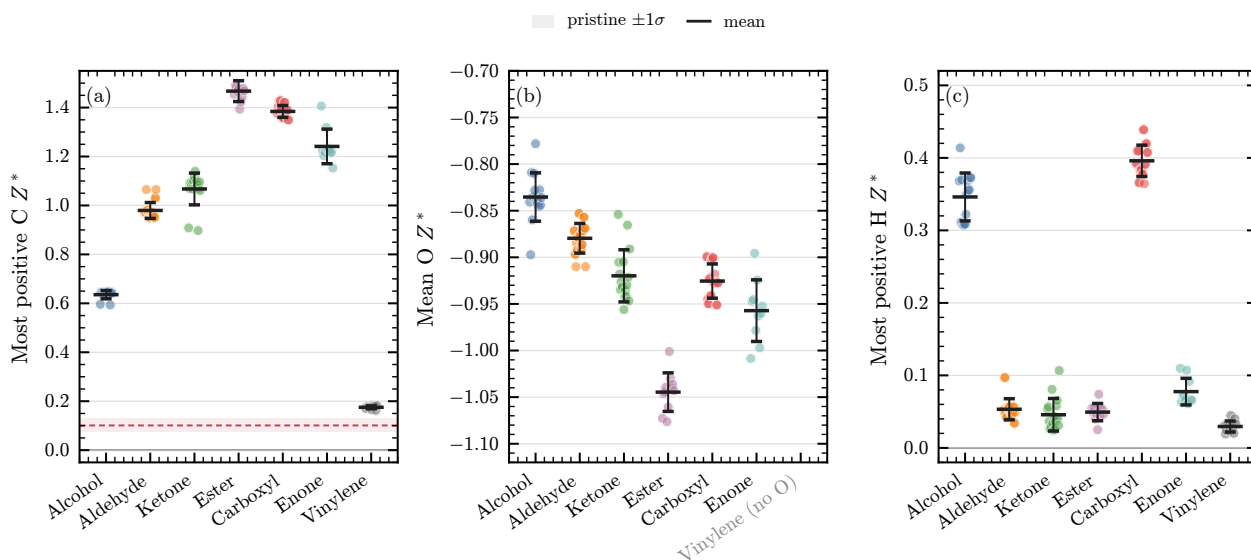


Figure 3.4: ASR-corrected Born effective charge summaries for 4 mol % defective PE. The panels show species-level proxies for chemically active atoms: the most positive carbon, the mean oxygen value, and the most positive hydrogen where applicable. Pristine PE carbon and hydrogen reference values are shown to indicate the weak dynamical polarity of the unmodified backbone. These species-level statistics run over every atom of the given element in the cell and are therefore not identical to the chemically assigned, role-resolved values of Table 3.3: panel (b) averages over all oxygens present, so that the ester entry is the mean of its carbonyl and bridging oxygens, and in panel (a) the most positive carbon of vinylene is a backbone carbon rather than the sp^2 defect carbon listed in Table 3.3. Vinylene contains no oxygen and is marked accordingly in panel (b).

son, the lattice contribution was decomposed into mode-resolved dielectric weights following the DFPT interpretation of phonon oscillator strengths [8, 9]. Each IR-active mode was assigned to a frequency bin, and the positive dielectric weights were summed within cumulative thresholds of 100, 200, and 400 cm^{-1} , so that each mode contributes to the lattice dielectric response within its corresponding frequency range. The cumulative fraction of the dielectric weight was then calculated to identify whether the ionic dielectric enhancement is primarily produced by low-frequency modes or by higher-frequency localized vibrations. A phonon mode can only contribute to the static dielectric constant when that mode produces a sizable oscillating dipole. The key quantity is the ratio between the oscillator strength of a mode, S_m , and the square of its phonon frequency, ω_m^2 . As a result, low-frequency collective motions of polar modes can contribute more strongly than high-frequency localized bond-stretching modes, even when the latter involve chemically polar bonds.

Table 3.4 summarizes the resulting mode-weight distribution averaged over all the defect positions. Among the defects studied, aldehyde shows the strongest low-frequency dielectric weight concentration, with 0.76 ± 0.09 of its positive mode weight below 100 cm^{-1} and 0.85 ± 0.06 below 200 cm^{-1} , together with a low dominant-mode frequency, $\omega_{\text{top}} = 25.0 \pm 17.0 \text{ cm}^{-1}$. This explains why aldehyde gives the largest ionic increment despite having carbonyl Born-charge isotropic averages smaller than those of ester or carboxyl: its relevant dynamical charges couple efficiently to soft collective modes of the defect-containing PE matrix. Alcohol has the second-largest ionic increment, but only 0.25 ± 0.07 of its positive mode weight lies below 100 cm^{-1} and 0.36 ± 0.14 lies below 200 cm^{-1} . Most of its cumulative contribution appears only by 400 cm^{-1} , indicating that its dielectric enhancement is distributed over moderately higher-frequency IR-active modes. Carboxyl, ketone, enone, and ester form an intermediate group, with $f_{\leq 100}$ values of 0.58 ± 0.11 , 0.64 ± 0.13 , 0.53 ± 0.12 , and 0.49 ± 0.12 , respectively. Vinylene is a clearly distinct case: only 0.15 ± 0.04 of its mode weight lies below 100 cm^{-1} , and its most common dominant frequency bin is 800–1600 cm^{-1} . This is consistent with its small Born-charge isotropic averages and weak static dielectric enhancement.

Overall, the combined Born-charge and mode-resolved analyses show that defect chemistry affects ϵ_0 through two coupled requirements. First, the defect must introduce dynamical charge so that atomic displacements create an oscillating dipole. Second, those dynamical charges must project onto low-frequency IR-active modes. The static dielectric ranking therefore cannot be inferred from functional-group polarity or Born-charge magnitude alone.

Table 3.4: Mode-resolved dielectric weight analysis at 4 mol %. $\sum_m \Delta\epsilon_m^+$: total positive mode-resolved dielectric weight; $f_{\leq 100}$, $f_{\leq 200}$, $f_{\leq 400}$: cumulative fraction of positive dielectric mode weight from modes below the indicated frequency threshold (in cm^{-1}); dominant frequency bin: the single bin carrying the largest weight fraction.

Defect	n	$\sum_m \Delta\epsilon_m^+$	$f_{\leq 100}$	$f_{\leq 200}$	$f_{\leq 400}$	Dominant bin
Aldehyde	12	0.87 ± 0.67	0.76 ± 0.09	0.85 ± 0.06	0.88 ± 0.04	(0, 100]
Alcohol	16	0.44 ± 0.11	0.25 ± 0.07	0.36 ± 0.14	0.78 ± 0.06	(200, 400]
Carboxyl	10	0.56 ± 0.14	0.58 ± 0.11	0.65 ± 0.08	0.66 ± 0.08	(0, 100]
Ketone	17	0.49 ± 0.18	0.64 ± 0.13	0.75 ± 0.09	0.79 ± 0.07	(0, 100]
Ester	11	0.40 ± 0.10	0.49 ± 0.12	0.56 ± 0.09	0.65 ± 0.06	(0, 100]
Enone	10	0.40 ± 0.11	0.53 ± 0.12	0.66 ± 0.08	0.71 ± 0.07	(0, 100]
Vinylene	12	0.10 ± 0.01	0.15 ± 0.04	0.25 ± 0.03	0.31 ± 0.03	(800, 1600]

3.2.5. Position-Dependent DFPT Tensor Response at 4 mol %

The 4 mol % calculations were used to test whether the same defect chemistry behaves differently when placed at different depths in the lamellar cell. Each cell contains two defect units. One defect

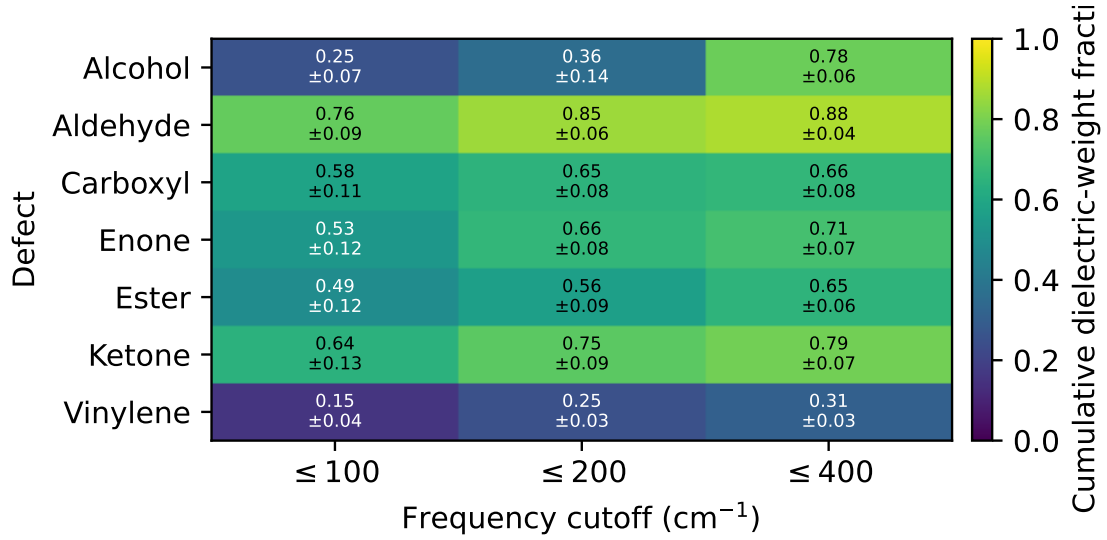


Figure 3.5: Low-frequency dielectric mode-weight fractions at 4 mol %. Larger fractions below 100–200 cm^{-1} indicate that a larger part of the lattice dielectric response is carried by soft IR-active modes.

is held fixed at the crystalline–amorphous interface while the second is placed at a range of positions spanning the crystalline core, the surface/interfacial region, and the amorphous region. The resulting ϵ_∞ and ϵ_0 values for each configuration of the mobile defect are plotted as a function of its position along the lamellar normal in Figure 3.6, one panel per defect type. Across all seven defect types the ϵ_∞ points form a tight and nearly flat band at all positions; the extracted 4 mol % isotropic-average ϵ_∞ ranges are only about 0.006–0.018, depending on defect type. This position-insensitivity of ϵ_∞ indicates that the electronic polarizability is governed primarily by local defect chemistry rather than the broader morphological environment. On the other hand, the ϵ_0 points scatter much more widely at every position. This contrast reflects the ionic contribution to ϵ_0 , which is sensitive to the local phonon environment that changes with morphological position.

For Alcohol, the ϵ_∞ points cluster tightly at 2.255, barely above the pristine reference and essentially invariant with position ($\epsilon_\infty^{\text{avg}} = 2.255$, spread < 0.01). The ϵ_0 points are distributed between 2.37 and 2.60, with an average of $\epsilon_0^{\text{avg}} = 2.41$, corresponding to an ionic increment $\Delta\epsilon = 0.16$. The largest ϵ_0 value (2.59) occurs when the mobile defect is located at the surface/interfacial zone. The scatter in ϵ_0 across the crystalline, interfacial, and amorphous positions shows no systematic directional trend, indicating that the –OH dipolar contribution is active throughout the slab but is maximized at surfaces. Aldehyde shows that ϵ_∞ forms a flat band at 2.20, which lies below the pristine reference at every position ($\epsilon_\infty^{\text{avg}} = 2.20$, 0.032 below the PE line). The ϵ_0 distribution is the widest among all defect types, spanning 2.34–2.54 with $\epsilon_0^{\text{avg}} = 2.44$ ($\Delta\epsilon = 0.24$). Notably, the highest ϵ_0 values (2.50–2.54) are concentrated in the crystalline region, unlike the other defects. For Carboxyl defects the ϵ_∞ points fall at 2.22–2.23, slightly below the pristine line at all positions ($\epsilon_\infty^{\text{avg}} = 2.22$, spread = 0.01). The ϵ_0 spans 2.36–2.43, with $\epsilon_0^{\text{avg}} = 2.38$ ($\Delta\epsilon = 0.16$), and the highest ϵ_0 values appear at the surface/amorphous boundary (2.43), whereas the crystal-region values (2.36–2.38) are the lowest in the distribution. Enone has the ϵ_∞ band lying at 2.245–2.265, slightly above the pristine reference ($\epsilon_\infty^{\text{avg}} = 2.255$, spread = 0.02). The ϵ_0 values span 2.35–2.46, with $\epsilon_0^{\text{avg}} = 2.38$ ($\Delta\epsilon = 0.12$). The highest ϵ_0 values (2.46) occur in the surface region, while the crystal-region values are the lowest in the distribution (2.35–2.38). For ester, ϵ_∞ is suppressed below the pristine reference at every position, while ϵ_0 lies above the pristine PE baseline. The ϵ_∞ points cluster tightly at 2.195–2.205 ($\epsilon_\infty^{\text{avg}} = 2.200$), give the lowest ϵ_∞ average in the series alongside aldehyde, and show no positional variation. The ϵ_0 values span 2.29–2.39 ($\epsilon_0^{\text{avg}} = 2.33$, $\Delta\epsilon = 0.13$); all data points sit above the ϵ_0^{PE} reference line. A rise in ϵ_0 is seen from the crystalline core (2.29–2.32) to the amorphous domain (2.35–2.39), indicating that the ionic response of the –COO– group grows as local chain disorder increases, while the electronic polarizability remains uniformly

suppressed regardless of position. The ε_∞ of ketone is tightly locked at 2.245–2.250, essentially coincident with the pristine reference at all positions ($\varepsilon_\infty^{\text{avg}} = 2.245$, spread < 0.01). The ε_0 distribution is the most broadly scattered, spanning 2.32–2.46 with $\varepsilon_0^{\text{avg}} = 2.375$ ($\Delta\varepsilon = 0.13$). The ketone ε_0 points are scattered throughout all three regions with no clear directional trend: elevated values appear in both the crystalline core (2.45–2.46) and the amorphous region (2.40–2.41), while intermediate values occur in the interfacial zone. Vinylene is set apart from all six oxygen-containing defects by its exceptionally narrow ε_0 distribution. The ε_∞ points fall at 2.230–2.246 ($\varepsilon_\infty^{\text{avg}} = 2.236$), close to the pristine reference. The ε_0 values are confined to the remarkably tight range 2.265–2.280 ($\varepsilon_0^{\text{avg}} = 2.270$), barely 0.012–0.022 above the pristine $\varepsilon_0^{\text{PE}}$. This gives the smallest ionic increment ($\Delta\varepsilon = 0.034$) in the series. The near-zero ionic increment, which is the same regardless of the morphological position of the defect, reflects the near-symmetric C = C bond. Consequently, the vinylene group contributes negligible additional polarization beyond the pristine backbone, irrespective of whether it is located in the ordered crystal or in the disordered amorphous region.

Across all seven defects, variation in defect position leaves ε_∞ nearly unchanged, confirming that the isotropic-average electronic polarizability is primarily a local chemical effect. The static ε_0 is more sensitive to position, but the direction and magnitude of this sensitivity are defect-specific. The strongest static values are not confined to one structural region: aldehyde and ketone have the highest values in the crystalline region, whereas carboxyl, enone, and ester reach their largest values toward the surface or amorphous side. Vinylene shows negligible positional variation in both concentrations.

3.3. Position-Dependent Dielectric Profile of Pristine Polyethylene

DFPT calculations provide macroscopic cell-averaged dielectric permittivities, but do not show the distribution of the response in the system. To resolve how the dielectric response varies through the PE matrix, a position-dependent dielectric profile $\varepsilon(z)$ was calculated using the linear-response finite-field formalism introduced by Giustino, Umari, and Pasquarello and implemented for slab geometries by Shi and Ramprasad [12, 13]. The planar average is first obtained over planes perpendicular to z , and the macroscopic average is then evaluated by smoothing the planar average over one repeat length following the standard macroscopic-averaging procedure [14]. In this approach, finite sawtooth electric fields of equal magnitude and opposite sign ($\pm\mathcal{E}$) are applied along the slab normal. The planar-averaged induced charge density is obtained from the difference between the two finite-field charge densities. Integration along z gives the induced polarization $\bar{P}(z)$, from which the local dielectric profile $\varepsilon(z)$ is constructed.

The reference system is a finite polyethylene segment with 20 carbon backbone atoms and CH₃ terminations on both sides, C₂₀H₄₂. The chain is placed in a supercell with vacuum at both chain ends along z , so that neighboring periodic images do not interact along the field direction. The PE20 model is used as a simplified reference to validate the dielectric-profile procedure before analyzing the folded lamella. The size of the supercell in the directions perpendicular to the chain is chosen to fix the inter-chain distance to 4.8 Å, close to the value in a crystalline lamella.

Figure 3.8 summarizes the induced charge density, polarization, and dielectric profile obtained for this model under a field amplitude of $E = 0.001$ a.u. The planar average shows oscillations associated with the CH₂ units, while the macroscopic average smooths these oscillations over one C–C repeat length. Both induced quantities decay to zero in the vacuum region. The polarization reaches a nearly constant plateau, and the resulting dielectric profile converges to $\varepsilon_{\text{bulk}} = 2.26$, consistent with the high-frequency dielectric constant of the semicrystalline polyethylene model. The vacuum region remains at $\varepsilon = 1.00$. The same profile analysis was then repeated after introducing alcohol, ketone, aldehyde, ester, carboxyl, enone, and vinylene defects into the chain.

Figure 3.9 compares the macroscopic $\varepsilon(z)$ profile for all seven defect chains against the pristine PE reference and shows the perturbation relative to the pristine profile, $\Delta\varepsilon(z) = \varepsilon_{\text{defect}}(z) - \varepsilon_{\text{pristine}}(z)$.

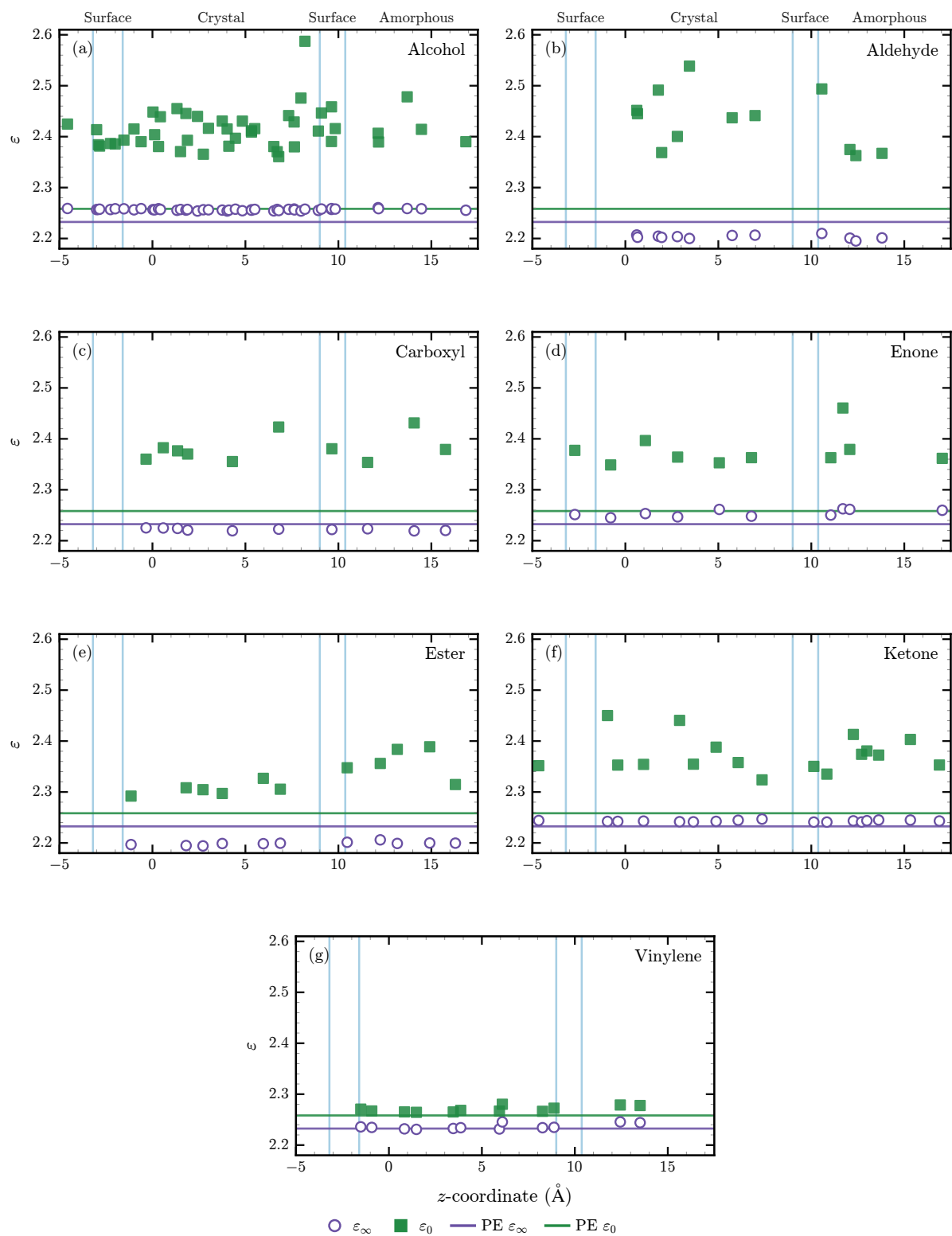


Figure 3.6: Position-dependent DFPT dielectric response at 4 mol % for all seven defect types. The x -axis gives the position of the defect along the lamellar normal; the second defect is fixed at the crystalline–amorphous interface.

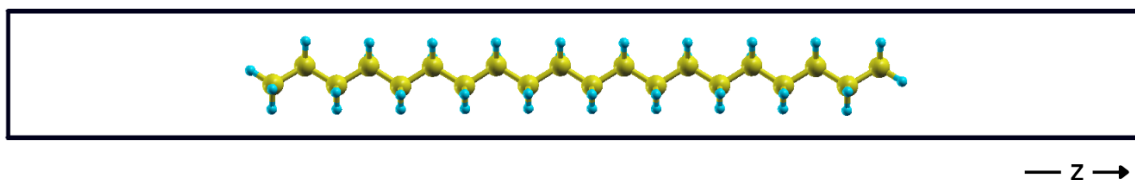
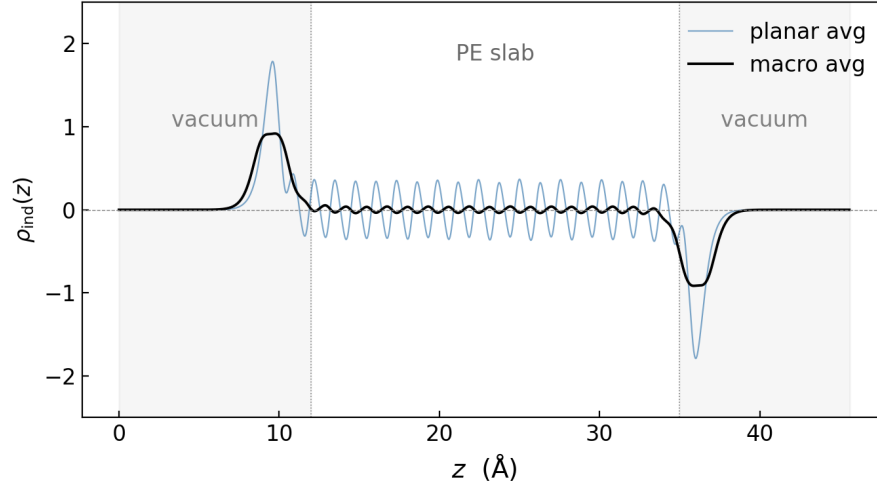


Figure 3.7: Isolated PE20 chain segment used as the reference model for position-dependent dielectric-profile calculations. The finite $C_{20}H_{42}$ chain is placed in a slab/vacuum field geometry with the chain axis and applied electric field along z .

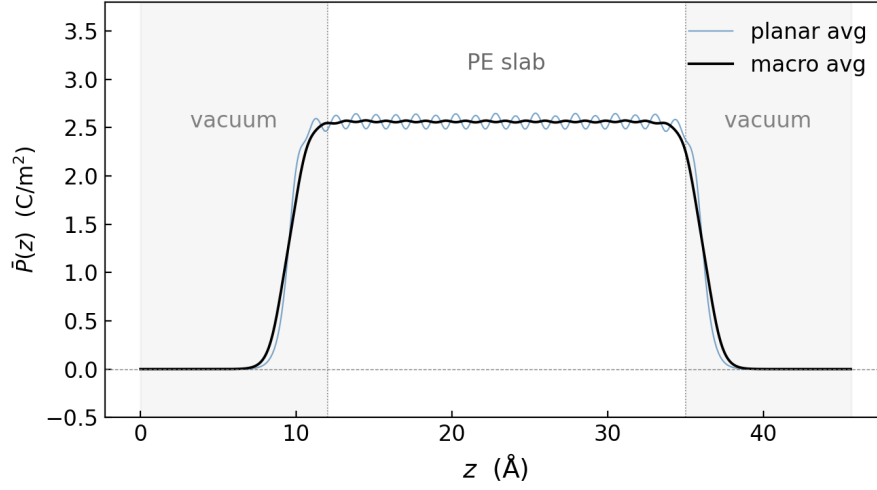
The defect systems follow two separate trends: those that produce a localized positive spike in $\varepsilon(z)$ centered on the substitution site (enone, vinylene, alcohol, ketone, and ester), and those that induce a negative dip (carboxylic acid and aldehyde). All perturbations are spatially confined within about 5 Å of the defect center, underscoring that no defect alters the dielectric profile beyond its immediate chemical neighborhood. The enone defect produces the single largest perturbation in the set, with a peak $\Delta\varepsilon = +1.46$ and a bulk-averaged increase of $\Delta\varepsilon_{\text{bulk}} = +0.185$ (an 8.2% enhancement relative to the pristine value; see Table 3.5). The vinylene defect produces a narrower but also large positive spike ($\Delta\varepsilon_{\text{peak}} = +0.71$) and a bulk increase of $\Delta\varepsilon_{\text{bulk}} = +0.104$ (+4.6%). The strong response of vinylene, despite the absence of any polar group, demonstrates that π -electron delocalization from unsaturation is a primary driver of local dielectric enhancement in PE. The remaining defects (alcohol, ketone, and ester) produce moderate positive perturbations ($\Delta\varepsilon_{\text{bulk}} = +0.039$, $+0.022$, and $+0.023$ respectively) that are well-localized within about 3 Å of the defect site. The carboxyl and aldehyde defects show a different response where the $\Delta\varepsilon(z)$ profile shows a positive spike followed by a corresponding negative dip that reaches $\Delta\varepsilon = -0.8$ for carboxyl and -0.7 for aldehyde. Consequently, both defects show a negligible bulk change ($\Delta\varepsilon_{\text{bulk}} = -0.004$ and -0.002 respectively), because the positive and negative lobes cancel out in the macroscopic average. However, their slab-wide root-mean-square deviations (RMSD), which account for the absolute magnitude of both positive and negative local variations, are among the largest in the set (0.203 and 0.195, respectively, compared to 0.044 for ketone). Despite their near-zero bulk permittivity change, both defects therefore introduce a strongly non-uniform dielectric environment across the PE chain.

Table 3.5: Dielectric-profile metrics for the seven PE20 defect variants. The pristine interior value is $\varepsilon_{\text{bulk}} = 2.255$. $\Delta\varepsilon_{\text{bulk}}$ is the signed change in the interior-region average of the macroscopic $\varepsilon(z)$ profile. Slab RMSD is the root-mean-square deviation of $\Delta\varepsilon(z)$ over the dielectric slab. Local $|\Delta\varepsilon|$ is the mean absolute perturbation within ± 1 Å of the defect center.

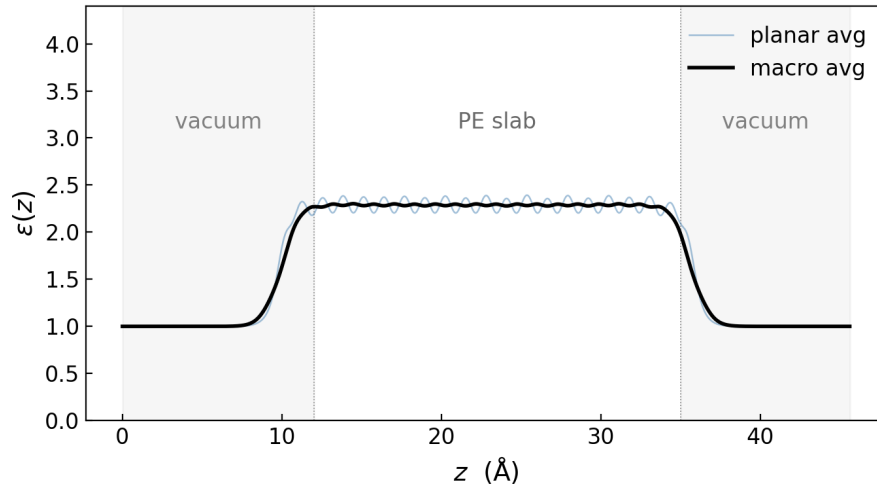
Defect	$\varepsilon_{\text{bulk}}$	$\Delta\varepsilon_{\text{bulk}}$	Slab RMSD	Local $ \Delta\varepsilon $	Max $ \Delta\varepsilon $
Pristine	2.255	–	–	–	–
Ketone	2.277	+0.022	0.044	0.138	0.187
Ester	2.278	+0.023	0.061	0.160	0.259
Alcohol	2.294	+0.039	0.077	0.264	0.337
Vinylene	2.358	+0.104	0.185	0.627	0.711
Enone	2.440	+0.185	0.349	0.565	1.459
Carboxyl	2.251	–0.004	0.203	0.322	0.759
Aldehyde	2.253	–0.002	0.195	0.327	0.732



(a) Induced charge density $\rho_{\text{ind}}(z)$.



(b) Macroscopic polarization $P_{\text{macro}}(z)$.



(c) Position-dependent dielectric function $\varepsilon(z)$.

Figure 3.8: Position-resolved dielectric response of the pristine PE20 chain to an applied field $E = 0.001$ a.u. along z . Grey shading marks vacuum regions and dashed vertical lines indicate the dielectric slab boundaries. Light blue curves are planar averages and black curves are macroscopic averages.

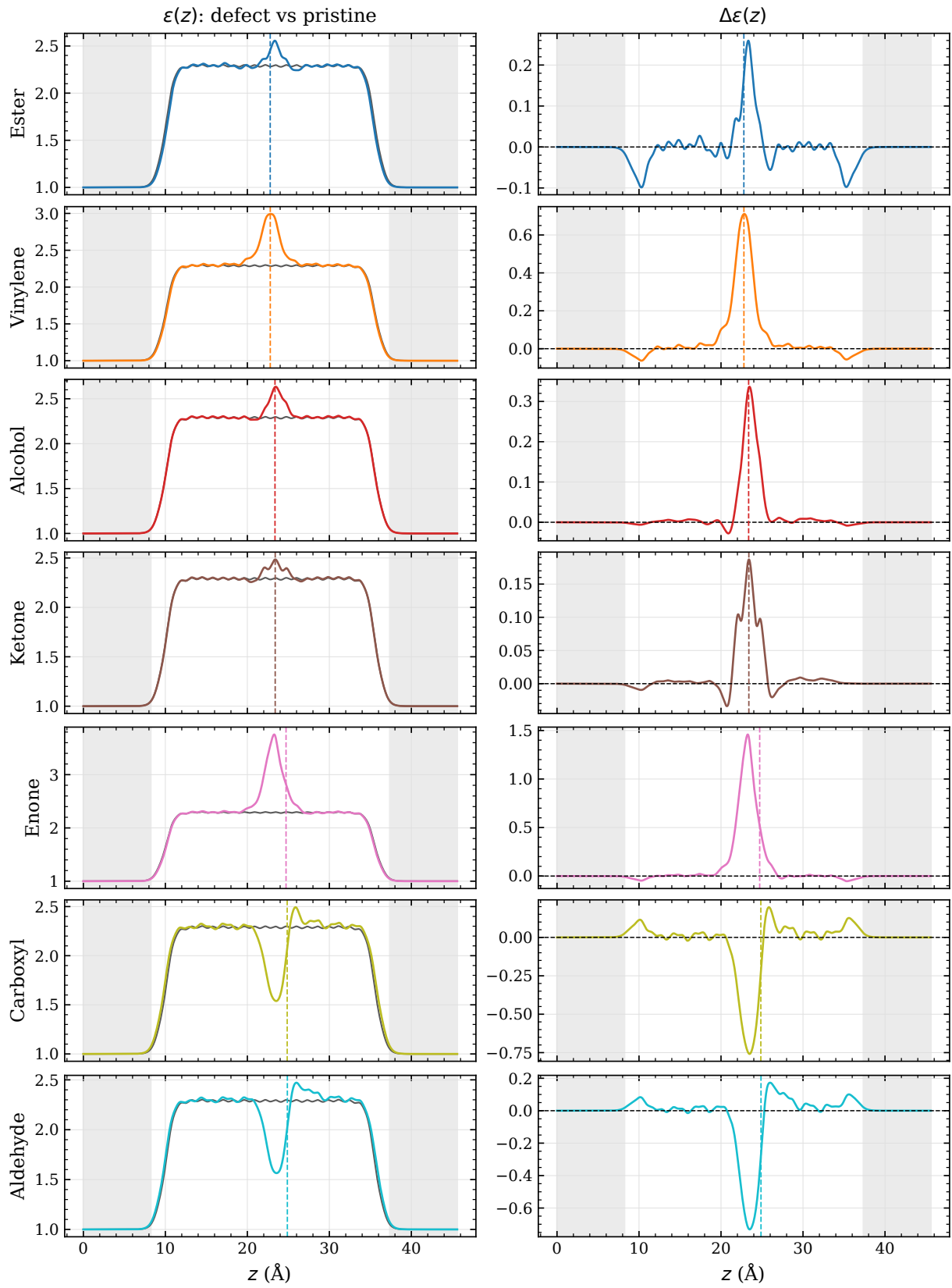


Figure 3.9: Macroscopic dielectric profiles for the seven PE20 defect variants compared with pristine PE20, together with differential profiles $\Delta\epsilon(z)$. Grey shading marks vacuum regions and the dashed vertical line in each panel marks the defect centre.

3.4. Dielectric Response of the Folded PE Lamella with Distributed Chemical Defects

Having established the position-dependent dielectric response of the isolated PE chain segment in Section 3.3, the same finite-field dielectric-profile analysis was extended to a folded polyethylene lamella. This model allows the intrinsic chemical effect of a defect to be separated from the effect of its local environment within a chain-folded morphology. A defect in the ordered crystalline interior experiences a different packing environment from the same functional group placed near a folded surface, where the chain curvature and local free volume are different. The folded PE model is a slab that is periodic in the perpendicular directions and separated by a vacuum of 5 Å on each side along z , allowing the saw-tooth electric field to be applied along the lamellar normal (Fig. 3.10). The dielectric profiles are computed from the macroscopically averaged induced response using the same finite-field method. With an applied field amplitude of $E = 0.0015$ a.u., the dielectric constant of the pristine PE lamellae is $\epsilon_{\text{bulk}}^{\text{pristine}} = 2.683$. Each defect structure was relaxed before the finite-field dielectric calculation. The dielectric profiles were calculated for 92 relaxed defect structures including ketone, alcohol, ester, carboxyl, aldehyde, enone, and vinylene. The full profile analysis of the semi-crystalline model is given in Appendix C.

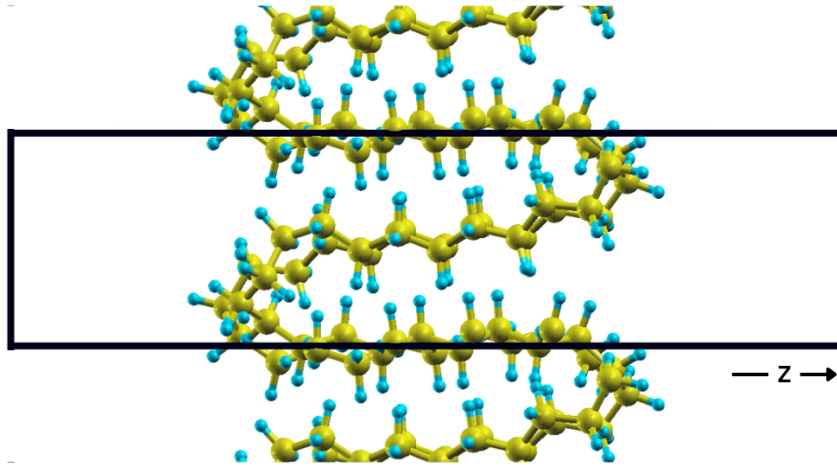


Figure 3.10: Folded PE lamella used for the position-dependent dielectric-profile calculations. The model contains ordered crystalline stems and folded-chain surface regions, with the finite electric field applied along the lamellar normal z .

3.4.1. Bulk-Region Dielectric Response and Full-Profile Perturbation

Here, $P_{\text{macro}}(z)$ denotes the Baldereschi-type macroscopic average of the induced polarization profile, and P_{max} is the maximum value of $P_{\text{macro}}(z)$ inside the dielectric slab. The plateau region is defined as the set of points for which $P_{\text{macro}}(z) > 0.70P_{\text{max}}$. The scalar bulk dielectric constant ϵ_{bulk} is then obtained by averaging $\epsilon(z)$ over this plateau region. The change in the bulk-averaged dielectric constant is calculated as

$$\Delta\epsilon_{\text{bulk}} = \epsilon_{\text{bulk}}^{\text{defect}} - \epsilon_{\text{bulk}}^{\text{pristine}}, \quad (3.1)$$

where ϵ_{bulk} is evaluated with the same $P_{\text{macro}}(z) > 0.70P_{\text{max}}$ plateau definition for the pristine and defect profiles. The mean response by defect group is shown in Fig. 3.11 and summarized in Table 3.6.

Enone produces the largest average enhancement, with $\langle\Delta\epsilon_{\text{bulk}}\rangle = +0.080$. Vinylene gives the second largest enhancement, with $\langle\Delta\epsilon_{\text{bulk}}\rangle = +0.039$. Both of these defect groups contain unsaturated bonding. Vinylene introduces a C=C bond into the PE backbone, whereas enone combines a carbonyl group with a neighboring unsaturated bond. Carboxyl and aldehyde exhibit the opposite trend. Carboxyl gives $\langle\Delta\epsilon_{\text{bulk}}\rangle = -0.040$, and aldehyde gives -0.043 . These negative shifts do not mean that

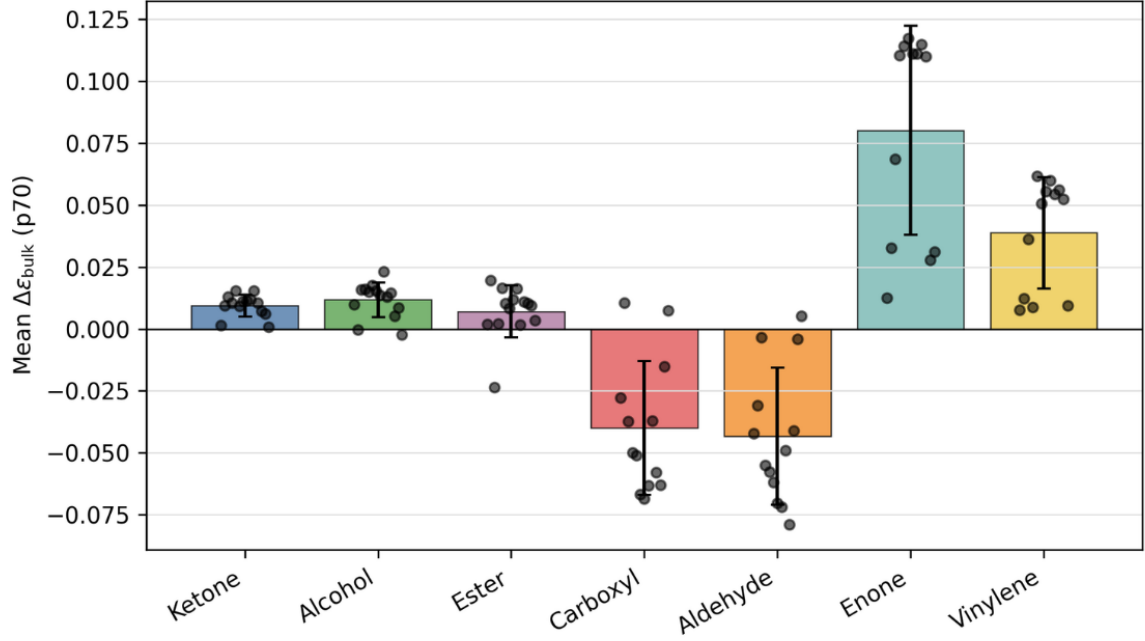


Figure 3.11: Average bulk-region dielectric shift for the seven defect groups in the folded PE lamella. Bars correspond to group means of $\Delta\epsilon_{\text{bulk}}$ calculated from the $P_{\text{macro}} > 0.70P_{\text{max}}$ interior-region criterion; black points correspond to values calculated for individual defect positions.

Table 3.6: Dielectric-profile metrics for the folded-PE lamella. N is the number of analyzed dielectric profiles. $\langle\epsilon_{\text{bulk}}\rangle$ and $\langle\Delta\epsilon_{\text{bulk}}\rangle$ use the $P_{\text{macro}} > 0.70P_{\text{max}}$ bulk-region criterion. σ is the standard deviation of ϵ_{bulk} over configurations. $\langle\text{RMSD}[\Delta\epsilon(z)]\rangle$ is the mean full-slab root-mean-square deviation of the dielectric perturbation.

Defect group	N	$\langle\epsilon_{\text{bulk}}\rangle$	σ	$\langle\Delta\epsilon_{\text{bulk}}\rangle$	$\langle\text{RMSD}[\Delta\epsilon(z)]\rangle$
Ketone	14	2.693	0.004	+0.010	0.020
Alcohol	14	2.695	0.007	+0.012	0.032
Ester	14	2.690	0.010	+0.007	0.042
Carboxyl	13	2.643	0.026	-0.040	0.104
Aldehyde	13	2.640	0.027	-0.043	0.100
Enone	12	2.764	0.040	+0.080	0.110
Vinylene	12	2.722	0.022	+0.039	0.059

the two groups have no dielectric response. Their $\Delta\epsilon(z)$ profiles contain adjacent positive and negative regions, so the local changes partly cancel when averaged over the plateau. They are therefore better described as producing strong local dielectric redistribution rather than bulk-permittivity enhancement. Ketone, alcohol, and ester occupy an intermediate regime. Their mean shifts are small and positive, +0.010, +0.012, and +0.007, respectively, showing that they perturb the dielectric profile but do not produce the larger enhancement observed for enone and vinylene. The narrow spread in Fig. 3.11 means that the dielectric response is relatively insensitive to the location of the defect, whereas a broad spread means that the position and relaxation geometry of the defect influence the dielectric profile. Enone shows a large positive mean and a sizable spread, indicating that it is a strong enhancer when its local response overlaps the interior plateau. Carboxyl and aldehyde have negative means, but their point distributions also show that their response is not uniformly weak; instead, their profiles contain strong local changes whose signed average becomes negative.

The bulk dielectric average is therefore only one part of the defect response. To quantify the spatial redistribution of the dielectric profile, the full-slab perturbation is defined as

$$\Delta\epsilon(z) = \epsilon_{\text{defect}}(z) - \epsilon_{\text{pristine}}(z), \quad (3.2)$$

This perturbation is summarized using the RMSD value over the inferred dielectric slab. Figure 3.12 compares this full-slab RMSD response across the seven defect groups.

The RMSD metric gives a different perspective for the interpretation of the data. The bulk average indicates whether a defect increases or decreases the average dielectric constant, whereas the RMSD value quantifies how strongly the defect redistributes the dielectric profile across the slab. Enone remains a strong perturbing defect, with $\langle \text{RMSD } \Delta\epsilon(z) \rangle = 0.110$, but carboxyl and aldehyde become comparable to it, with mean RMSD values of 0.104 and 0.100. Thus, although carboxyl and aldehyde lower the plateau-averaged dielectric constant, they produce some of the largest spatial redistributions of the dielectric response in the slab. A single averaged dielectric constant would hide this effect because it does not distinguish between positive and negative changes in the dielectric response. The individual extremes show the same point. The largest positive bulk shift occurs for an enone motif placed in the inner core part of the lamella, where the defect response overlaps strongly with the crystalline plateau and gives $\Delta\epsilon_{\text{bulk}} = +0.117$. The most negative bulk shift occurs for an aldehyde motif in a subsurface-to-core region, giving $\Delta\epsilon_{\text{bulk}} = -0.079$. The strongest full-profile perturbation is found for a carboxyl motif in a similar subsurface-to-core region, with $\text{RMSD } \Delta\epsilon(z) = 0.190$. In contrast, the weakest profile perturbations occur for motifs close to a folded surface, where only a small part of the local disturbance projects into the dielectric slab. These examples show that the strongest local dielectric distortion does not necessarily coincide with the largest positive bulk shift. Defects near the folded surface sample a less densely packed region, and part of their response can extend toward the vacuum side of the slab. The defects in the core crystalline regions overlap more directly with the crystalline plateau. This distinction changes the measured bulk average without changing the basic chemical classification, where enone and vinylene remain positive dielectric enhancers when their local response projects into the slab interior, whereas carboxyl and aldehyde remain strong local-redistribution groups whose positive and negative contributions reduce the averaged response.

Figure 3.13 visualizes the correlation between the local mean absolute perturbation within $\pm 2 \text{ \AA}$ of the defect center and the full-slab RMSD response. Most points on the figure suggest a near-linear correlation, indicating that the local response near the defect is the dominant contribution to the dielectric profile. Other points that deviate from this trend indicate that the perturbation extends beyond the immediate defect center or contains oscillatory positive and negative regions away from the defect. This is particularly relevant for carboxyl and aldehyde, where large full-slab RMSD values can coexist with negative plateau shifts. Enone and vinylene generally show strong local perturbations that also contribute positively to the bulk dielectric constant. Carboxyl and aldehyde occupy a different region of the plot, where they can produce large local and full-slab perturbations while still giving negative plateau shifts. This suggests that their response is not only a local dipole effect, but

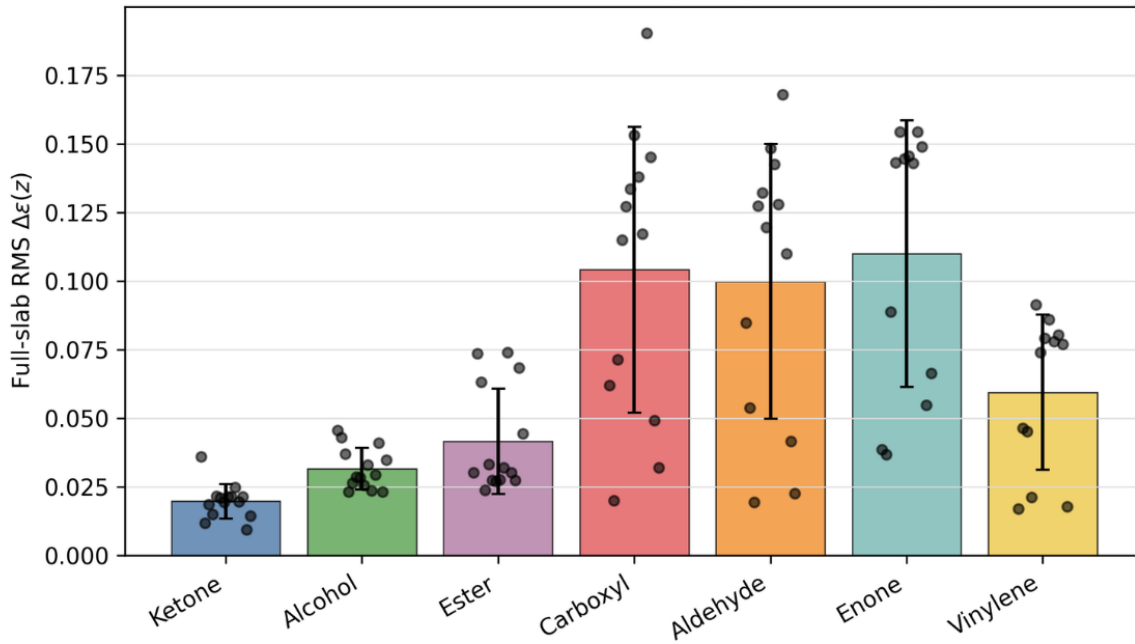


Figure 3.12: Full-slab RMSD of the dielectric perturbation $\Delta\epsilon(z)$ for the seven folded-PE defect groups. RMSD measures the magnitude of local profile redistribution and does not cancel positive and negative lobes.

also includes structural rearrangement of nearby chain segments that creates alternating positive and negative regions in $\Delta\epsilon(z)$.

3.4.2. Absolute-Position and Defect-Centered Profiles

The absolute-position profiles in Fig. 3.14 show how the same local perturbation contributes differently depending on where the defect sits in the lamella. The curves are colored by the relaxed defect position along z . The color scale orders the curves by absolute z -position of the defect, so a progression from surface to interior can be followed within each type of defect. In enone and vinylene, the positive peaks contribute the most to $\Delta\epsilon_{\text{bulk}}$. In carboxyl and aldehyde, the same locations show strong local positive and negative lobes that can cancel in the plateau average. A defect placed near the surface of the slab restricts dielectric perturbations mostly to the slab-vacuum interface without strongly affecting the core region, and its contribution to the extracted $\Delta\epsilon_{\text{bulk}}$ is relatively small. In contrast, the same type of defect positioned deep within the crystalline core produces perturbations that overlap significantly with the plateau region, contributing more directly to the bulk dielectric shift. This is why the same chemical group can give different bulk shifts at different positions.

The defect-centered profiles in Fig. 3.15 remove this absolute-position information by shifting each curve so that the defect center lies at $z - z_{\text{defect}} = 0$. This representation emphasizes the shape and spatial extent of the perturbation. Enone and vinylene are dominated by positive perturbations near the defect center, so their local response can increase the plateau average. Carboxyl and aldehyde show broader profiles with neighboring positive and negative regions, creating a strong local dielectric inhomogeneity while reducing the average response. Ketone, alcohol, and ester remain intermediate; ketone is weak and narrow, alcohol is more sensitive to the hydroxyl geometry, and ester perturbs the local profile more than ketone, but does not give a clear bulk enhancement.

3.4.3. Orientation Dependence of the Local Dielectric Profile

The orientation analysis tests whether the local dielectric perturbation depends on the alignment of the defect's polar or polarizable axis with the applied field. The applied electric field is along z , so

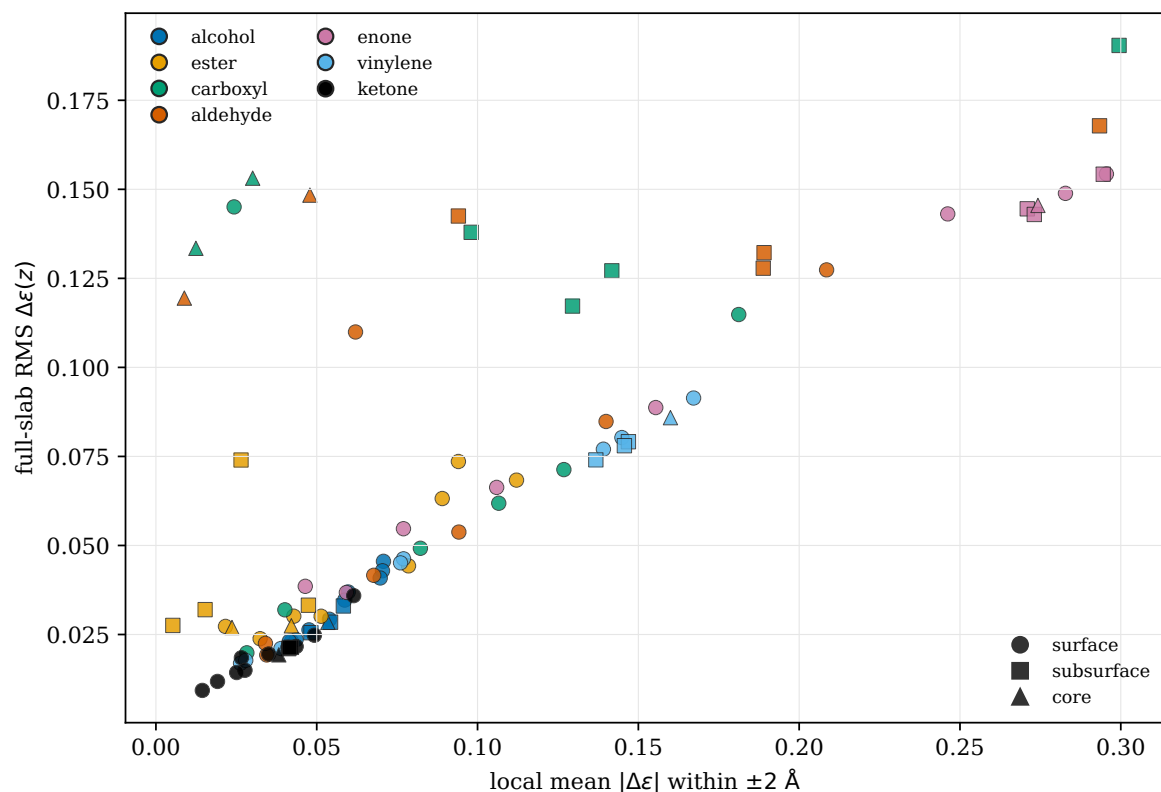


Figure 3.13: Relationship between local and slab-wide dielectric perturbations. The local metric is the mean absolute $\Delta\epsilon$ within ± 2 Å of the defect center, and the full-slab metric is $\text{RMSD}[\Delta\epsilon(z)]$ over the dielectric slab.

the projection of the defect's polarizable axis along the direction of the electric field is relevant to the local dielectric response. Carbonyl-containing defects are described by the C=O direction, alcohol by the C-O and O-H directions, and vinylene and the unsaturated part of enone by the C=C direction. For defect groups with more than one chemically relevant vector, the response cannot be reduced to a single orientation parameter. The clearest single-vector cases are ketone and vinylene: ketone has one dominant C=O vector and vinylene has one dominant C=C vector.

The relaxed final orientation in the presence of the electric field is not necessarily the same as the orientation of the defect without the field. Table 3.7 summarizes the mean relaxed angle to the field direction and the mean reorientation during relaxation. Ketone reorients only weakly, by about 6° , indicating that its C=O vector remains constrained by the surrounding chain environment. Carboxyl and aldehyde reorient much more strongly, by about 37° , showing that the polar groups can rotate substantially during relaxation. Vinylene has the smallest mean angle to z , about 42° , because the C=C motif follows the backbone direction more closely.

Figure 3.16 provides the corresponding dielectric profiles as a function of the orientation of each defect in the PE lamellae. Each defect-centered curve is colored by its relaxed primary-vector angle relative to the field direction. Small angles indicate a more field-aligned motif, while angles near 90° indicate a more transverse motif. The strongest dependence on orientation is visible for enone, vinylene, carboxyl, and aldehyde, whereas ketone remains weak over most of its orientation range. Vinylene shows this behavior: the more aligned C=C bond vector produces stronger positive peaks in the dielectric profile. Ketone does not show the same strong enhancement because most C=O vectors remain perpendicular, and the response stays localized and weak. Carboxyl and aldehyde show strong orientation-sensitive profiles, but their positive and negative lobes make the bulk average decrease rather than increase.

The single-vector profile maps in Figs. 3.17 and 3.18 show how the relaxed vector projection con-

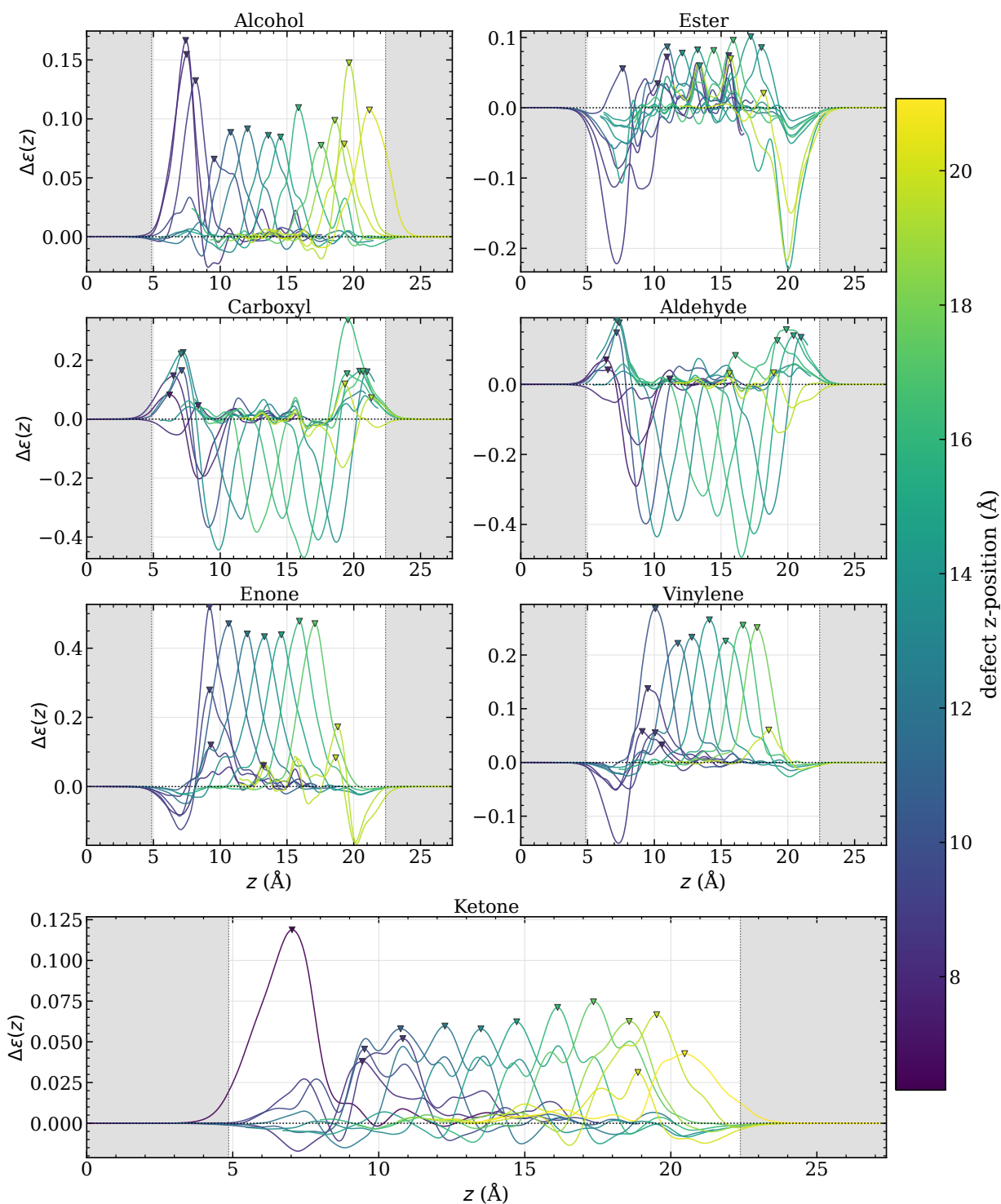


Figure 3.14: Absolute-position $\Delta\epsilon(z)$ profiles for the seven defect groups. Each panel shows one defect group in the original folded-lamella coordinate system. The color scale gives the relaxed defect position along z , allowing surface and interior profiles to be distinguished within each group. Grey shading marks vacuum regions.

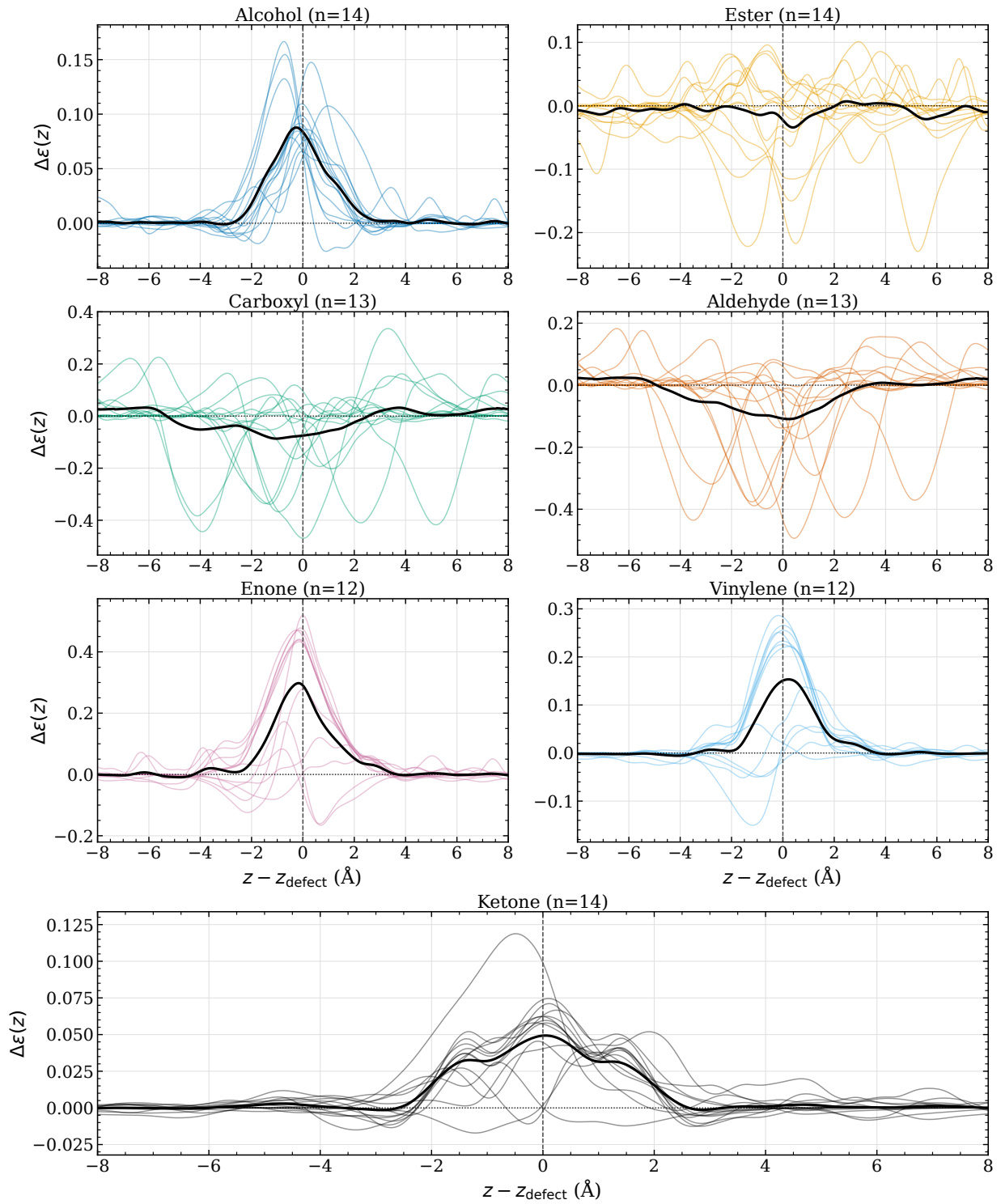


Figure 3.15: Defect-centered $\Delta\epsilon(z)$ profiles for all seven folded-PE defect groups. Thin curves show individual defect profiles shifted so that the defect center is at zero; the black curve shows the group mean. The value of N in each panel is the number of analyzed profiles for that defect group.

nects to the dielectric profile. Each curve is colored by the signed projection of the defect vector along z . Ketone remains a weak perturbation for most orientations. Its largest profile changes are localized near the carbonyl position and do not generate a large plateau shift, consistent with the small positive mean $\Delta\epsilon_{\text{bulk}}$ in Table 3.6. Vinylene gives a clearer positive orientation response. The C=C vector is part of the backbone and is therefore more aligned with the lamellar direction than the ketone C=O vector. When this unsaturated bond projects strongly along z , the local positive perturbation overlaps with the dielectric plateau, giving the second-largest positive mean bulk shift among the seven defect groups. This comparison shows that a nonpolar unsaturated motif can produce a stronger field-directed response than a constrained polar carbonyl.

Table 3.7: Mean orientation and reorientation of the primary defect vector in the folded-lamella dataset. N is the number of analyzed dielectric profiles. Angles are measured relative to the applied z -directed field used in the dielectric-profile calculations, $E = 0.0015$ a.u. The last column gives the mean full-slab RMSD of $\Delta\epsilon(z)$.

Defect group	N	Mean angle to z	Mean reorientation	Mean RMSD
Ketone	14	75.5°	6.4°	0.020
Alcohol	14	72.7°	9.0°	0.032
Ester	14	53.3°	30.7°	0.042
Carboxyl	13	65.7°	37.0°	0.104
Aldehyde	13	64.6°	36.4°	0.100
Enone	12	73.1°	22.4°	0.110
Vinylene	12	42.3°	19.1°	0.059

The folded-lamella results show that the dielectric response of chemically modified PE cannot be reduced to the presence of a polar functional group. The chemical structure of the defect controls the sign and scale of the mean bulk response, but the full position-resolved profile is needed to understand the local effect of each defect. Enone and vinylene are the clearest positive enhancers because their unsaturated motifs generate positive local perturbations that can project onto the crystalline plateau. Alcohol, ketone, and ester give small positive mean shifts. Ketone is especially weak because its in-chain carbonyl is geometrically constrained and remains perpendicular to the applied field, while alcohol and ester depend more strongly on the relaxed local geometry of their C–O, O–H, and carbonyl components. Carboxyl and aldehyde define a different response class. They are strongly polar oxygenated groups, yet they reduce the mean plateau dielectric constant. Their importance appears in the full dielectric profile rather than in the scalar bulk average. Both defects create broad local perturbations with positive and negative regions around the defect site, producing large RMSD changes even when the bulk average decreases. This behavior shows that a polar defect can create strong dielectric inhomogeneity without increasing the bulk dielectric constant.

The orientation analysis connects these group-level trends to the relaxed defect geometry. Field-aligned polarizable motifs give larger local $\Delta\epsilon(z)$ perturbations, especially for enone, vinylene, carboxyl, and aldehyde. The plateau-averaged response also depends on where the defect sits in the folded lamella, because a surface or subsurface defect does not overlap the dense crystalline region in the same way as an interior defect. The most consistent interpretation is therefore that orientation controls the strength and shape of the local dielectric perturbation, while defect placement controls how much of that perturbation contributes to the averaged plateau response.

In the PE chain, each defect is tested in a single local environment, so the chemical response appears as a direct defect-specific perturbation. In the folded lamella, the same motif samples multiple packing environments and relaxed orientations. The group trends remain visible, with enone and

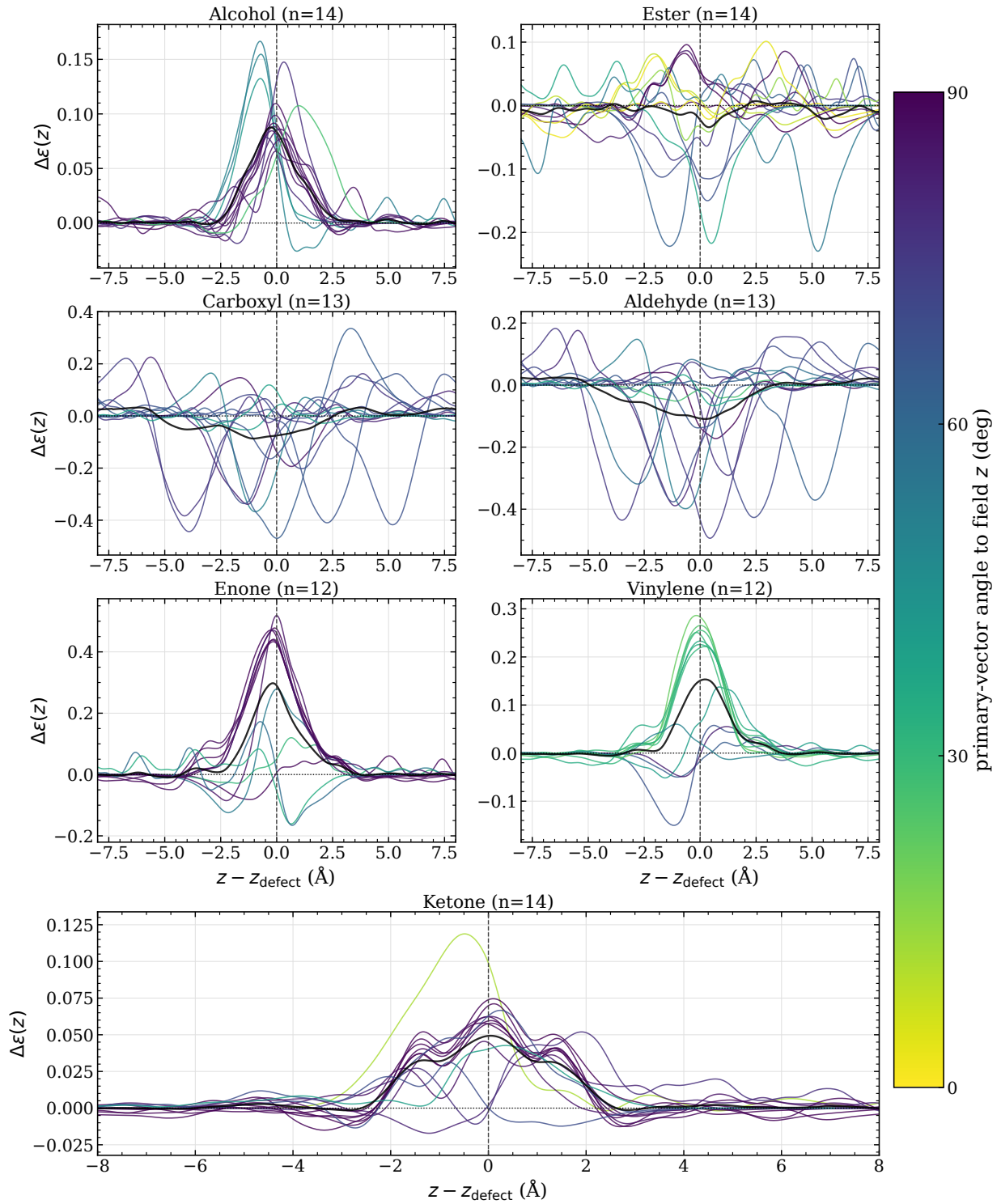


Figure 3.16: Defect-centered $\Delta\epsilon(z)$ profiles grouped by relaxed primary-vector orientation relative to the applied z -directed field. The vertical dashed line marks the defect center. Curves are colored by the relaxed primary-vector angle to the field, as shown on the color bar.

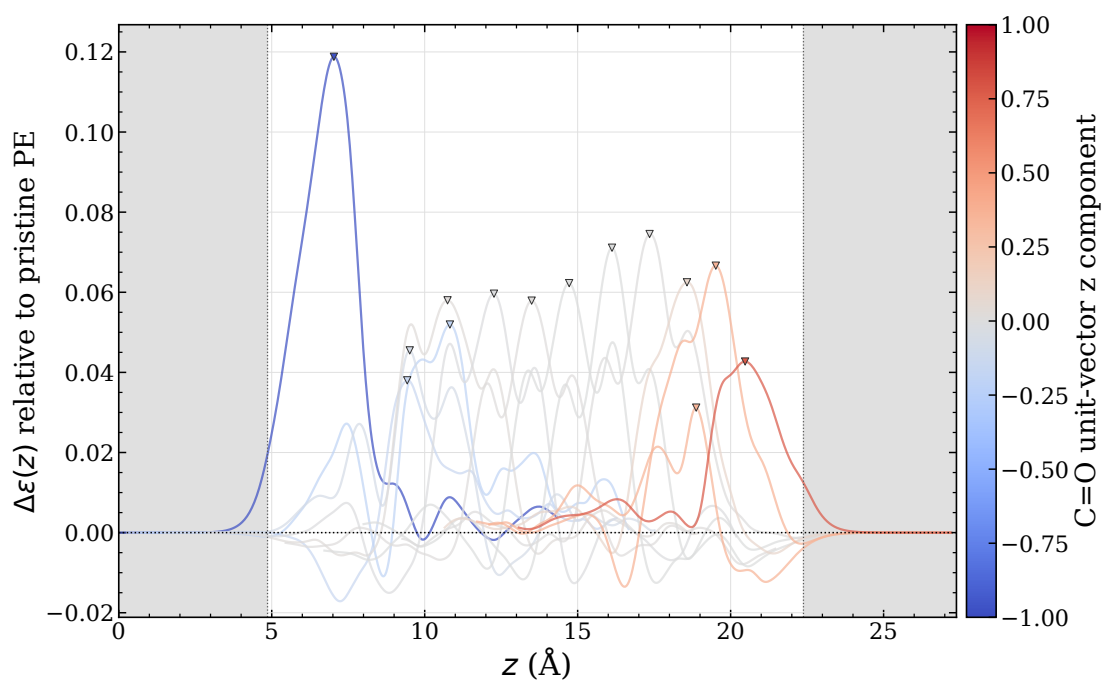


Figure 3.17: Ketone $\Delta\varepsilon(z)$ profiles grouped by the signed projection of the C=O unit vector along z .

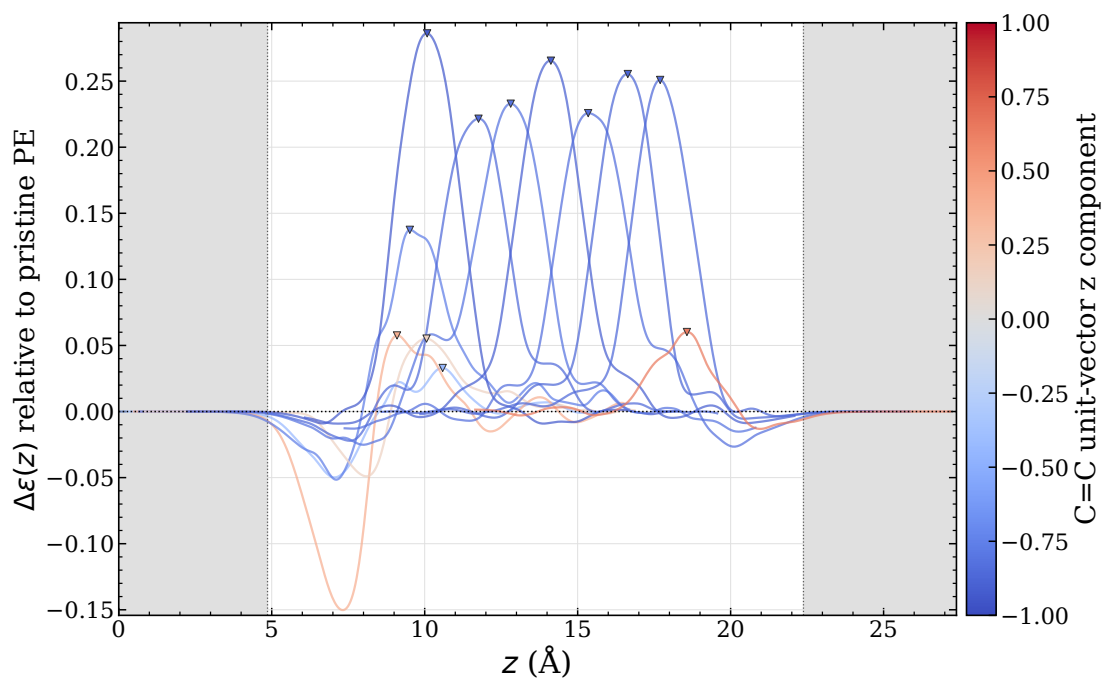


Figure 3.18: Vinylene $\Delta\varepsilon(z)$ profiles grouped by the signed projection of the C=C unit vector along z .

vinylene acting as positive enhancers and carboxyl and aldehyde producing strong local dielectric redistribution, but the folded morphology broadens the response within each group.

3.5. Chapter Conclusions

The combined DFPT and position-resolved dielectric analyses show that defected polyethylene cannot be interpreted using a single chemical descriptor. The concentration-dependent DFPT calculations show that ϵ_{∞} changes only weakly across the defect series, whereas ϵ_0 is more sensitive because oxygenated defects can introduce additional IR-active lattice-polarization channels. Born effective charges identify the atoms capable of generating dynamical polarity, and the mode-resolved analysis shows that the largest static response occurs only when those dynamical charges couple to low-frequency polar modes.

The position-dependent profiles add a second level of interpretation. A scalar bulk-region dielectric value indicates whether the selected interior average increases or decreases, but it does not show how the response is distributed around the defect. Enone and vinylene are the clearest positive enhancers when their local perturbations project into the interior polymer region. Carboxyl and aldehyde create a strong local dielectric redistribution with positive and negative profile changes that reduce the signed average. Ketone, alcohol, and ester form an intermediate group whose response depends more strongly on local orientation and packing.

The position-resolved dielectric profile is therefore useful because it shows that the same average dielectric constant can hide very different local responses. Defect chemistry controls the possible polarization mechanism, morphology controls how much of that mechanism contributes to the bulk-region average, and relaxed orientation controls the magnitude and shape of the local dielectric perturbation. This combined picture is the most defensible interpretation of the calculated dielectric response of chemically modified semicrystalline PE.

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4 – Finite-Temperature Dielectric Response from Molecular Dynamics

4.1. Introduction

The preceding first-principles chapter, particularly Sections 3.2 and 3.2.2, used density functional perturbation theory (DFPT) to calculate the dielectric constant of polyethylene and to analyse the influence of seven chemical defect groups on its dielectric response. These calculations resolved the dielectric constant at the high-frequency limit ϵ_∞ , in which the electronic density responds while the nuclei remain fixed, and at the DFPT static limit ϵ_0 , which additionally contains the harmonic lattice-vibrational contribution.

The DFPT approach has several limitations in calculating the dielectric permittivity of a material. A density functional calculation is computationally expensive, so the semicrystalline model must remain small, and these models cannot capture the range of chain conformations, fold surfaces, and amorphous regions that determine a real semicrystalline polymer. The second limitation is that the DFPT calculations describe a static structure at zero temperature. The ionic contribution obtained from perturbation theory only captures bond stretching and angle bending, but not the large-amplitude motion by which a whole polar group changes its orientation. In pristine polyethylene, the chains carry no permanent dipole to reorient, but once oxidation introduces carbonyl or hydroxyl groups with a permanent dipole, and at room temperature, the chains are mobile enough for the reorientation of these defect dipoles. Another limitation of DFPT is that these calculations say nothing about the intermediate frequency range between the two extreme limits.

Molecular dynamics addresses the second and third of these limitations directly, and the first in part. Integrating Newton's equations for a classical force field is computationally cheap enough to allow polymer chains of several thousand atoms, which can support a lamellar morphology with genuine crystalline and amorphous regions. The simulations can also be run at a chosen finite temperature, so the chains slide, the folds rearrange, and the defect dipoles reorient as they would in the real material. Because the trajectory is long compared with the reorientation time, a wider frequency range becomes accessible.

The simulations reported here use the all-atom OPLS force field [1] with fixed partial charges, applied through Moltemplate [2] and LAMMPS [3]. Fixed charges cannot polarize, so the electronic contribution to the permittivity is absent from the model by construction. It is therefore taken from the DFPT results in Section 3.2.1, whereas molecular dynamics is used to compute the finite-temperature orientational contribution $\Delta\epsilon$. This combination follows the established MD treatments in which a separately supplied electronic permittivity is combined with the response obtained from total-dipole fluctuations [4, 5]. The simulations follow the time-dependent cell dipole moment for semicrystalline polyethylene containing alcohol, aldehyde, ester and ketone oxidation products. Each defect type was introduced separately into the melt at concentrations of 2 and 4 mol % before quenching.

The analysis focuses on how defect chemistry changes the finite-temperature dielectric response. It establishes the orientational dielectric contribution for each oxidation product, tests whether the ranking follows the local polarity of the defect group, separates the response into defect, matrix and defect-matrix correlation terms, and connects the same mechanisms to dielectric loss. The dielectric properties are studied at 280, 300, and 320 K to assess how they depend on temperature. The calculations at 300 K are also repeated in a progressive-addition protocol, in which defects are added to an equilibrated pristine PE configuration in increments of 1 mol %, followed by a 50 ns trajectory at each concentration. This series shows how the structural and dielectric observables evolve as the defect content is increased sequentially. Section 4.2 and Section 4.3 describe the systems and their full dielectric analysis at 300 K. Section 4.4 repeats the analysis at 280 and 320 K. Section 4.5 reports a sep-

arate set of simulations in which the defects are introduced progressively into an already equilibrated cell.

4.2. Defect Systems and Their Morphology

Separate molecular-dynamics systems were prepared for alcohol, aldehyde, ester, and ketone defects so that the effect of each defect group on the dielectric response could be evaluated independently. The general simulation protocol, including the force field, melt-quench preparation, thermostat settings, and dielectric-fluctuation formulae, is given in Chapter 2, Sections 2.3.2, 2.3.3, and 2.3.5. Every system in this chapter is built from a single linear polyethylene chain of 2000 methylene units, assembled with Moltemplate [2], described by the all-atom OPLS force field [1] and equilibrated in LAMMPS [3]. A semicrystalline morphology was generated from the melt by the quench protocol described in Section 2.3.3. Defect concentration is defined relative to 1000 ethylene repeat units. Thus the 2 and 4 mol % systems contain 20 and 40 defect sites, respectively, in the 2000-methylene-unit chain.

The four groups studied here differ in structural characteristics that directly influence both their chemistry and dielectric response. The ketone, $-\text{C}(=\text{O})-$, and the aldehyde, $-\text{CHO}$, both carry a carbonyl group and thus possess large permanent dipoles. The ester, $-\text{C}(=\text{O})-\text{O}-$, carries two oxygens, and the alcohol carries the strongly polarized $\text{O}-\text{H}$ bond. The alcohol defect is introduced into the PE chain by replacing one hydrogen atom attached to a backbone carbon by a hydroxyl group. The oxygen and hydrogen of the hydroxyl group carry charges of $-0.683 e$ and $+0.418 e$, respectively. Alcohol is also the only defect in this set that can form hydroxyl-hydroxyl hydrogen bonds. The ketone defects are formed on backbone carbons by removing two hydrogens, with the $\text{C}=\text{O}$ bond pointing away from the polymer chain. The ester group is introduced as a $-\text{C}(=\text{O})-\text{O}-$ linkage in the backbone where its carbonyl and ether oxygens carry local dipoles that do not point in the same direction. The aldehyde differs structurally from the other groups. It is a terminal group, so introducing it breaks the polymer chain and replaces a single continuous chain with two shorter ones. Alcohol, ester, and ketone preserve the continuous backbone and leave the chain intact. The contrast between chain-preserving and chain-cutting defects affects the ease with which the material reorganizes during quench.

4.2.1. Morphology of the Equilibrated Cells

Figure 4.1 shows the equilibrated pristine PE cell and the four 2 mol % defect cells after equilibration at 300 K. Crystallinity is quantified with the local orientational order parameter defined in Chapter 2, Section 2.3.4 and Equation (2.31). Green chain segments mark locally ordered crystalline regions, while blue segments mark disordered amorphous regions. The oxygen atoms in each defect group are highlighted in red. In pristine PE, the chains adopt a well-ordered lamellar arrangement with a global crystallinity of 48.85% under the common 7 Å neighbour-shell and $P_2 > 0.7$ convention, and a density of $0.91 \pm 0.01 \text{ g/cm}^3$. The crystalline fractions of the defect configurations are shown in Figure 4.2. At 2 mol % they are 36.9% for alcohol, 39.9% for aldehyde, 47.8% for ester, and 58.7% for ketone. Raising the concentration to 4 mol % lowers the crystalline fraction to 21.0% for alcohol, 30.2% for ester and 36.8% for ketone, while the aldehyde crystalline fraction increases to 69.4%. For the alcohol, ester and ketone, adding more defects reduces the crystalline fraction, consistent with polar side groups and backbone modifications interrupting regular chain packing [6]. The aldehyde follows a different trend because its insertion cuts the backbone into shorter passivated segments. The greater mobility of those shorter aldehyde segments during the quench provides a plausible explanation for the more ordered 4 mol % configuration.

The defect oxygen atoms are mainly located at lamellar interfaces and in disordered regions rather than deep inside ordered stacks. This placement is physically consistent with the strong obstruction that crystalline lamellae present to gas transport and with oxidation pathways that are consequently favoured in the more accessible amorphous fraction [7, 8]. Here those positions are obtained directly

from the structures summarized in Table 4.1, which shows that the defect sites are predominantly in locally amorphous environments. This distinction matters because orientational polarization requires both a permanent dipole and sufficient local segmental mobility for that dipole to explore different directions.

Table 4.1: Local environment of the defect groups at 300 K, compared with the composition of the cell that contains them. The depletion factor is the fraction of defect groups in a crystalline environment divided by the crystalline fraction of the cell, so unity would mean the defects follow the cell and values below unity mean they are excluded from the ordered domains.

Defect	mol%	Groups	Cell (%)		Defect groups (%)		Depletion
			Cryst.	Amor.	Cryst.	Amor.	
Alcohol	2	20	36.9	63.1	33.3 ± 5.8	66.7 ± 5.8	0.90
	4	40	21.0	79.0	15.0 ± 4.3	85.0 ± 4.3	0.71
Aldehyde	2	20	39.9	60.1	0.0	100.0	0.00
	4	40	69.4	30.6	0.0	100.0	0.00
Ester	2	20	47.8	52.2	0.0	100.0	0.00
	4	40	30.2	69.8	0.0	100.0	0.00
Ketone	2	20	58.7	41.3	15.0	85.0	0.26
	4	40	36.8	63.2	3.8 ± 1.8	96.2 ± 1.8	0.10

Crystalline is $P_2 > 0.6$ and amorphous below it, on the orientation vector defined in Section 4.2.1.

4.3. Dielectric Response at 300 K

Each of the eight systems was simulated in the canonical (NVT) ensemble at 300 K with a fixed cell volume, and the total dipole moment of the cell was recorded every 0.1 ps. Table 4.2 records the thermodynamic state of all systems during the production run. The orientational contribution $\Delta\epsilon$ is obtained from the equilibrium fluctuation of the total cell dipole moment [9], as described in Chapter 2, Section 2.3.5.1. During each production run the total dipole moment of the cell, $\mathbf{M}_{\text{tot}} = \sum_i q_i \mathbf{r}_i$, is calculated from the fixed partial charges and the instantaneous atomic positions. Because the charges are fixed, every change in $\mathbf{M}_{\text{tot}}$ comes from atomic motion; the total dipole therefore fluctuates about a mean even without an applied field.

Dipole fluctuations are converted into permittivity through the fluctuation formula. This is the additional static permittivity generated by reorientation of permanent defect dipoles and nearby polarized chain segments. The key quantity is the variance of the total dipole moment, calculated as the difference between the mean-squared magnitude $\langle M^2 \rangle$ and the squared magnitude of the mean vector $\langle \mathbf{M}_{\text{tot}} \rangle^2$. When dipoles fluctuate freely across all orientations, $\langle \mathbf{M}_{\text{tot}} \rangle^2$ approaches zero, resulting in a large variance and a strong dielectric response. Conversely, if dipoles remain in a preferred direction, $\langle \mathbf{M}_{\text{tot}} \rangle^2$ remains large and subtracts much of $\langle M^2 \rangle$. This reduces the net variance and weakens the response, even when the individual defect dipoles are large. The ratio $|\langle \mathbf{M}_{\text{tot}} \rangle|^2 / \langle M^2 \rangle$ therefore measures how much of the polarization is available as a time-averaged offset; it is defined below as the remnant fraction.

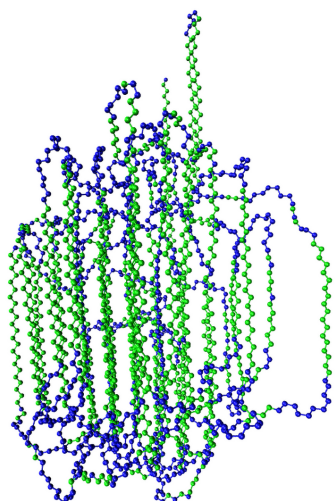
4.3.1. Convergence of the static permittivity

Dipole-fluctuation estimates converge slowly because configurations separated by less than a relaxation time are correlated and do not constitute independent orientational samples. As a result,

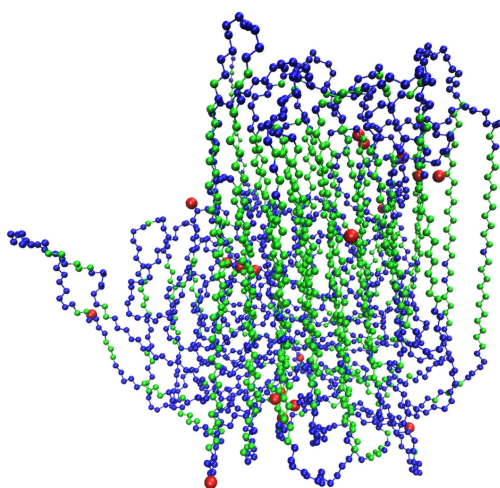
(a) Pristine polyethylene

All cells at 300 K, defects at 2 mol%

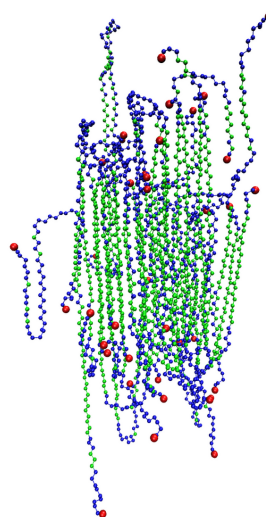
- ordered chain segment
- disordered chain segment
- defect oxygen



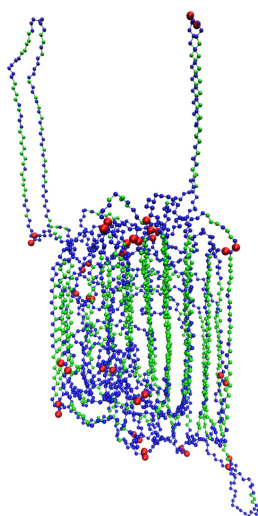
(b) Alcohol



(c) Aldehyde



(d) Ester



(e) Ketone

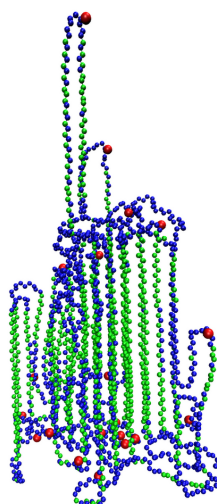


Figure 4.1: Equilibrated cells at 300 K: (a) pristine polyethylene and (b)–(e) the four defect systems at 2 mol %. Chain segments are colored green where the local orientational order parameter identifies an ordered environment and blue where it does not; defect oxygen atoms are shown in red.

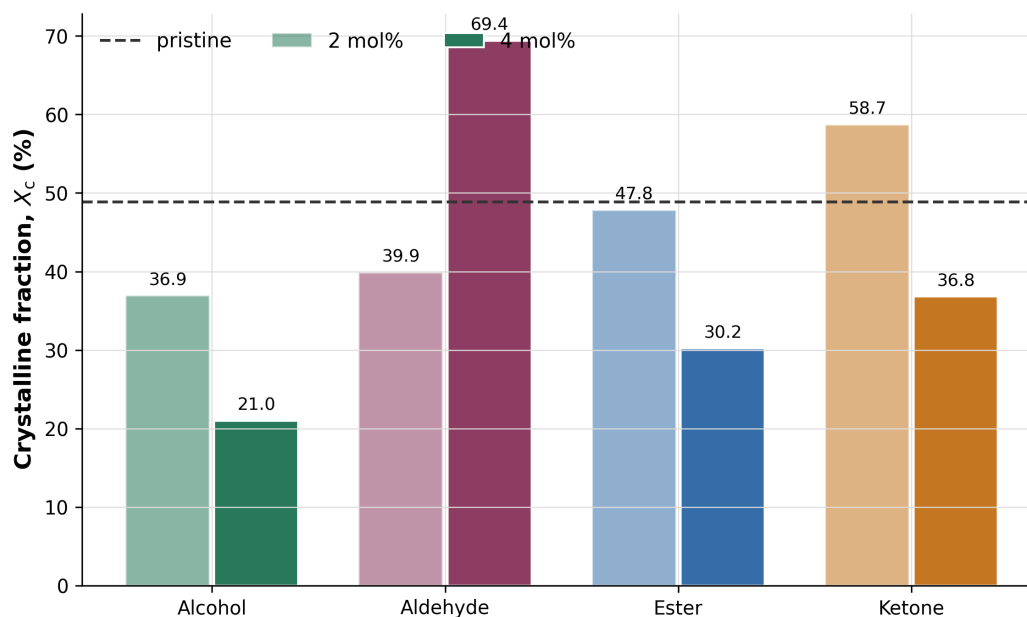


Figure 4.2: Crystalline fraction of the eight fixed-defect configurations at 300 K; the dashed line marks the pristine PE reference.

Table 4.2: Thermodynamic state of the eight fixed-defect cells during the 300 K production runs. The temperature is quoted as the mean over the analyzed trajectory with its standard deviation about that mean; the runs are at fixed cell volume, so the density and volume are constant by construction.

Defect	mol%	T (K)	ρ (g cm ⁻³)	V (Å ³)
Alcohol	2	299.99 ± 3.16	0.8595	54819.2
	4	300.01 ± 3.15	0.8734	54558.4
Aldehyde	2	300.00 ± 3.16	0.8470	55589.3
	4	299.99 ± 3.17	0.8585	55425.0
Ester	2	300.01 ± 3.19	0.8277	56929.1
	4	300.01 ± 3.20	0.8409	56661.2
Ketone	2	299.98 ± 3.17	0.8254	57008.9
	4	300.00 ± 3.17	0.8226	57761.6

the running fluctuation estimate can require tens of nanoseconds to stabilize. Convergence was evaluated from the evolution of the accumulated static permittivity and from the absence of a systematic drift near the end of the production trajectory. Because fixed-charge force fields neglect electronic polarization, the high-frequency dielectric constant (ϵ_∞) was taken from the previous DFPT calculations (Table 3.2). Figure 4.3 shows the static permittivity computed from the 100 ns production runs. The running estimates become visually stable within approximately 40–80 ns. The ketone at 4 mol % takes longest to settle and continues to fluctuate until about 60 ns. This absence of a sustained late-time drift supports use of the full production record.

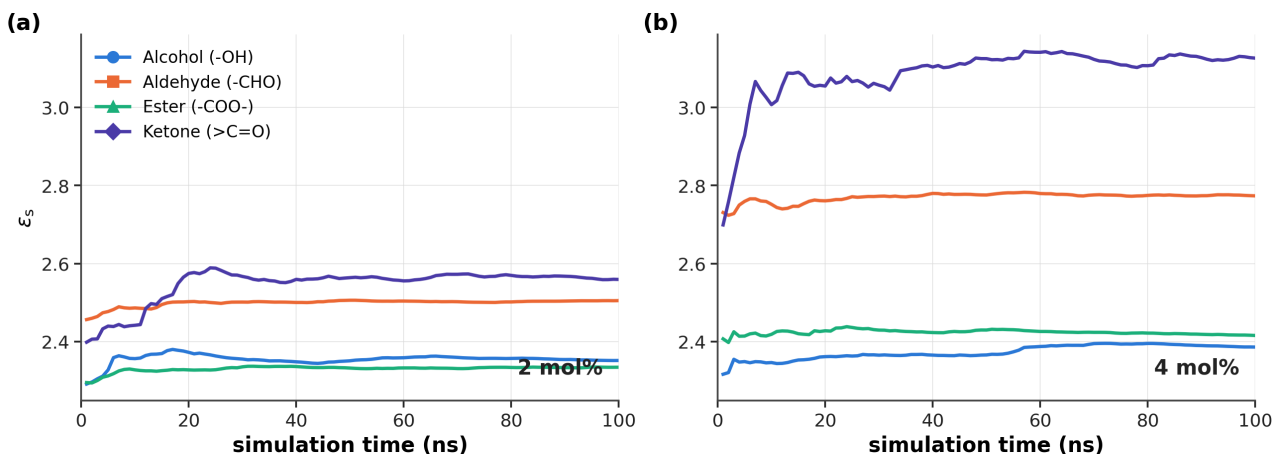


Figure 4.3: Static permittivity ϵ_s computed for each defect group at 300 K, for (a) 2 mol % and (b) 4 mol %.

Table 4.3: Terms of the fluctuation formula and the resulting static response at 300 K. $\langle M^2 \rangle$ is the mean square of the total cell dipole moment, $\langle \mathbf{M} \rangle^2$ the squared magnitude of its mean, and their difference is the fluctuation that generates the orientational response through $\Delta\epsilon = (\langle M^2 \rangle - \langle \mathbf{M} \rangle^2) / (3\epsilon_0 V k_B T)$.

Defect	mol%	$\langle M^2 \rangle$ ($\text{e}^2 \text{\AA}^2$)	$\langle \mathbf{M} \rangle^2$ ($\text{e}^2 \text{\AA}^2$)	$\langle M^2 \rangle - \langle \mathbf{M} \rangle^2$ ($\text{e}^2 \text{\AA}^2$)	$\Delta\epsilon$	ϵ_∞	ϵ_s
Alcohol	2	2.691	0.148	2.543	0.108	2.244	2.352
	4	6.390	3.358	3.032	0.130	2.257	2.387
Aldehyde	2	6.996	0.188	6.808	0.286	2.220	2.506
	4	13.807	0.265	13.541	0.570	2.203	2.773
Ester	2	3.536	0.631	2.905	0.119	2.216	2.335
	4	5.846	0.572	5.274	0.217	2.199	2.416
Ketone	2	9.174	1.281	7.892	0.323	2.236	2.560
	4	22.782	0.931	21.852	0.883	2.243	3.126

Figure 4.5(a) and Table 4.3 give the orientational contribution $\Delta\epsilon$ added by each oxidation product at 2 and 4 mol %. At 2 mol % the ketone gives the largest response, $\Delta\epsilon = 0.323$, followed by the aldehyde at 0.286; the ester and the alcohol are close together at 0.119 and 0.108. At 4 mol % the order is unchanged, but the separation is larger, with ketone at 0.883, aldehyde at 0.570, ester at 0.217 and alcohol at 0.130. The strongest and weakest defects therefore differ by a factor of 6.8 at the same concentration.

The total static permittivity spans three clear groups. The lowest values occur for ester and alcohol at 2 mol %, with $\epsilon_s = 2.339$ and 2.348, respectively. Intermediate values are obtained for alcohol

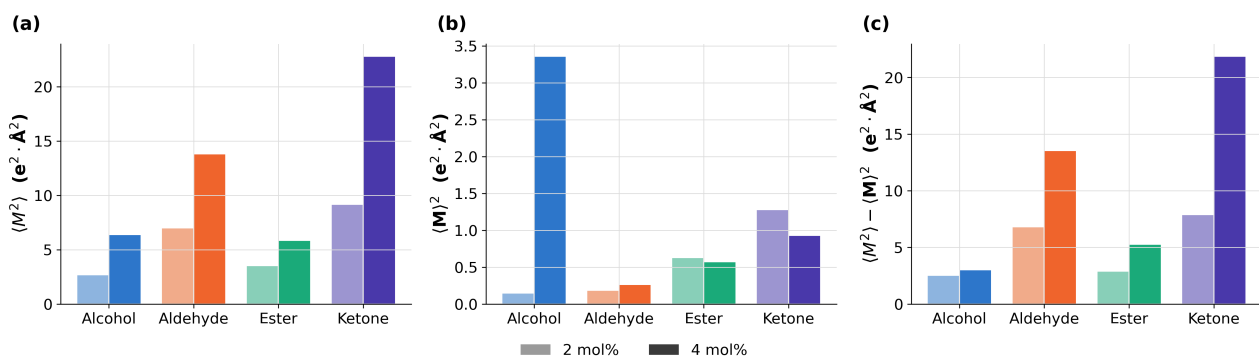


Figure 4.4: Dipole-moment statistics at 300 K: (a) the mean square dipole moment, (b) the squared mean dipole moment, and (c) their difference.

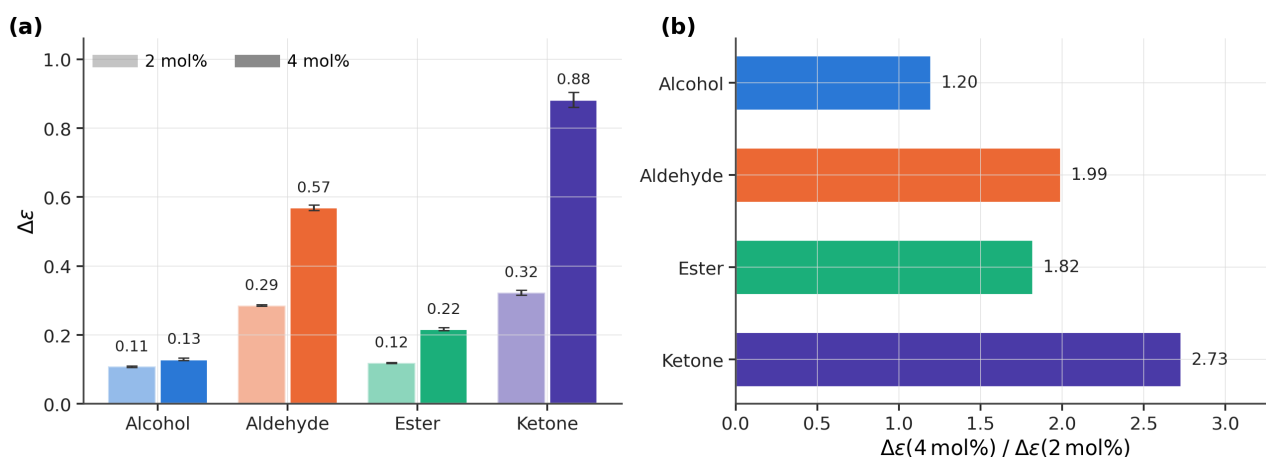


Figure 4.5: (a) Orientational contribution $\Delta\epsilon$ at 300 K for the four defects at 2 and 4 mol%; error bars are block standard errors. (b) The ratio of the 4 mol % value to the 2 mol % value for each defect. A value of two would mean that doubling the number of defects doubles the response.

and ester at 4 mol %, followed by aldehyde and ketone at 2 mol %. The largest values occur at 4 mol %, with aldehyde reaching 2.770 and ketone reaching 3.123. Against the pristine polymer, for which Section 3.2.2 gives $\epsilon_\infty = 2.23$ and a static constant of 2.26, these correspond to increases of between 3.5% for the ester at 2 mol % and 38% for the ketone at 4 mol %. Within the additive multiscale construction used here, most of this increase is assigned to the finite-temperature orientational increment sampled by MD. The comparison does not imply that DFPT contains no ionic response: DFPT includes harmonic lattice vibrations, while the additional MD term represents slower, large-amplitude orientational and correlated segmental fluctuations.

The comparison with crystallinity is shown in Figure 4.6. The ketone at 4 mol % has the largest orientational response even though its crystalline fraction is only 36.8%, whereas the aldehyde at 4 mol % is much more crystalline at 69.4% but gives a smaller response. The alcohol at 4 mol % is the least crystalline system and also has the smallest $\Delta\epsilon$. Crystallinity therefore modifies the environment sampled by each defect but does not order the dielectric response by itself. This lack of ordering by crystallinity shifts the interpretation from morphology alone to the molecular features of each defect. Ketone and ester both contain a carbonyl bond, while ester additionally contains an ether oxygen. Nevertheless, ketone gives about four times the ester response at 4 mol %. The number and magnitude of local partial charges therefore do not determine the orientational response without their geometry, mobility, and correlations. The alcohol contains the most strongly charged single atom in the force field, and it gives the smallest response of the four defects studied. If each defect contributed independently of the others, doubling their number would double $\Delta\epsilon$. Figure 4.5(b) shows that only the aldehyde behaves in this way, with a ratio of 1.99. The ketone grows faster, by a factor of 2.73, and the alcohol much more slowly, by a factor of 1.20; the ester lies in between at 1.82. This scaling differs materially from the DFPT lattice-vibrational increments in Figure 3.3. On doubling the concentration from 2 to 4 mol %, the DFPT lattice contribution changes by factors of 2.00, 1.89, 1.64, and 1.70 for aldehyde, alcohol, ketone, and ester, respectively, whereas the corresponding MD orientational factors are 1.99, 1.20, 2.73, and 1.82. Thus aldehyde is nearly linear in both descriptions and ester is broadly similar, but alcohol is substantially more sublinear and ketone is superlinear only in the finite-temperature MD response. This is not a contradiction: DFPT probes small-amplitude harmonic ionic displacements in optimized cells, whereas MD probes large-amplitude orientational fluctuations, intermolecular correlations, and morphology-dependent segmental motion. The concentration dependence of one contribution therefore cannot be used as a proxy for the other.

4.3.2. Dipole magnitude, fluctuation and remnant dipole

The static response is calculated from the fluctuation of the cell dipole moment about its mean, so it depends on two properties of the dipole trajectory: how widely the dipole moment fluctuates and how much of the dipole moment is a fixed offset that does not fluctuate at all. Table 4.4 and Figure 4.7 report how these quantities vary with defect chemistry and concentration.

Table 4.4: Dipole moment statistics at 300 K. The variance of the cell dipole is the quantity that enters the fluctuation formula directly.

Defect	mol%	$\langle M \rangle$ (eÅ)	$\sigma_{ M }$ (eÅ)	Variance (e ² Å ²)	Remnant (%)
Alcohol	2	1.52	0.63	0.39	5.5
	4	2.37	0.87	0.76	35.9
Aldehyde	2	2.44	1.02	1.03	5.5
	4	3.42	1.45	2.10	< 0.05
Ester	2	1.74	0.72	0.52	11.5
	4	2.23	0.93	0.87	9.9
Ketone	2	2.79	1.18	1.39	12.7
	4	4.42	1.81	3.27	3.9

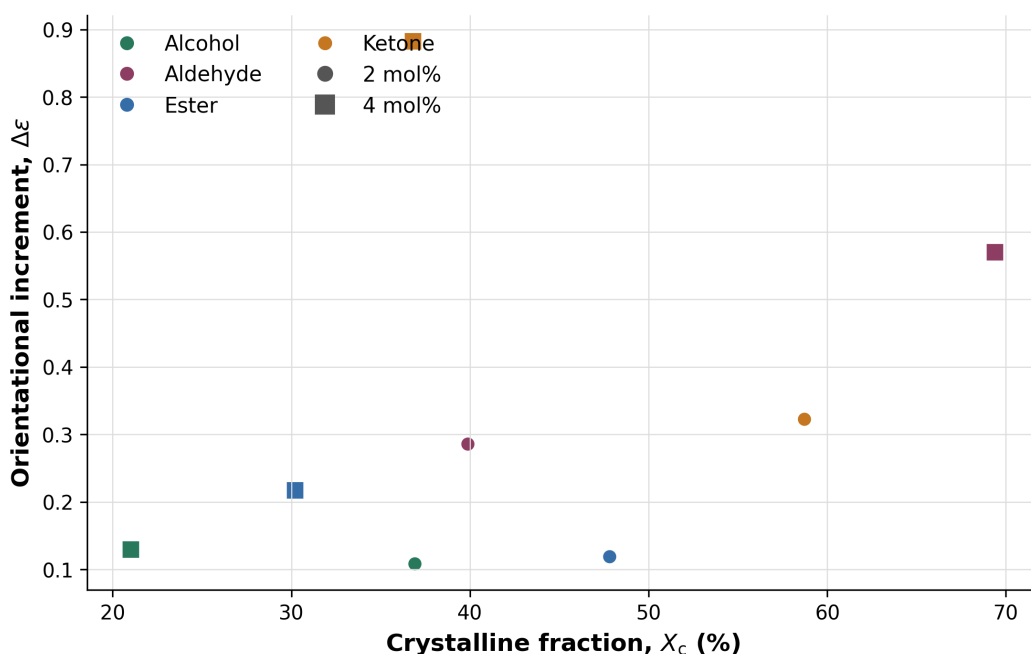


Figure 4.6: Crystalline fraction compared with the 300 K orientational contribution $\Delta\epsilon$. Open symbols are 2 mol % systems and filled symbols are 4 mol % systems.

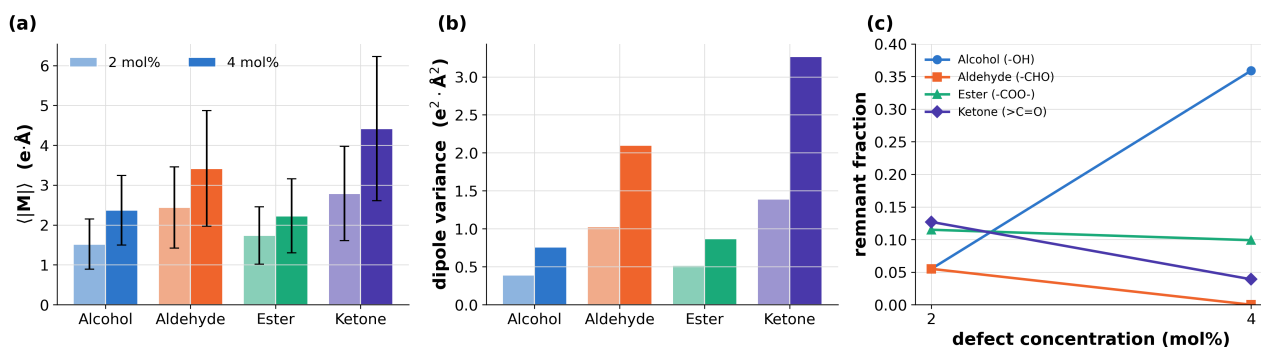


Figure 4.7: Properties of the cell dipole moment at 300 K, showing (a) mean magnitude, with the bars showing the standard deviation, (b) the variance of the magnitude, and (c) the remnant fraction.

The mean dipole magnitude rises with defect concentration for every defect, from $1.52 e\text{\AA}$ for the alcohol at 2 mol % to $4.42 e\text{\AA}$ for the ketone at 4 mol %; from largest to smallest, the order is ketone, aldehyde, ester and alcohol. The variance of the magnitude follows the same order, running from 0.39 to $3.27 e^2\text{\AA}^2$. Since the response is determined by the size of the fluctuations, this is the expected relationship. The ratio of $\Delta\epsilon$ to the variance is between 0.23 and 0.28 for seven of the eight systems. The one system that deviates from this proportionality is the alcohol at 4 mol %, where the ratio falls to 0.17. This deviation arises from the remnant fraction, which measures how much of the mean squared dipole moment is retained during time averaging. A value near zero means that the dipole explores all directions during the run, while a value near one means that a greater part of the dipole remains as a non-fluctuating offset and is removed by mean subtraction. For alcohol, the remnant fraction increases from 5.5% at 2 mol % to 35.9% at 4 mol %. At the higher concentration, a large fraction of alcohol dipoles are in a static offset that does not contribute to the fluctuation, and the alcohol produces a smaller dielectric response. Among the other systems, the reported remnant fractions are 0–5.5% for aldehyde, 9.9–11.5% for ester, and 3.9–12.7% for ketone. A large remnant fraction indicates either an orientational constraint that locks the dipole or incomplete sampling when the simulation trajectory is short relative to the slowest relaxation process. The alcohol has the slowest

relaxation of the four defect types, and the 4 mol % alcohol system also has the largest remnant fraction. Hydrogen bonding between hydroxyl groups is therefore a plausible microscopic source of the constraint, consistent with earlier work on hydroxyl-functionalized polyolefins [5, 10, 11].

4.3.3. Direction dependence of the response

The permittivity of a material with aligned lamellae need not be the same along all three axes of the cell, and if it were strongly anisotropic then a single number $\Delta\epsilon$ would be a poor summary of it. Figure 4.8 shows the three diagonal Cartesian components of the response for each system, and the last column of Table 4.5 gives the ratio of the largest to the smallest of them.

Table 4.5: Direction dependence of the orientational response at 300 K. $\Delta\epsilon_{xx}$, $\Delta\epsilon_{yy}$ and $\Delta\epsilon_{zz}$ are the diagonal components of the response along the three axes of the simulation cell.

Defect	mol%	$\Delta\epsilon_{xx}$	$\Delta\epsilon_{yy}$	$\Delta\epsilon_{zz}$	$\Delta\epsilon_{\max}/\Delta\epsilon_{\min}$
Alcohol	2	0.1131	0.1031	0.1085	1.10
	4	0.1601	0.1026	0.1263	1.56
Aldehyde	2	0.2611	0.3030	0.2932	1.16
	4	0.5734	0.6373	0.4994	1.28
Ester	2	0.1430	0.0984	0.1158	1.45
	4	0.2017	0.2195	0.2303	1.14
Ketone	2	0.3744	0.2732	0.3214	1.37
	4	0.9599	0.8023	0.8857	1.20

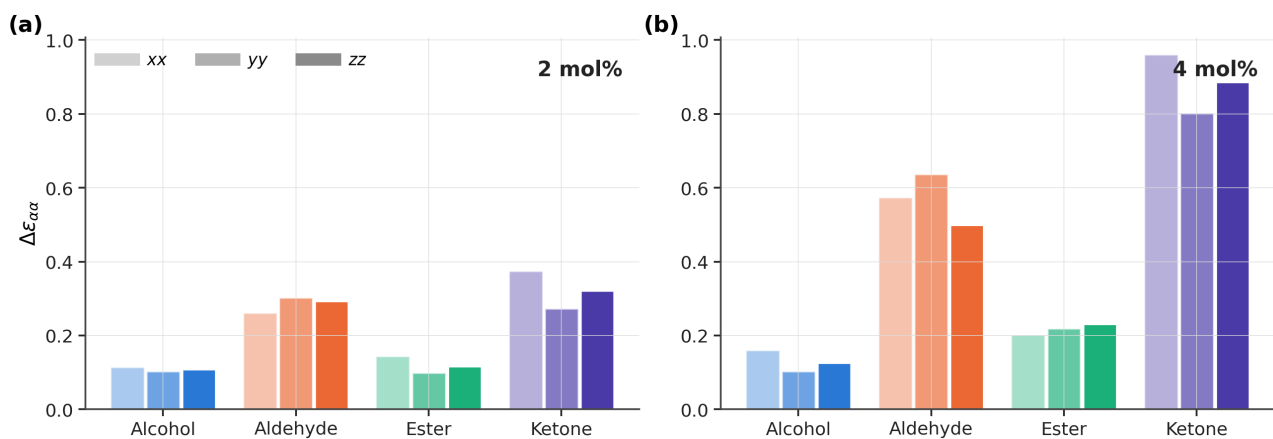


Figure 4.8: Diagonal Cartesian components $\Delta\epsilon_{xx}$, $\Delta\epsilon_{yy}$ and $\Delta\epsilon_{zz}$ of the orientational response at 300 K, at (a) 2 mol % and (b) 4 mol %.

The ratio lies between 1.10 and 1.56 across the eight systems. The largest values occur for the alcohol at 4 mol % (1.56) and the ester at 2 mol % (1.45), and the smallest for the alcohol at 2 mol % (1.10). There is no systematic preference for one Cartesian direction. The largest component is xx for five of the eight systems, yy for two and zz for one, and the direction that is largest changes with concentration only for the ester. This is what would be expected of a cell in which the lamellae were formed by a quench from the melt without any imposed alignment, so that the lamellar normal bears no fixed relation to the axes of the simulation box. The residual anisotropy of 10–56% is smaller than the factor of 6.8 that separates the defects, and it is not systematic, so the scalar average $\Delta\epsilon$ used in the rest of the chapter is an adequate description of the response.

4.3.4. Relaxation of the dipole correlation function

The static response says how much additional polarization a defect can store, but not how quickly it can be stored. Since PE is operated over a wide range of frequencies, both the size and the speed of the response matter. The normalized autocorrelation function $\phi(t)$ is calculated from fluctuations $\delta \mathbf{M}_{\text{tot}}(t) = \mathbf{M}_{\text{tot}}(t) - \langle \mathbf{M}_{\text{tot}} \rangle$, using the definition in Chapter 2, Section 2.3.5.2 and Equation (2.33). It measures how much memory the fluctuating cell dipole retains of its direction at the time origin. By normalization, $\phi(0) = 1$; it then decays as successive configurations lose orientational correlation.

Figure 4.9 shows $\phi(t)$ for the eight systems on a logarithmic time axis. The four defect systems behave very differently. The alcohol curve stays high for the first hundred picoseconds and then decays over several nanoseconds. The ketone starts to decay earlier than the alcohol but remains slower than the aldehyde and ester. The aldehyde and the ester have already lost a large part of their correlation within the first ten picoseconds and then decay slowly over the remaining decades.

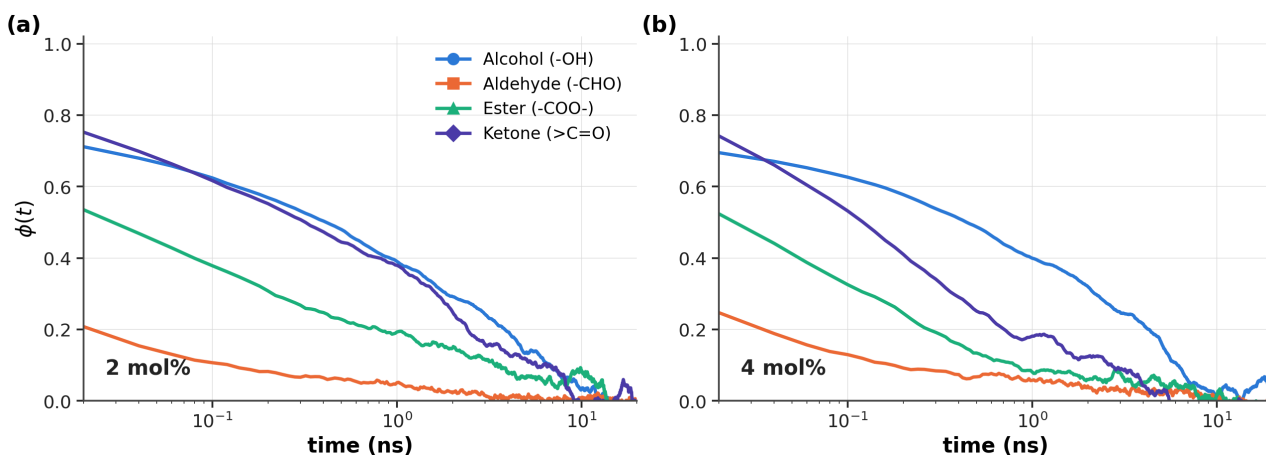


Figure 4.9: Dipole autocorrelation function $\phi(t)$ at 300 K, at (a) 2 mol % and (b) 4 mol %.

The relaxation curves are represented by the Kohlrausch–Williams–Watts (KWW) stretched exponential defined in Equation (2.34) [12, 13]. Here τ_{KWW} sets the time scale, while $0 < \beta \leq 1$ describes the breadth of the relaxation-time distribution: $\beta = 1$ is a single exponential and smaller values represent a broader, more heterogeneous decay. The reported mean relaxation time $\langle \tau \rangle$ is calculated with Equation (2.35). The conversion from the fitted time-domain correlation to $\epsilon''(\omega)$ follows Section 2.3.5.4. This procedure is consistent with established molecular-dynamics calculations in which dipole autocorrelation functions are transformed into frequency-dependent dielectric response functions [4, 5]. Appendix E compares five definitions of the relaxation time on these same trajectories.

Table 4.6 gives the fitted parameters obtained from the same 100 ns trajectory and 10 ps exported ACF grid used for the temperature series. Alcohol relaxes on a few-nanosecond time scale, with $\langle \tau \rangle = 2.95$ and 3.04 ns at 2 and 4 mol %, respectively. Ketone changes more strongly with concentration, from 2.344 to 0.887 ns, while its β decreases from 0.496 to 0.39. Aldehyde has the shortest quoted mean times, 0.17 and 0.38 ns, but its fitted amplitudes exceed one, which signals that part of the initial decay occurs below the 10 ps grid and makes its KWW parameters less robust. The broad ester fits have the same short-time limitation and show a non-Debye response, and $\langle \tau \rangle$ falls from 3.039 to 0.76 ns as the concentration is doubled.

4.3.5. Dielectric loss

The loss spectrum describes how much energy the material dissipates per cycle at each frequency. A defect contributes to the loss over a band of frequencies centered near the inverse of its relaxation time, and the height of that band scales with the amount of polarization the defect can store. A material may therefore be penalized either by a large loss concentrated in a narrow band or by a smaller loss spread over many decades. The spectra discussed here cover the orientational response of the

Table 4.6: Stretched-exponential (KWW) relaxation parameters and derived loss characteristics at 300 K. FWHM is the full width at half maximum of the loss peak, in decades of frequency.

Defect	mol%	A	τ_K (ns)	β	$\langle\tau\rangle$ (ns)	R^2	f_{pk} (Hz)	ε''_{pk}	FWHM (dec.)
Alcohol	2	0.78	2.02	0.61	2.95	0.992	6.3×10^7	0.03	1.74
	4	0.75	2.27	0.66	3.04	0.984	5.5×10^7	0.03	1.64
Aldehyde	2	1.13	0.003	0.22	0.17	0.985	3.0×10^{10}	0.04	4.16
	4	1.14	0.006	0.22	0.38	0.990	1.7×10^{10}	0.08	4.47
Ester	2	1.04	0.10	0.24	3.04	0.990	9.5×10^8	0.02	4.40
	4	1.12	0.045	0.27	0.76	0.991	2.3×10^9	0.04	4.04
Ketone	2	0.89	1.15	0.50	2.34	0.993	9.8×10^7	0.08	2.03
	4	1.03	0.25	0.39	0.89	0.995	4.4×10^8	0.20	2.74

classical trajectories. The complementary vibrational region, obtained from Car-Parrinello trajectories of the same defect chemistries, is reported in Appendix D.

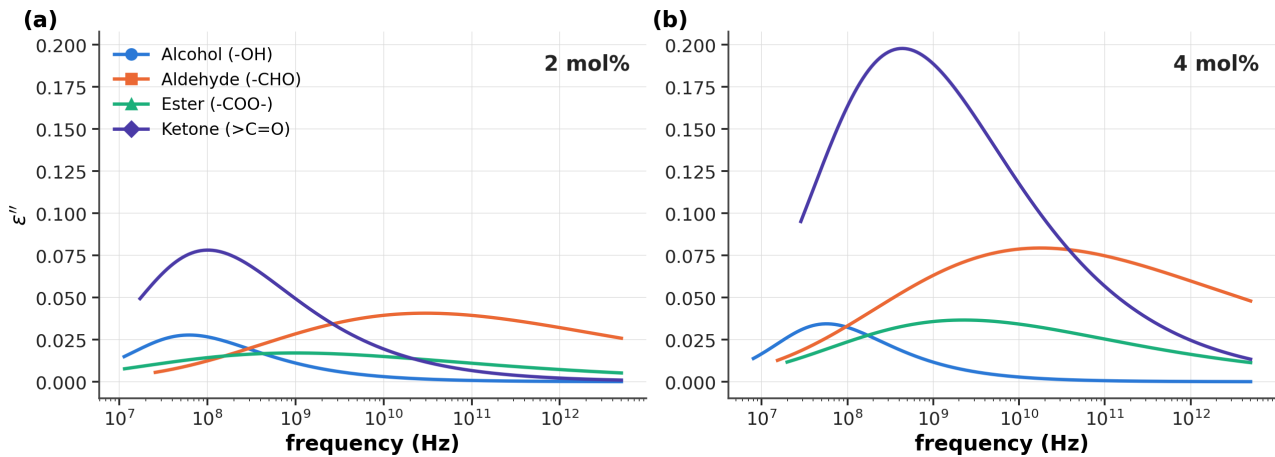


Figure 4.10: Dielectric loss spectra at 300 K, at (a) 2 mol % and (b) 4 mol %.

Figure 4.10 shows the loss spectra at both concentrations, and the last two columns of Table 4.6 give, in that order, the peak position f_{pk} and peak height ε''_{pk} . Alcohol has peaks at 6.34×10^7 and 5.53×10^7 Hz, with heights of 0.028 and 0.034 at 2 and 4 mol %, respectively. Ketone reaches 0.078 and 0.198 at 9.83×10^7 and 4.41×10^8 Hz, giving the largest peak at each concentration. The aldehyde peak occurs at much higher fitted frequencies, 2.95×10^{10} and 1.73×10^{10} Hz. Ester remains low in amplitude, at 0.017 and 0.037, despite its broad response. Overall, ketone has both the highest static response and the largest loss peak, whose position lies in the 10^8 – 10^9 Hz range. Alcohol and ester produce the smallest losses of the four defect groups. For these systems, the ranking of loss amplitude is similar to that of the stored orientational polarization, while the peak frequency remains controlled by the relaxation dynamics.

Choice of relaxation model

Equation (2.34) is not the only form that can describe a decay of this kind, and a single stretched exponential is a strong assumption when the cell contains two physically distinct populations of dipoles, the defect groups and the matrix around them. Two alternatives were therefore fitted to the same correlation functions: a simple sum of two exponentials, and a two-component model in which each

population relaxes with its own stretched exponential. Figure 4.11 and Tables 4.7 and 4.8 compare them.

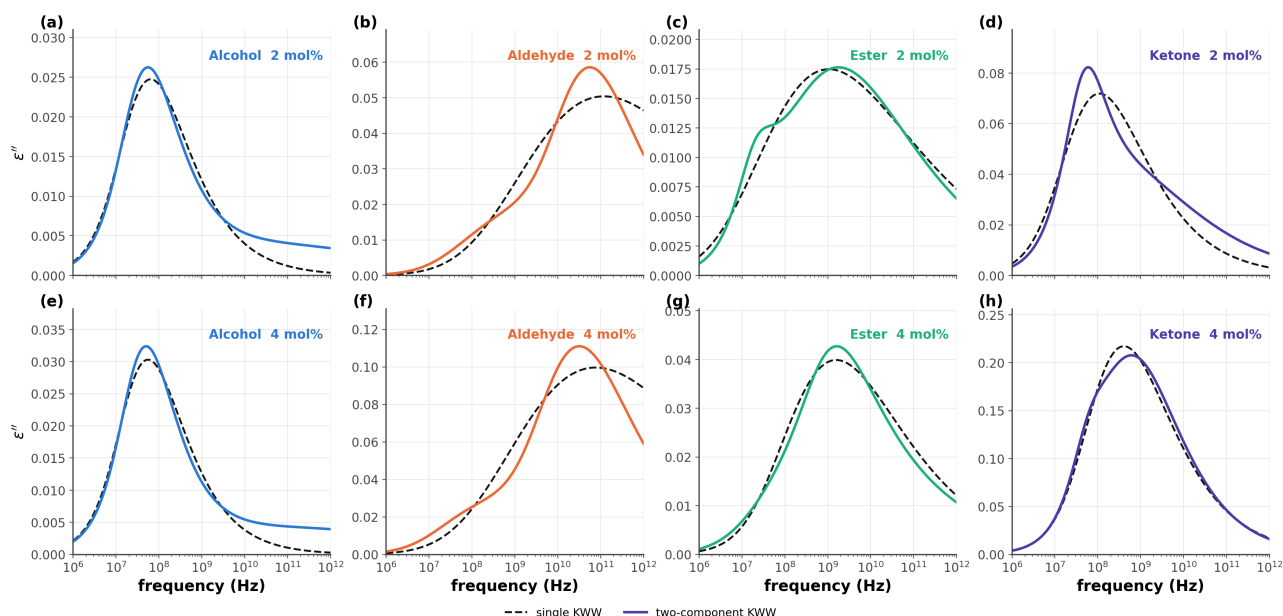


Figure 4.11: Comparison of the single stretched-exponential fit with a two-component model, in the time domain and after transformation to the loss spectrum.

Table 4.7: Comparison of the single- and two-component stretched-exponential descriptions of the 300 K dipole autocorrelation. Timescales are mean relaxation times. 4.6.

Defect	mol %	A (single)	Fast weight	τ_{fast} (ns)	τ_{slow} (ns)
Alcohol	2	0.78	0.33	0.440	3.28
	4	0.75	0.35	1.385	3.44
Aldehyde	2	1.50	0.69	0.004	0.70
	4	1.50	0.78	0.009	1.98
Ester	2	1.05	0.89	0.536	7.69
	4	1.02	0.29	0.119	1.17
Ketone	2	0.90	0.61	0.804	3.17
	4	0.99	0.83	0.296	2.61

The single stretched exponential is retained for the main analysis. It uses fewer parameters, it reproduces the correlation functions well across the whole set, and the resulting mean relaxation time is the quantity compared between defects. The two-component fits are reported because they show where the single form is a simplification: two distinct time scales improve the empirical description, with the largest separation in systems whose single-form β is smallest.

4.3.6. Defect-matrix decomposition

The total dipole moment of the cell is written as the sum of the dipole moment carried by the defect groups, M_{def} , and that carried by the remaining PE matrix, M_{mat} . Following self/cross decompositions used in molecular-dynamics analyses of orientational correlations [14], the response is separated into defect self, matrix self, and defect-matrix cross terms. The complete definition and normalization are given in Chapter 2, Section 2.3.5.3 and Equation (2.36). The cited glycerol study is a methodological precedent for separating self and cross orientational correlations. A positive cross

Table 4.8: Dielectric-loss consequences of replacing the single-KWW description by the two-component KWW model for the high-resolution 300 K autocorrelation functions.

Defect	mol%	A (single)	ΔAIC	ε''_{pk} single	ε''_{pk} two	f_{pk} two (Hz)
Alcohol	2	0.78	105	0.025	0.026	5.62×10^7
	4	0.75	110	0.030	0.032	5.11×10^7
Aldehyde	2	1.50	347	0.050	0.059	5.62×10^{10}
	4	1.50	332	0.100	0.111	3.16×10^{10}
Ester	2	1.05	89	0.017	0.018	1.78×10^9
	4	1.02	116	0.040	0.043	1.62×10^9
Ketone	2	0.90	270	0.072	0.082	6.19×10^7
	4	0.99	32	0.217	0.208	6.19×10^8

term means that correlated matrix fluctuations add to the defect fluctuations, whereas a negative term means that their covariance cancels part of the response. This is a statistical statement about correlated motion and does not require the two instantaneous dipoles to be exactly parallel or antiparallel. Figure 4.14 and Table 4.9 give the three terms for all eight systems. Figures 4.12 and 4.13 show the same decomposition resolved in time, with each component normalized to its own value at $t = 0$ and scaled by its dielectric weight, so that the weighted components sum to the total correlation function.

Table 4.9: Decomposition of the 300 K orientational contribution into defect self, matrix self and defect-matrix cross contributions.

Defect	mol%	$\Delta\varepsilon$	Defect self	Matrix self	Cross	Cross (%)
Alcohol	2	0.108	0.106	0.013	−0.012	−10.7
	4	0.130	0.125	0.014	−0.010	−7.3
Aldehyde	2	0.286	0.245	0.014	0.026	9.2
	4	0.570	0.505	0.017	0.049	8.6
Ester	2	0.119	0.082	0.016	0.021	17.4
	4	0.217	0.165	0.021	0.031	14.3
Ketone	2	0.323	0.247	0.014	0.062	19.3
	4	0.883	0.686	0.022	0.175	19.8

The matrix term is small and nearly the same in every system, between 0.013 and 0.022. It accounts for between 2.5% and 13.4% of the total, and it does not vary in step with the defect types. It is 0.014 for both the aldehyde at 2 mol % and the ketone at 2 mol %, whose totals differ by 13%. This is consistent with the matrix being non-polar hydrocarbon, which has no permanent dipole of its own to reorient and contributes only through the weak polarity of its C–H bonds. The differences between the defects are therefore not produced by the matrix acting on its own. The defect term, in contrast, varies over the same range as the total, from 0.106 for the alcohol at 2 mol % to 0.686 for the ketone at 4 mol %. It sets the scale of the response; however, it does not by itself reproduce the ordering of the total dielectric response, because the cross term modifies it by different amounts.

Figure 4.15(a) shows this by plotting the total against the defect self term. Points above the diagonal contain a positive combined matrix and cross contribution; points below it contain a negative combined contribution. At the scale of panel (a), the alcohol symbols lie only slightly above the diagonal and appear visually almost coincident with it because the positive matrix self term nearly offsets the negative cross term. The cross term's sign is resolved quantitatively in panel (b) and Table 4.9: the alcohol cross term is −0.012 at 2 mol % and −0.010 at 4 mol %, corresponding to −10.7% and

Weighted correlation-function components, 2 mol%

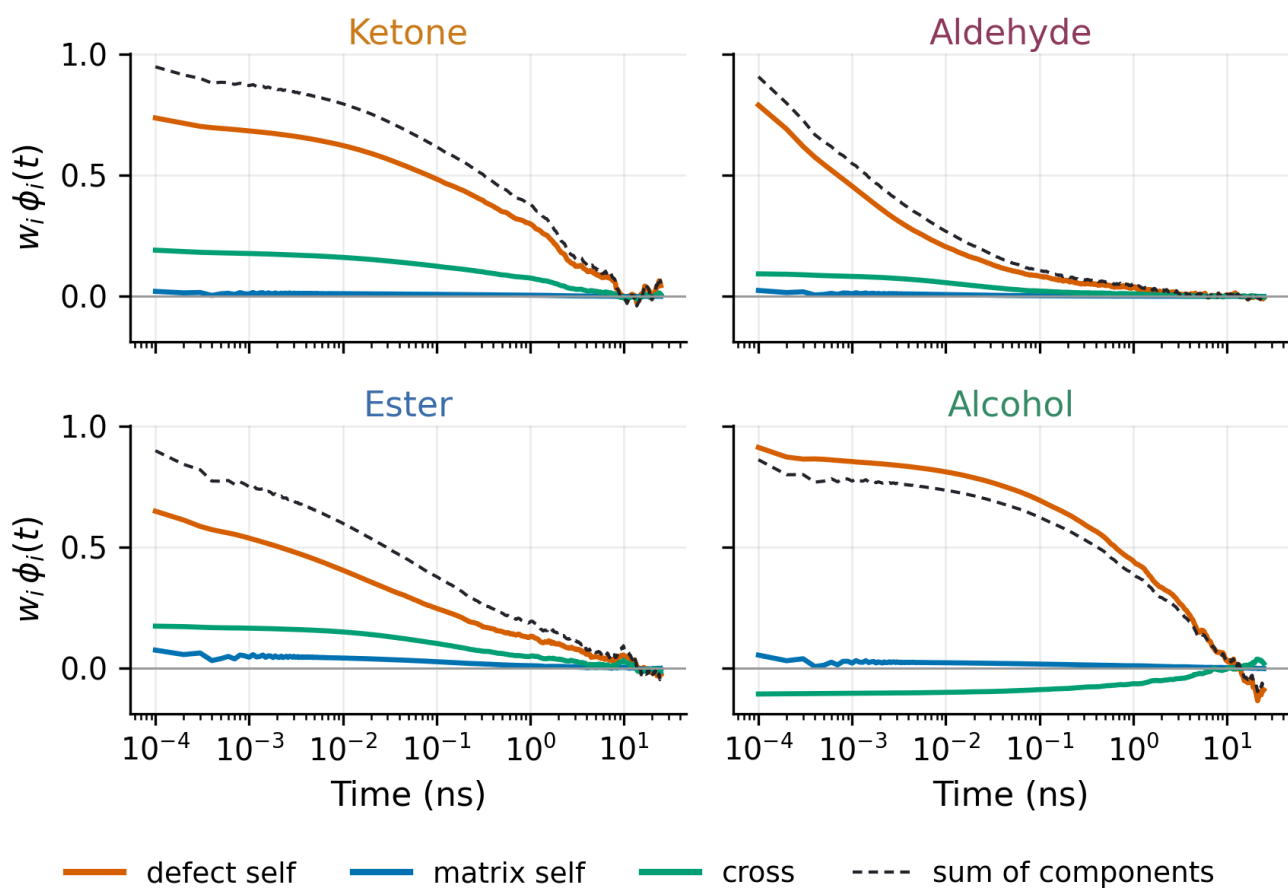


Figure 4.12: Amplitude-weighted correlation functions of the three terms of Equation (2.36) at 2 mol %, showing how each contributes to the decay of the total.

Weighted correlation-function components, 4 mol%

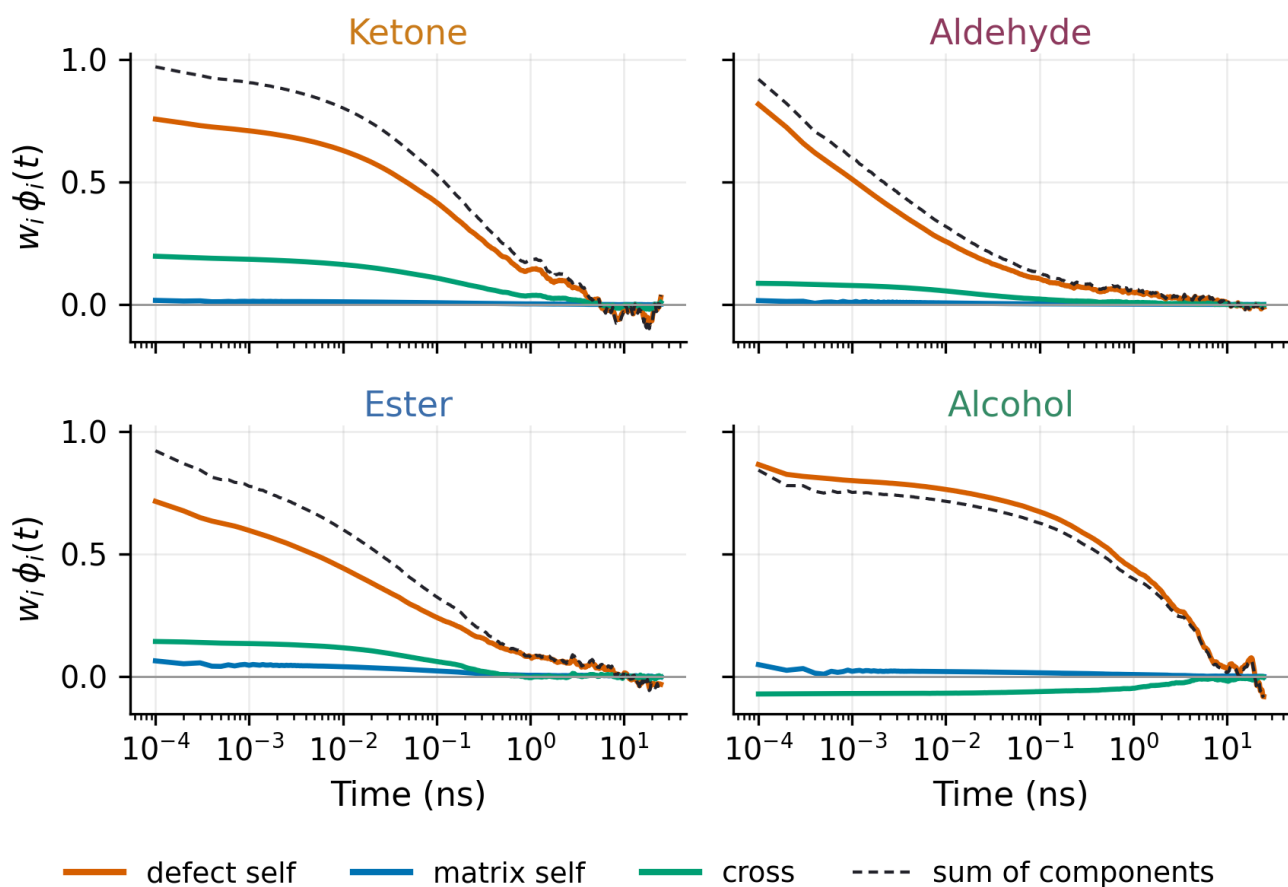


Figure 4.13: Amplitude-weighted correlation functions at 4 mol %.

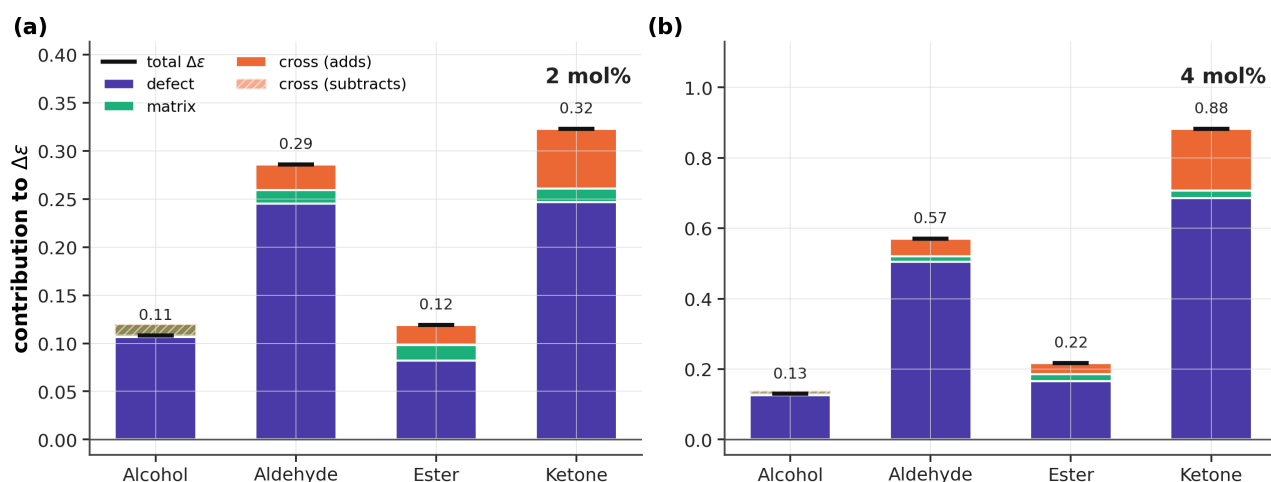


Figure 4.14: Decomposition of the 300 K orientational contribution into the defect, matrix and cross terms of Equation (2.36), at (a) 2 mol % and (b) 4 mol %. The cross term is hatched where it is negative. Black markers give the total, which the three terms reproduce by construction.

−7.3% of the total. The associated defect-matrix directional correlations are also negative, −0.154 and −0.115. For the other three defect types, the cross term is positive: +9.2% and +8.6% for the aldehyde, +17.4% and +14.3% for the ester, and +19.3% and +19.8% for the ketone, the last with defect-matrix correlations of +0.531 and +0.715.

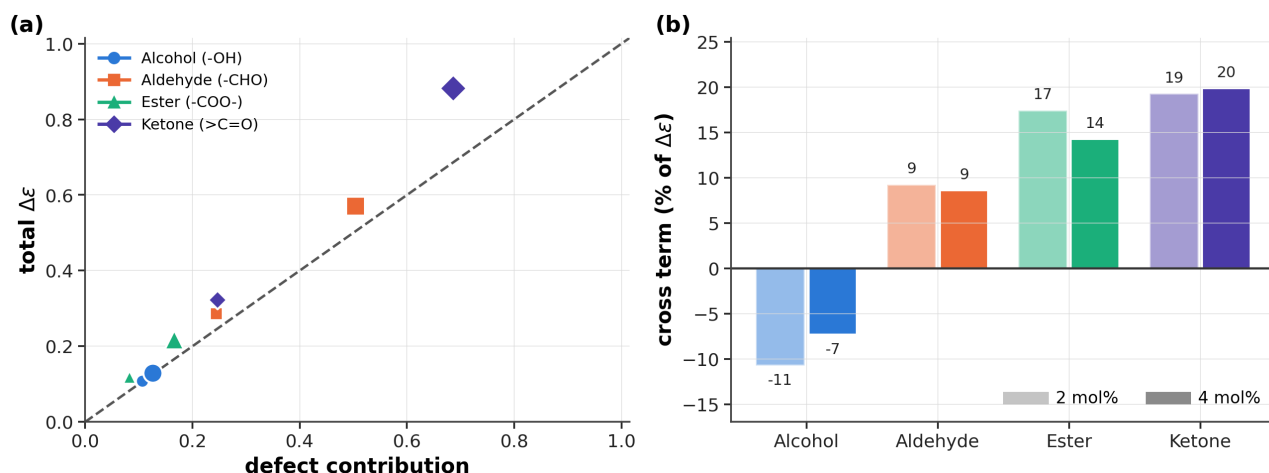


Figure 4.15: (a) Total orientational contribution against the defect self term of Equation (2.36); the dashed diagonal is a visual reference for equality between those two quantities. Because the matrix self term is also present, the signed cross percentages in panel (b), rather than visual distance from the diagonal alone, determine the sign of defect-matrix coupling. Larger symbols are 4 mol %. (b) The cross term as a percentage of the total.

The correlations behind these numbers are shown group by group in Figure 4.16. Alcohol is the only defect with a negative defect-matrix correlation. Ester instead shows an internal cancellation channel: its carbonyl and ether-bond contributions have correlation coefficients of −0.59 and −0.56 at 2 and 4 mol %, respectively.

The ketone exceeds the ester although both contain a carbonyl because its defect self term is larger, 0.686 against 0.165 at 4 mol %, and because its positive cross term adds a further 0.175. The ester's smaller defect term has a specific origin visible in Figure 4.16. Its carbonyl subgroup taken alone contributes 0.245 at 2 mol %, whereas the corresponding value for the complete ester group is 0.082. This reduction occurs because the carbonyl and ether oxygen dipoles are anti-correlated at −0.59 and partially cancel each other before the group has any opportunity to couple to the matrix. Thus, the ester response is limited by internal cancellation within the group rather than by weak polarity.

The alcohol falls below the other three despite its large atomic charge because it is the only defect for which the defect-matrix covariance is negative. This negative covariance cancels about one tenth of the defect-associated response; it does not mean that the matrix possesses an independent dipole of the same magnitude pointing permanently in the opposite direction. Slow relaxation, a large remnant fraction, and a negative cross term are consistent with hydrogen-bonding constraints. A hydrogen-bonded hydroxyl network could couple local O–H reorientation to compensating chain motion, and such constrained hydroxyl dynamics are plausible in light of earlier work [5, 10, 11]. The structural evidence for that interpretation—hydroxyl-hydroxyl contact statistics, polar contacts with the matrix, and the persistence of the O–H orientation—is examined in Appendix G. The defect-matrix correlation of the ketone rises from +0.531 to +0.715 when the concentration is increased to 4 mol %, indicating stronger coupling at higher ketone concentration and a faster-than-proportional growth in response. For alcohol, the correlation remains negative at both concentrations while the defect term grows only from 0.106 to 0.125, and the response grows more slowly than proportionally. The aldehyde, whose cross term is essentially unchanged at +9.2% and +8.6%, is the only defect that scales proportionally.

The same decomposition can be transformed into the frequency domain. Figure 4.17 shows that

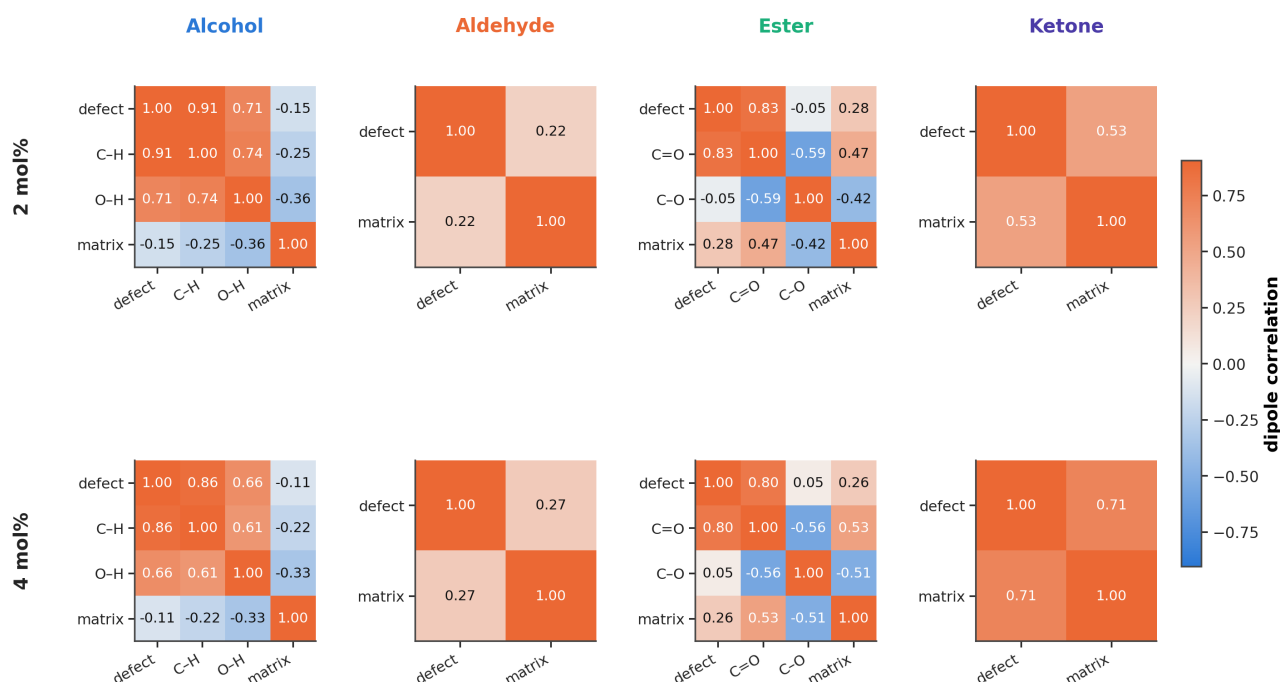


Figure 4.16: Correlations between the dipole moments of the chemical constituents at 300 K. In every panel, defect denotes the dipole of the complete defect group and matrix denotes the remainder of the PE chain after all atoms assigned to that motif have been excluded. The alcohol panel additionally resolves the motif into its O – H bond and adjacent backbone C – H bonds; the ester panel resolves it into its carbonyl C = O and ether C – O bonds. Aldehyde and ketone are not subdivided, which is why their panels contain only the complete motif and matrix.

the defect self term carries most of the loss intensity, while the matrix self term is small across the frequency range. The cross contribution preserves the sign of the static mechanism. It is negative for the alcohol near the loss band, reducing the total below the defect-self spectrum, and positive for the aldehyde, ester and ketone. Consequently, the ketone combines the largest defect-self loss contribution with the largest positive cross contribution, whereas the alcohol has a modest defect-self contribution that is further suppressed by anti-correlated matrix motion.

4.4. Temperature Dependence

The 300 K systems were extended to temperatures of 280 and 320 K to determine how both their semicrystalline structure and dielectric properties change over this interval. The comparison follows crystallinity, orientational dielectric strength, dipole relaxation, and dielectric loss for the same defect groups and concentrations. The fluctuation formula includes an explicit $1/T$ factor, which reduces the orientational permittivity contribution $\Delta\epsilon$ with increasing temperature under constant dipole variance. At the same time, increasing the temperature can accelerate barrier crossing by defect groups and polymer segments, allowing a trajectory to sample a wide range of orientations, which can increase the overall dipole variance. Changes in local packing and semicrystalline order can further shift the constraints on those motions. Dielectric-relaxation theory and studies of PE and hydroxyl-containing PE all support the coexistence of activated local reorientation and broader chain/morphology effects [5, 11, 15, 16]. Those references establish plausible competing mechanisms; they do not select the dominant mechanism at any individual state point in the present data. The comparison is therefore preliminary: the fixed-volume calculations isolate changes at constant density and do not include thermal expansion.

Figure 4.18 and Table 4.10 show no universal monotonic temperature dependence of crystallinity. Alcohol loses order between 280 and 320 K at both concentrations, but other defect groups show

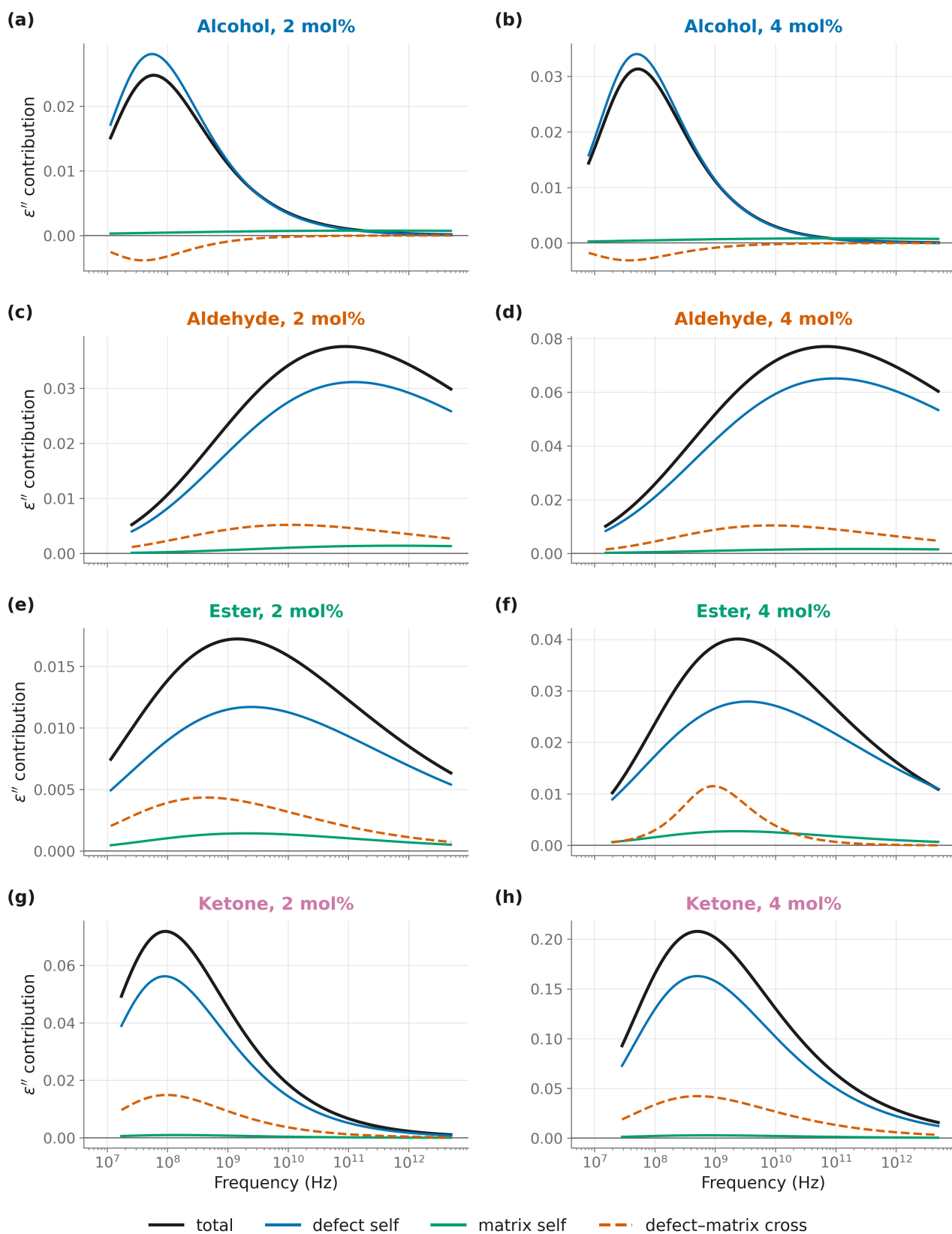


Figure 4.17: Frequency-domain decomposition of the 300 K dielectric loss into the defect self, matrix self and defect-matrix cross contributions.

Table 4.10: Temperature dependence of the eight defect systems. $\Delta\epsilon$ is the orientational contribution obtained from a 100 ns production window, with its standard error from ten contiguous 10 ns blocks; $\epsilon_s = \epsilon_\infty + \Delta\epsilon$ uses the defect-specific DFPT high-frequency constant of Table 3.2; and X_c is the crystalline fraction of the corresponding cell.

Defect	mol%	T (K)	$\Delta\epsilon$	SEM	ϵ_s	X_c (%)
Alcohol	2	280	0.0657	0.0027	2.3095	44.80
		300	0.1082	0.0046	2.3521	36.92
		320	0.1216	0.0053	2.3654	39.25
	4	280	0.1218	0.0042	2.3786	21.35
		300	0.1297	0.0060	2.3865	21.00
		320	0.1508	0.0072	2.4076	19.35
Aldehyde	2	280	0.2958	0.0043	2.5153	41.05
		300	0.2858	0.0027	2.5053	39.88
		320	0.2665	0.0037	2.4860	40.60
	4	280	0.5698	0.0046	2.7730	56.80
		300	0.5701	0.0082	2.7733	69.38
		320	0.5482	0.0110	2.7515	63.30
Ester	2	280	0.1078	0.0034	2.3236	33.08
		300	0.1191	0.0021	2.3349	47.81
		320	0.1172	0.0032	2.3331	30.91
	4	280	0.2164	0.0072	2.4153	27.50
		300	0.2172	0.0041	2.4161	30.20
		320	0.2348	0.0041	2.4337	25.20
Ketone	2	280	0.4052	0.0233	2.6416	40.10
		300	0.3230	0.0174	2.5595	58.70
		320	0.4366	0.0150	2.6730	34.25
	4	280	1.2227	0.1057	3.4657	31.50
		300	0.8826	0.0211	3.1256	36.80
		320	0.8595	0.0166	3.1025	17.95

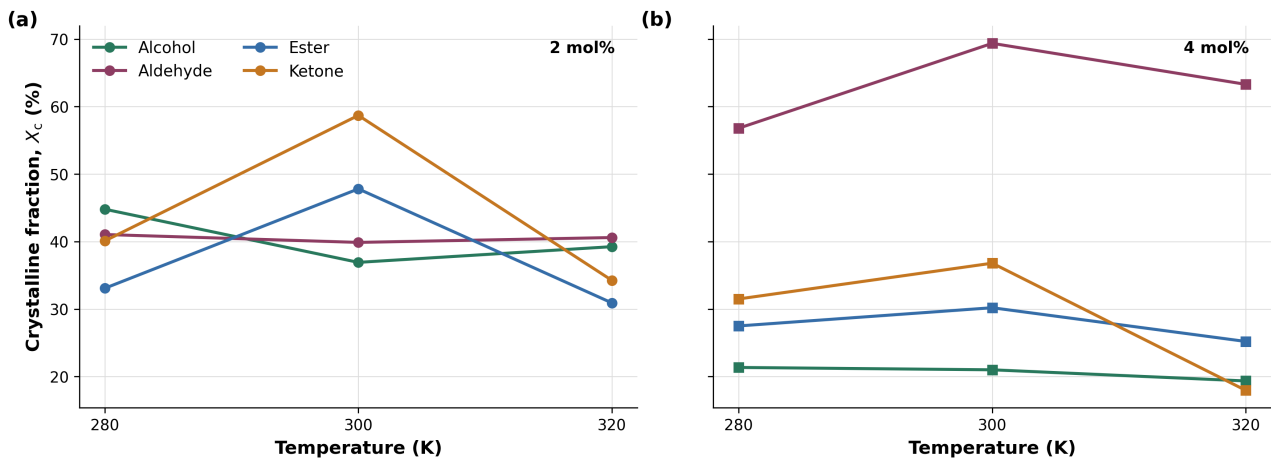


Figure 4.18: Crystalline fraction against measured temperature at (a) 2 mol % and (b) 4 mol %, using the common 7 Å neighbour shell and $P_2 > 0.6$ convention.

plateaus or reversals, particularly around 300 K. The 4 mol % aldehyde cells remain ordered throughout the series, consistent with their distinct morphology.

4.4.1. Static response at 280, 300 and 320 K

Figure 4.19 and Table 4.10 show that the most robust result is the separation by chemistry: ketone and aldehyde give the two largest $\Delta\epsilon$ values at both concentrations and all three temperatures, whereas alcohol and ester remain lower. The detailed temperature dependence is not universal. For example, ketone at 2 mol % gives $\Delta\epsilon = 0.405, 0.323$, and 0.437 at 280, 300, and 320 K, respectively. Alcohol generally increases across the interval, whereas aldehyde decreases modestly. These patterns may reflect different balances between activated orientational sampling and morphology-dependent constraints. Because hydrogen-bond statistics, chain alignment, and independent morphology replicas were not measured, the data do not justify assigning any of these mechanisms as the unique cause of an individual trend.

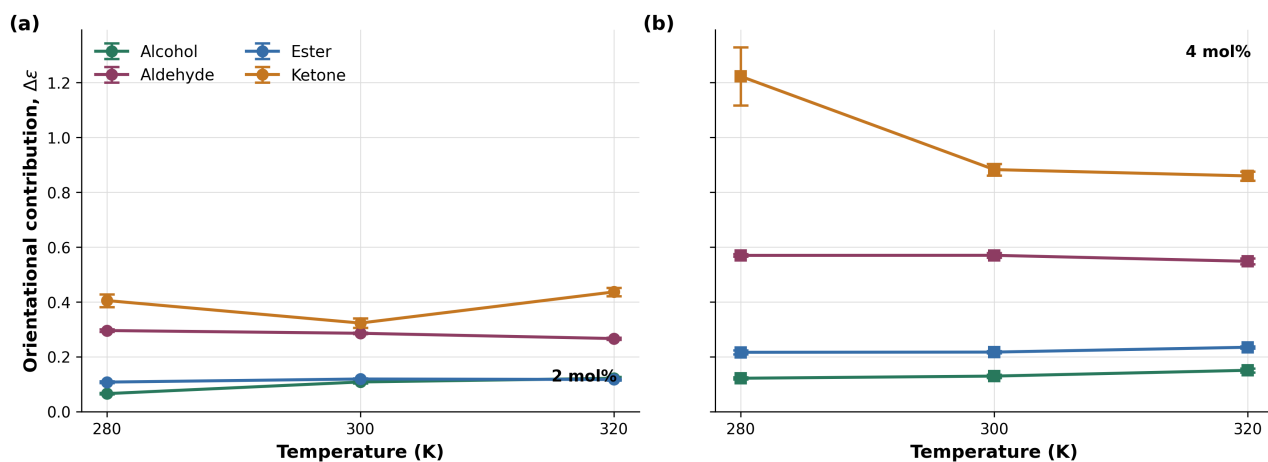


Figure 4.19: Orientational contribution $\Delta\epsilon$ against measured temperature at (a) 2 mol% and (b) 4 mol %. Error bars are standard errors from ten contiguous 10 ns blocks.

4.4.2. Relaxation and loss at 280, 300 and 320 K

Table 4.11 gives the relaxation and loss parameters from a 100 ns analysis window and 10 ps exported ACF grid for all 24 state points. Only two of eight series show a monotonic decrease in $\langle\tau\rangle$ from 280 to 320 K: alcohol at 4 mol% and ketone at 4 mol%. The fitted peak frequency is likewise not temperature-invariant. Therefore, this three-temperature series supports neither a universal Arrhenius-like decrease of $\langle\tau\rangle$ nor a nearly constant f_{pk} . The broad chemical ordering is clearer than the temperature slopes: alcohol remains mainly in the 10^7 – 10^8 Hz range, while the fast, under-resolved aldehyde fits place its peak near 10^{11} Hz.

Figure 4.20 shows the complete spectra so that frequency shifts can be assessed without inferring them solely from $\langle\tau\rangle$. The spectra do not all shift monotonically to higher frequency with temperature. The most robust amplitude result is that ketone has the largest loss peak at every temperature and both concentrations, reaching $\epsilon''_{pk} = 0.365$ at 280 K and 4 mol%, while alcohol and ester remain lower. Thus the chemical ranking of loss amplitude is comparatively stable, whereas the detailed temperature dependence of peak position remains preliminary and model-sensitive.

4.5. Progressive Defect Addition

The fixed-defect systems above were quenched after all defects had already been introduced. A separate progressive defect-addition protocol starts from an equilibrated pristine cell. Ten defects are then inserted at a time, and a 50 ns trajectory is recorded after each stage from 1 to 4 mol %.

Table 4.11: Relaxation and loss parameters at the three temperatures. All 24 state points are fitted over a matched 100 ns window on a common 10 ps autocorrelation grid.

Defect	mol%	T (K)	β	$\langle \tau \rangle$ (ns)	f_{pk} (Hz)	$\varepsilon''_{\text{pk}}$
Alcohol	2	280	0.610	2.13	5.64×10^7	0.0142
		300	0.555	2.59	6.29×10^7	0.0248
		320	0.490	4.38	4.53×10^7	0.0259
	4	280	0.513	6.23	2.62×10^7	0.0253
		300	0.620	2.49	5.06×10^7	0.0313
		320	0.517	1.99	8.74×10^7	0.0327
Aldehyde	2	280	0.185	0.56	4.45×10^{10}	0.0312
		300	0.192	0.31	5.53×10^{10}	0.0314
		320	0.172	0.38	1.33×10^{11}	0.0262
	4	280	0.189	0.58	3.20×10^{10}	0.0616
		300	0.198	0.44	2.87×10^{10}	0.0644
		320	0.125	18.19	2.29×10^{11}	0.0393
Ester	2	280	0.332	2.19	2.61×10^8	0.0176
		300	0.253	2.67	8.68×10^8	0.0170
		320	0.288	1.24	9.68×10^8	0.0190
	4	280	0.386	0.96	3.62×10^8	0.0409
		300	0.326	0.47	1.50×10^9	0.0398
		320	0.329	0.71	9.68×10^8	0.0433
Ketone	2	280	0.616	1.21	1.35×10^8	0.1155
		300	0.470	2.36	9.75×10^7	0.0718
		320	0.486	0.67	3.62×10^8	0.1111
	4	280	0.587	2.46	7.02×10^7	0.3646
		300	0.438	0.74	4.04×10^8	0.2136
		320	0.567	0.43	4.50×10^8	0.2503

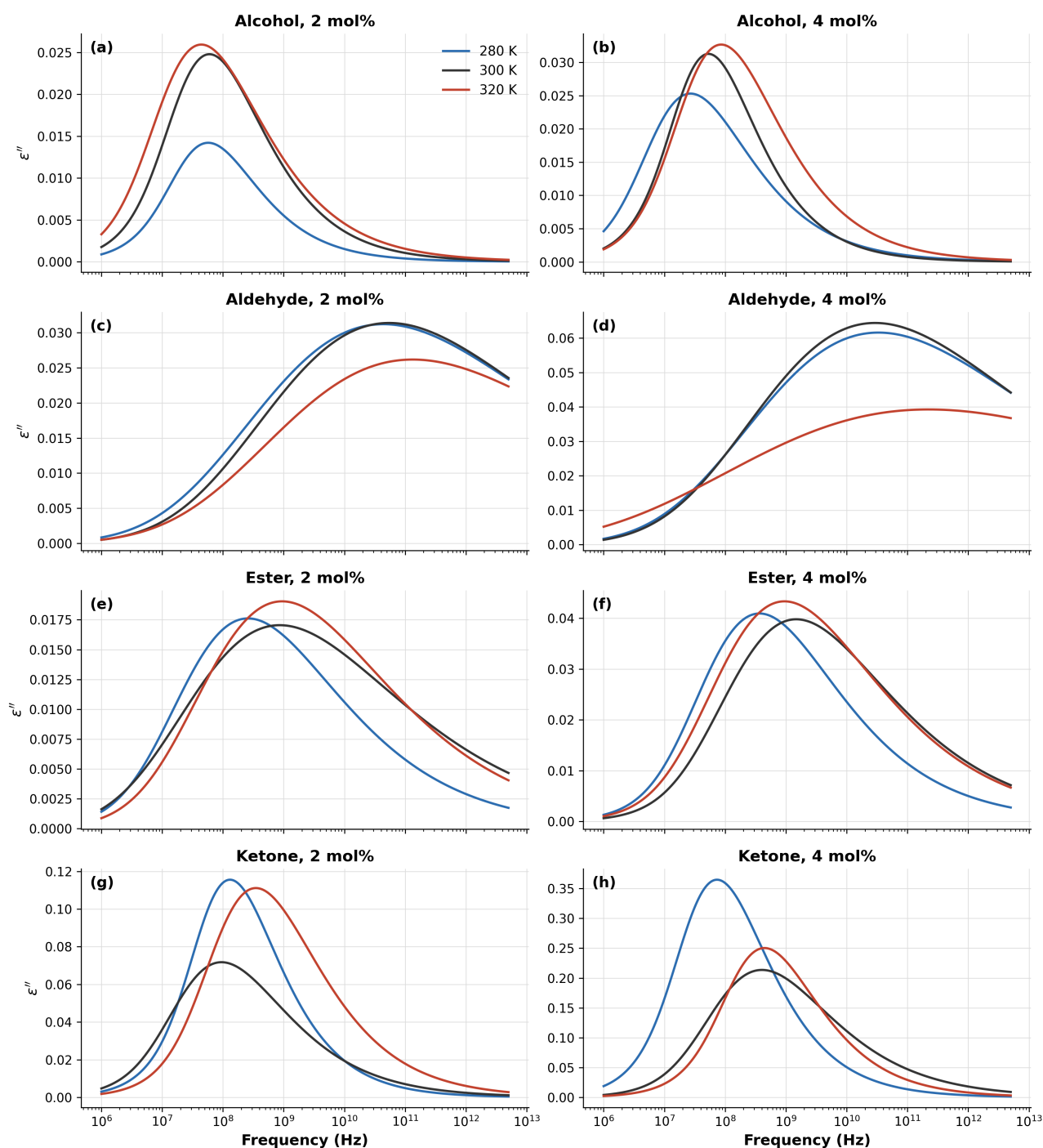


Figure 4.20: Dielectric-loss spectra at 280, 300, and 320 K for alcohol, aldehyde, ester, and ketone at 2 and 4 mol%. The spectra are calculated from the fitted dipole autocorrelation functions listed in Table 4.11.

These progressive-addition calculations are exploratory: only one insertion sequence and one trajectory were generated for each chemistry, so the calculations do not quantify variability with insertion site, order, or independently prepared morphology. Sequential insertion followed by relaxation is conceptually analogous to atomistic defect-accumulation protocols used to study progressive irradiation damage [17]. The analogy is methodological only: the cited work concerns Frenkel-pair accumulation in a ceramic, whereas the present calculation inserts prescribed chemical motifs in PE. It neither simulates oxygen transport and chemical reaction kinetics nor maps 50 ns of MD time onto a physical aging time. The equilibration checks for these runs, and the structural descriptors that show how the defects are distributed at each stage, are given in Appendix F.

4.5.1. Permittivity with defect content

Table 4.12: Static permittivity during sequential defect addition at 300 K, from 1 to 4 mol% of inserted polar groups.

Defect	1 mol%	2 mol%	3 mol%	4 mol%	Δ (1→4 mol%)
Alcohol (-OH)	2.326	2.352	2.398	2.494	0.169
Aldehyde (-CHO)	2.369	2.487	2.614	2.759	0.390
Ester (-COO-)	2.279	2.312	2.325	2.368	0.089
Ketone (>C=O)	2.413	2.570	2.749	2.806	0.392

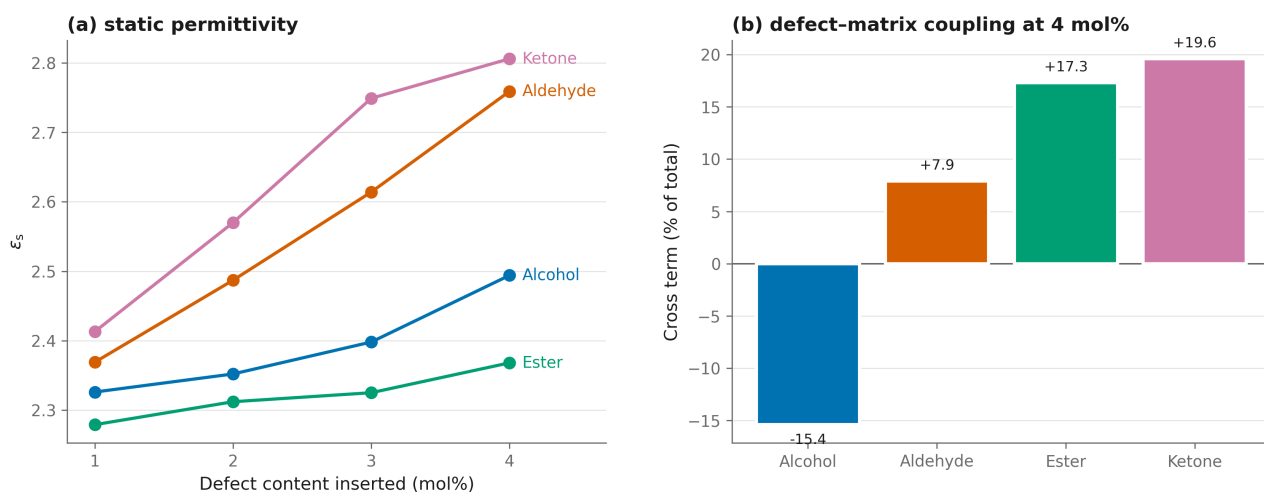


Figure 4.21: Progressive defect addition at 300 K: (a) static permittivity against inserted defect content, and (b) the defect-matrix cross term as a percentage of the total at the 4 mol % end point.

Table 4.12 and Figure 4.21(a) report values from the complete 50 ns stage records; the error bars are standard errors from ten contiguous 5 ns blocks. Static permittivity rises with the added concentration for every defect group, and ketone and aldehyde remain above ester and alcohol. The comparison with the fixed-defect systems is deliberately restricted to this ordering. Table 4.12 reports ϵ_s over the progressive 1–4 mol % interval, whereas Section 4.3 reports $\Delta\epsilon$ for separately quenched 2 and 4 mol % cells. Here an *endpoint* means a value evaluated at the end of a concentration stage, once that concentration has been reached, and not the end of the whole run. Subtracting unmatched endpoints would mix different observables, concentration intervals, and preparation histories and would therefore have no controlled quantitative interpretation.

Figure 4.23 tracks the crystalline fraction across successive addition stages relative to the pristine starting state. Although all final configurations exhibit higher crystallinity than the initial state, only

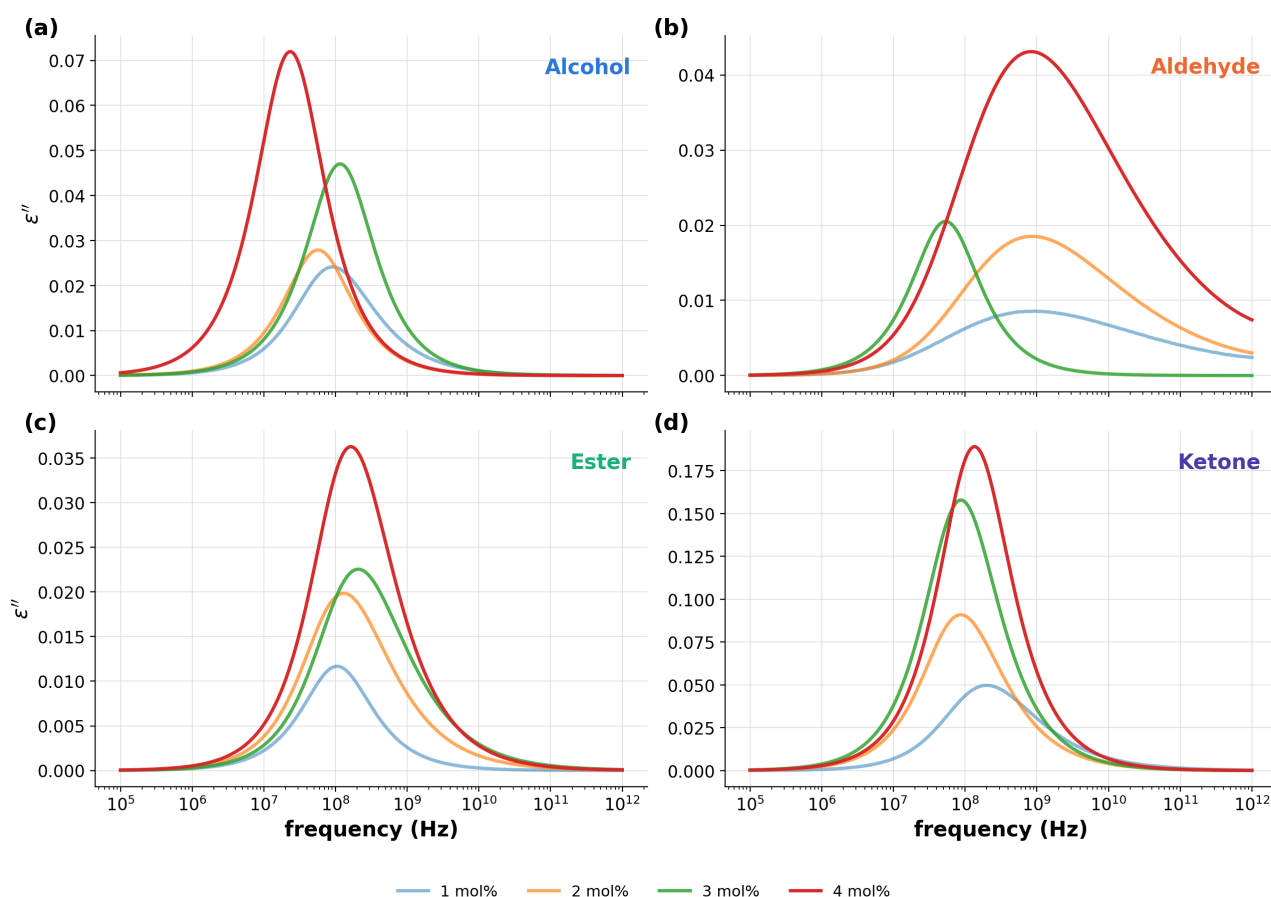


Figure 4.22: Dielectric-loss spectra for progressive 1–4 mol% addition: (a) alcohol, (b) aldehyde, (c) ester, and (d) ketone.

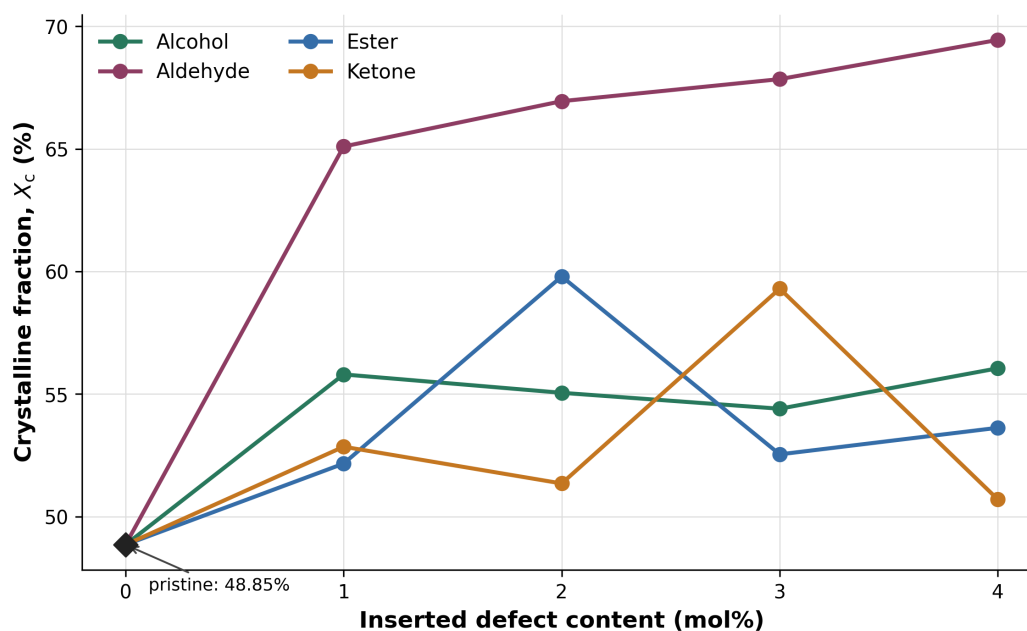


Figure 4.23: Crystalline fraction of the progressive-addition cells at each stage of defect insertion, using the P_2 convention of Section 2.3.4. All four curves begin at the same pristine cell (48.85%).

the aldehyde shows a steady upward trend, increasing from 65.1% to 69.5% across the four stages. Alcohol changes by less than two percentage points after its first stage, while ester and ketone fluctuate without a clear trend.

4.5.2. Defect-matrix coupling during progressive addition

The decomposition of Equation (2.36) was also applied to these systems, providing the most direct test of the mechanism. Figure 4.21(b) and Table 4.13 give the result.

Table 4.13: Decomposition and relaxation of the progressive-addition cells at the 4 mol % end point.

Defect	$\Delta\epsilon$	Defect self	Matrix self	Cross	Cross (%)	β	$\langle\tau\rangle$ (ns)	f_{pk} (Hz)
Alcohol	0.238	0.259	0.015	−0.037	−15.4	1.000	4.131	2.39×10^7
Aldehyde	0.555	0.495	0.017	0.044	7.9	0.394	0.162	8.30×10^8
Ester	0.169	0.121	0.019	0.029	17.3	0.824	0.489	1.65×10^8
Ketone	0.563	0.434	0.019	0.110	19.6	0.942	0.824	1.37×10^8

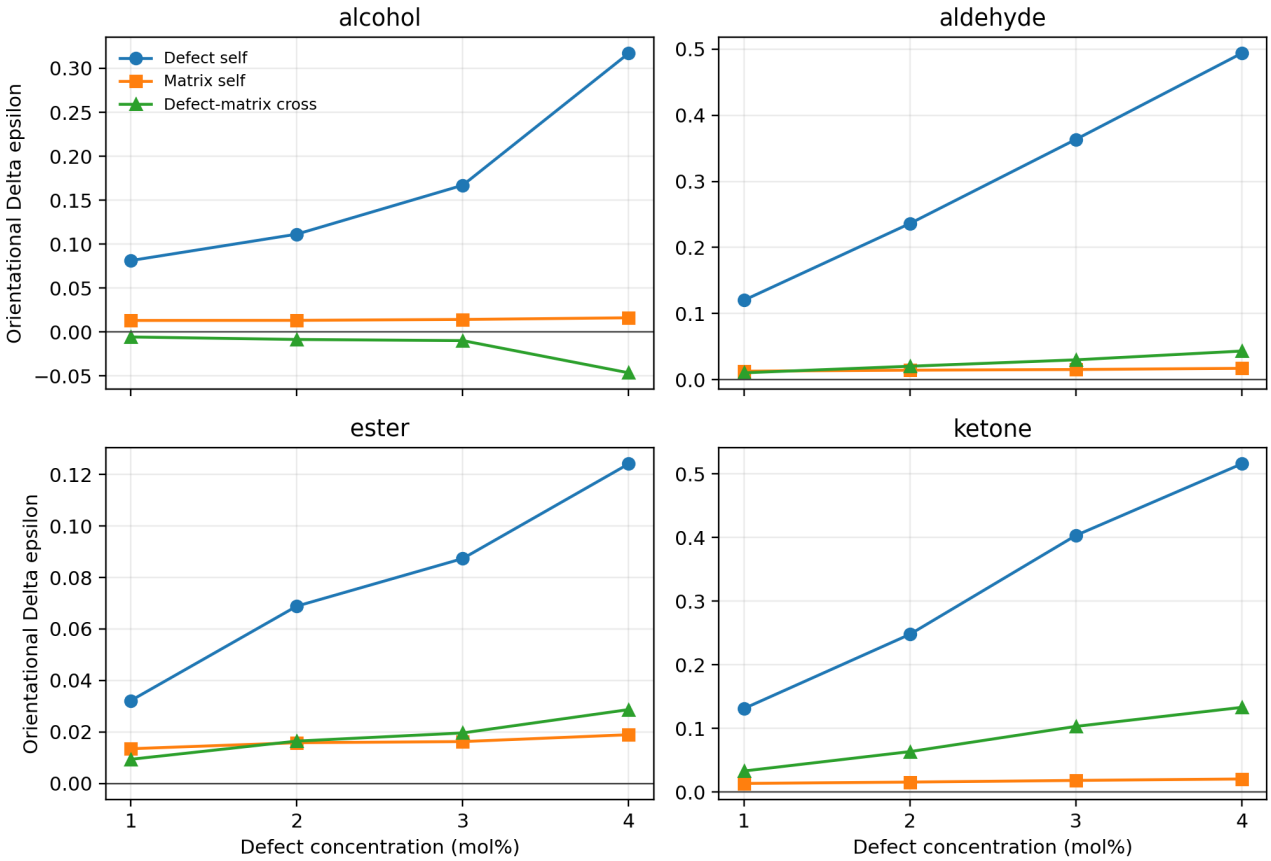


Figure 4.24: Defect self, matrix self and cross contributions against inserted defect content for the progressive-addition cells.

At the 4 mol % endpoint, the progressive cross term is −15.4% of the total for alcohol, +7.9% for aldehyde, +17.3% for ester, and +19.6% for ketone. The signs and ordering agree with the fixed-defect results, including the negative alcohol term and the strong positive ketone term. This is a valid comparison because the same normalized cross contribution is evaluated at the same concentration in both routes. The magnitude of the alcohol effect is preparation-sensitive, whereas the other three

agree within approximately three percentage points. The progressive-addition series therefore supports the reproducibility of the coupling sign. However, a single trajectory per route cannot establish the molecular origin of that coupling or its statistical distribution over morphologies.

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5 – Conclusion

This thesis investigates how chemical degradation products formed during the radio-oxidation of polyethylene modify its electronic, vibrational, and orientational polarization. It also examines how these products redistribute the local dielectric response in space. The work is motivated by the use of polyethylene-based materials as insulation in nuclear power-plant cable systems, where long-term exposure to heat, ionizing radiation, oxygen, and moisture can alter both the chemistry and morphology of the insulation. Since dielectric behavior is a direct functional property of cable insulation, the central aim is to connect specific oxidation defects to measurable dielectric changes using an atomistic computational framework.

The conclusion of this work is that the dielectric response of oxidized polyethylene cannot be predicted from the presence of a polar functional group alone. While defect chemistry is fundamental, its influence depends on the operational polarization mechanism. The dielectric response must be separated according to its physical origin. Electronic polarization arises from redistribution of the electron density with the nuclei fixed, while ionic polarization results from field-induced atomic displacements and depends on the mode effective charges and vibrational frequencies. At finite temperature, molecular dynamics separately describes orientational polarization from fluctuations of permanent dipoles. Aged polyethylene must therefore be interpreted as a coupled chemical, morphological, and dynamical system rather than as a non-polar matrix containing independent polar additives.

The introduction establishes the scientific and technological need for this analysis. Experimental studies of thermally and radiochemically aged polyethylene and cross-linked polyethylene show that oxidation produces alcohol, ketone, aldehyde, ester, carboxylic acid, enone, and other unsaturated species, and that these chemical changes correlate with changes in real and imaginary permittivity. Radio-oxidation also produces transient, short-lived alkyl, peroxy, and alkoxy radicals, although the present work focuses on the more persistent degradation products that can be represented as structural defects. Previous first-principles studies clarify how defects modify the electronic structure of polyethylene, while molecular-dynamics studies show that morphology and dipolar motion can strongly affect the dielectric response. However, these lines of work do not fully connect realistic radio-oxidation chemistry, semicrystalline morphology, position within the lamella, and the separate electronic, ionic, and orientational contributions to permittivity. This thesis addresses that gap by combining DFT/DFPT calculations with classical molecular dynamics and by treating polyethylene as a semicrystalline material containing crystalline, interfacial, and amorphous environments.

The methodology chapter develops the multiscale framework needed for this purpose. Density functional theory and density functional perturbation theory are used to relax pristine and defected polyethylene structures and to calculate the high-frequency dielectric tensor, the static dielectric tensor, Born effective charges, and mode-resolved ionic contributions. Position-dependent dielectric profiles were obtained by comparing the planar-averaged electrostatic response to equal electric fields applied in opposite directions across the lamella. Unlike the cell-averaged dielectric constant, these profiles distinguish the local responses of different regions inside the lamella. Classical molecular dynamics was used to calculate the orientational dielectric contribution from fluctuations of the total dipole moment. Auto-correlating the total dipole trajectory and transforming it into the frequency domain gives the relaxation behavior and dielectric loss spectrum. The decomposition of the dipole fluctuations into defect, matrix, and defect-matrix cross terms then identifies whether the surrounding polymer amplifies or suppresses the contribution of a defect. The defects were studied at 2 and 4 mol % concentrations, and progressive-addition simulations from 1 to 4 mol % test whether inferred trends persist as defects are introduced sequentially.

The first results chapter shows that polymer morphology significantly governs dielectric behavior. The fully crystalline polyethylene cell exhibited the highest DFPT dielectric constants and was strongly

anisotropic along its chains, whereas the amorphous model was nearly isotropic. The semicrystalline lamellar model containing both ordered and disordered regions within a single unit cell yielded an effective permittivity close to the experimental range for polyethylene, which makes it the reference for the subsequent defect calculations. These comparisons show that the dielectric response of polyethylene is governed by chain orientation, packing, density, and the crystalline–amorphous partition. Analysis of the DFPT calculations on defected polyethylene shows that electronic and ionic dielectric mechanisms make distinct contributions. The high-frequency dielectric constant changes only weakly across the defect series, with all defective systems remaining close to the pristine value. Alcohol, enone, ketone, and vinylene slightly increase the electronic response, whereas aldehyde, ester, and carboxylic acid slightly reduce it. Thus, adding an oxygenated group does not automatically increase the purely electronic polarizability of the polyethylene matrix. By contrast, the static DFPT response, which includes ionic lattice contributions, increases for all seven defect groups. At 4 mol %, aldehyde gives the largest static dielectric constant, followed by alcohol, carboxyl, enone, ketone, ester, and vinylene. The comparison between high-frequency and static values demonstrates that the defect-induced enhancement in the dielectric response arises from IR-active lattice modes rather than from electronic polarization alone. Mode-resolved analysis and Born effective charges provided deeper insight into this behavior. Oxidized functional groups introduced significantly larger dynamical charges than pristine polyethylene, particularly within carbonyl- and hydroxyl-containing units. However, the magnitude of the Born effective charge alone did not dictate the final dielectric ranking. For instance, the aldehyde exhibited the largest ionic dielectric increment despite possessing a smaller carbonyl Born effective charge than other groups, primarily because its dynamical charges coupled strongly to low-frequency IR-active modes. In contrast, the ester exhibited strong carbonyl dynamical charges but only a moderate ionic contribution. A higher static dielectric contribution requires both dynamical charge and a strong coupling to soft polar modes. The position-dependent calculations showed how the local environment influences the dielectric response. Aldehyde and ketone can give high values in the crystalline regions, whereas carboxyl, enone, and ester groups achieved larger contributions nearer to the surface. The carboxyl and aldehyde profiles contain positive and negative lobes whose contributions mostly canceled upon macroscopic averaging. Thus, rather than uniformly raising bulk permittivity, these polar groups introduce local dielectric heterogeneity. This distinction is critical for aged electrical insulation, where spatial field distortions and local dielectric heterogeneity can accelerate breakdown even if the bulk dielectric constant appears only modestly altered.

The results reported in the molecular-dynamics chapter extend the analysis from harmonic, zero-temperature response to finite-temperature orientational polarization. For alcohol, aldehyde, ester, and ketone defects, the simulations show that orientational contributions can be much larger than the electronic and ionic increments obtained from DFPT. At 300 K and 4 mol %, ketone gives the largest dielectric relaxation strength, followed by aldehyde, ester, and alcohol. When the DFPT high-frequency contribution is added to the MD orientational increment, the static permittivity reaches values above 3 for ketone at 4 mol %, compared with values near 2.2–2.3 for pristine polyethylene. This shows that the strongest low-frequency dielectric enhancement in oxidized polyethylene comes from finite-temperature dipole fluctuations and defect–matrix coupling.

The MD results also show why the magnitude of a defect’s dipole moment is not a reliable predictor of its dielectric contribution. In the alcohol systems, a large fraction of the total dipole remains after the fluctuating part is removed. The hydroxyl bond in alcohol is strongly polar, yet it produced the smallest orientational response among the four defects studied. The slow relaxation of the alcohol systems and the negative defect–matrix cross term indicate that hydroxyl motion is constrained by its local environment. Ester was similarly constrained by the internal mechanism where the carbonyl and ether-oxygen dipoles were anti-correlated, reducing the effective fluctuation of the whole defect group. Ketone behaves differently. Its defect self term is the largest of the four systems, and its positive cross term shows that the matrix fluctuates cooperatively with the ketone dipole. Aldehyde falls

between these cases and combines fast relaxation with an approximately proportional concentration dependence.

The frequency-domain analysis connects these microscopic mechanisms to the dielectric-loss spectra. Ketone has the highest loss maximum at 300 K, while the restricted hydroxyl motion gives alcohol the smallest loss. Aldehyde and ester form lower-amplitude bands. Across 280, 300, and 320 K, the chemical ranking is more robust than the fitted peak positions or relaxation times: only two of the eight temperature series show a monotonic decrease of the mean relaxation time. The temperature dependence should therefore be interpreted as a comparative trend rather than a universal Arrhenius-like shift. The progressive defect-addition simulations provide an independent test of the mechanisms obtained from the fixed-defect systems. As defects are added from 1 to 4 mol %, the permittivity generally increases, with chemistry-specific and sometimes non-linear concentration dependence. Ketone and aldehyde produce the largest responses, while alcohol and ester remain weaker. At 4 mol %, the signs and ordering of the defect-matrix cross terms are reproduced: alcohol remains negative, ketone remains strongly positive, and aldehyde and ester remain intermediate. Because one insertion sequence and one trajectory were used for each chemistry, this agreement supports the reproducibility of the coupling sign but does not establish a statistical distribution over morphologies.

Taken together, the thesis makes three principal contributions to the understanding of polymer dielectric behavior. First, it establishes a chemically resolved hierarchy of radio-oxidation defects in polyethylene across multiple dielectric mechanisms. In the static harmonic regime (DFPT), aldehyde and alcohol groups act as strong enhancers due to their effective coupling with IR-active vibrational modes, while vinylene exhibits a weak effect. In the finite-field local-profile analysis, enone and vinylene are strong positive local enhancers, whereas carboxyl and aldehyde drive significant spatial dielectric redistributions through canceling positive and negative regions. In the finite-temperature MD regime, ketone and aldehyde dominate the orientational contribution, while alcohol and ester are limited by environmental and internal cancellation. Second, the thesis demonstrates that morphology and position of the semicrystalline structure control the baseline dielectric response, affect how local perturbations project into the bulk dielectric region, and shape the dynamical environment sampled by defect dipoles. Third, the thesis establishes defect-matrix coupling as a practical mechanism for understanding dielectric aging: oxidation products do not act independently, but interact with the surrounding chain environment in ways that can amplify, suppress, or redistribute the dielectric response.

These conclusions change how dielectric monitoring of aged polymer insulation should be interpreted. A change in dielectric constant or loss cannot be mapped onto a single generic "oxidation level", because the measured response reflects the identities, concentrations, locations, and dynamical environments of the degradation products. Chemical characterization, including carbonyl and hydroxyl signatures, is therefore needed alongside dielectric spectroscopy. More importantly, service-aged polyethylene contains several defect types simultaneously. The response of such a mixture cannot yet be inferred from the present single-defect calculations by simply weighting and adding their individual contributions: neighboring functional groups may alter local packing, form specific interactions, align or cancel their dipole fluctuations, and change the way each defect couples to the polymer matrix. The single-defect systems used here provide the controlled reference required to identify these non-additive effects, but mixed-defect interactions are the essential next level of the problem.

The limitations of the work follow directly from its computational choices. The DFPT calculations describe electronic and harmonic ionic response in relaxed structures, but they do not include finite-temperature orientational motion. The MD simulations capture orientational dynamics over nanosecond time scales, but use a fixed-charge, non-polarizable force field; electronic polarization is therefore not generated dynamically and is incorporated through the DFPT contribution. The accessible size of the polymer and trajectories are smaller and shorter than real cable insulation, and the simulated

concentrations are idealized representations of chemically modified polyethylene rather than direct replicas of a service-aged cable. In addition, each simulated system contains one defect class at a time. This isolation is useful for assigning mechanisms, but excludes cross-correlations and structural interactions between different oxidation products. The hydrogen-bond interpretation for alcohol is likewise supported only indirectly by relaxation behavior, remnant dipoles, and defect-matrix correlations. Finally, although the finite-field profiles resolve atomistic dielectric redistribution, connecting these local fields to macroscopic breakdown, space-charge transport, or lifetime prediction requires additional modeling.

The principal perspective is therefore to simulate realistic mixtures of defect types. The most direct test would hold the total defect content fixed and compare a mixed system with the corresponding single-defect references. Changing the proportions of alcohol, ketone, aldehyde, ester, carboxyl, enone, and vinylene would then reveal whether a composition follows a simple additive rule. Defects should also be placed at different parts of the lamella so that isolated pairs, clusters, and interfacial arrangements can be compared. The dipole decomposition used in this thesis can be adapted to these mixtures by resolving cross terms between defect species as well as between each species and the polyethylene matrix. It would then be possible to test specific explanations, including hydroxyl-carbonyl association, mutually canceling dipole orientations, and restrictions caused by local packing. Experimental measurements should guide both the mixture compositions and the spatial distributions whenever such information is available. Explicit analysis of hydrogen bonding and local packing around hydroxyl and carboxyl defects would directly test the proposed mechanisms for constrained orientational motion.

Integrating a polarizable force field would include part of the electronic response during the MD trajectory; machine-learned potentials or hybrid QM/MM calculations provide other routes to reduce the present separation between the DFPT and MD descriptions. Larger lamellar cells would represent morphology more comprehensively, while longer trajectories and a broader temperature range would refine the calculated relaxation and loss spectra. A later stage should combine these dielectric calculations with models of trapping, space-charge transport, and breakdown. Ultimately, the central outcome of this thesis is not a static ranking of oxidation products, but a unified framework for determining how chemistry, morphology, and molecular dynamics reinforce one another. Extending this framework to complex, multi-defect distributions provides the foundational step toward accurately modeling the dielectric response of polyethylene under realistic nuclear aging conditions.

Appendices

A – Alcohol Defect Formation Energy

This appendix reports the formation energy of alcohol defects in the semicrystalline polyethylene model, and the spread of that energy across the local environments the cell contains. It supports the discussion of defect formation by comparing hydroxylated configurations under one consistent oxygen reference, and by showing that the relative stability depends on where the oxygen is placed in the lamella.

All calculations here use the same relaxed 151-atom $C_{51}H_{100}$ semicrystalline cell, the optB86b-vdW exchange–correlation functional, and 80/320 Ry wavefunction/charge-density cutoffs.

A.1. Formation-Energy Definition

The formation energy was evaluated by comparing the relaxed hydroxylated polyethylene cell with the relaxed pristine polyethylene reference and an oxygen reservoir. Hydroxylation converts a C–H unit into a C–OH unit, so the carbon and hydrogen counts are unchanged and only oxygen is added: pristine $C_{51}H_{100}$ becomes $C_{51}H_{100}O$ at 2 mol % and $C_{51}H_{100}O_2$ at 4 mol %. The formation energy per defect is therefore

$$E_{\text{form}} = \frac{E_{\text{defect}} - E_{\text{PE}} - n_O \mu_O}{n_O}, \quad (\text{A.1})$$

where E_{defect} is the final relaxed total energy of the alcohol–polyethylene cell, $E_{\text{PE}} = -700.7988$ Ry is the final relaxed total energy of the pristine cell, n_O is the number of oxygen atoms added, and $\mu_O = \frac{1}{2}E(\text{O}_2) = -31.9095$ Ry is the oxygen chemical potential taken from a spin-polarized O_2 calculation with the same functional and cutoffs. Reporting the value per defect allows the one- and two-alcohol systems to be compared on the same scale.

Equation A.1 defines a formation energy within one chosen oxygen-reference convention. Because the absolute zero of this scale depends on the oxygen chemical potential and on the exchange–correlation functional, the robust quantities here are the relative differences between configurations and between concentrations, all evaluated with the same reference.

The one-alcohol configurations have a mean formation energy of -1.46 ± 0.15 eV per defect over 50 configurations, while the selected two-alcohol configurations have a mean of -1.59 ± 0.06 eV per defect over 18 configurations (Table A.1).

Table A.1: Formation energies of alcohol defects in semicrystalline polyethylene, reported per inserted oxygen. Values are computed from Eq. A.1 over the relaxed configuration sets described in the text.

System	N	Mean	SD	Min	Median	Max
(eV per inserted oxygen)						
One alcohol defect (2 mol%)	50	−1.46	0.15	−1.75	−1.47	−1.07
Two alcohol defects (4 mol%)	18	−1.59	0.06	−1.70	−1.59	−1.43

The oxygen position was projected onto the lamellar direction z in order to analyse the energetic spread associated with the local morphology of the semicrystalline cell (Fig. A.2). The spread of the formation energies shows that local morphology changes the defect stability. An alcohol group placed near a chain fold, a surface-like region, or a less ordered segment does not experience the same steric and electrostatic environment as an alcohol group placed in a more ordered chain segment. The formation-energy distribution therefore provides an independent check that the semicrystalline cell contains multiple local chemical environments, and supports the use of many configurations rather than a single representative geometry.

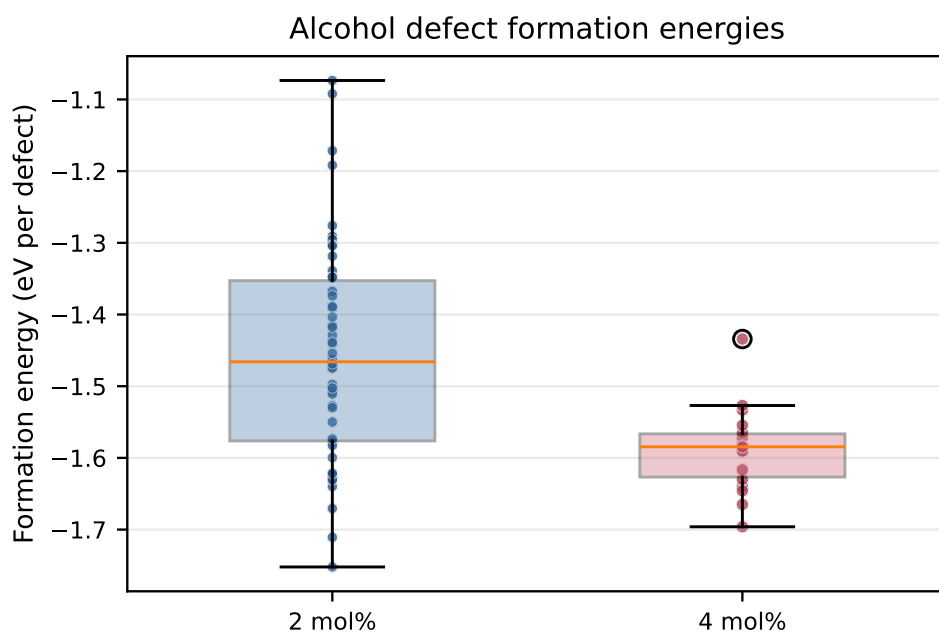


Figure A.1: Distribution of alcohol-defect formation energies for the one- and two-alcohol semicrystalline polyethylene configurations.

The one-alcohol set covers a wider range of both position and formation energy than the two-alcohol set, but that comparison should not be read as a purely physical result. Three effects contribute. The one-alcohol set contains 50 configurations against 18; it spans a wider sampled z window (-3.2 to 16.8 Å against 2.6 to 13.2 Å); and, most importantly, both quantities plotted for the two-alcohol cells are already averages over the two oxygens in the cell, which mechanically reduces their variance. The narrower two-alcohol distribution is therefore consistent with, but not evidence for, a genuinely more uniform insertion energy at 4 mol %.

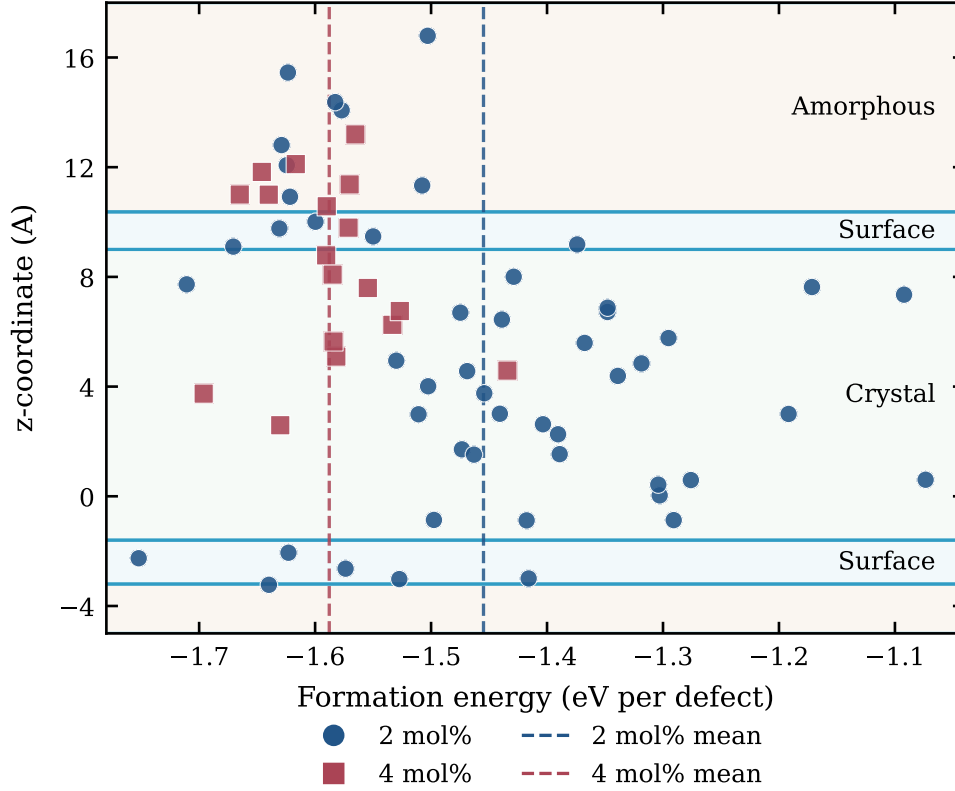


Figure A.2: Alcohol-defect formation energy plotted against the oxygen position along the lamellar direction (energy on the abscissa, position on the ordinate). For the two-alcohol cells the plotted position is the mean of the two oxygen z coordinates. The shaded bands are the crystallinity classification of *this* relaxed cell, assigned by distance along z : crystalline for $-1.6 \leq z \leq 9.0$ Å, fold-surface for $-3.2 \leq z < -1.6$ Å and $9.0 < z \leq 10.4$ Å, and amorphous outside that range. This classification and its z origin are specific to the formation-energy cell and are not the morphology regions used in Appendix C, which are defined on a different and larger cell. Dashed lines mark the mean formation energy of each concentration set.

B – Finite-Field and Macroscopic-Averaging Checks

This appendix documents the finite-field and macroscopic-averaging checks that establish the post-processing convention used for the position-dependent dielectric profiles. The checks were performed on a pristine folded polyethylene slab whose polymer region spans z -values from 4.86 to 22.38 Å in its cell. That cell is smaller than the semicrystalline lamella used in Appendix C, so the numerical values of ε reported here are not the reference values used there; what carries over is the choice of field amplitude and averaging window. Section C.3 states the scope of that correspondence.

B.1. Finite-Field Linear Response

The induced polarization was obtained by integrating the macroscopically averaged induced charge density along the slab-normal direction, following the finite-field slab-profile approach used for atomic-scale dielectric profiles [1, 2]. Let $\rho_{+E}(z)$ and $\rho_{-E}(z)$ denote the macroscopically averaged field-induced charge-density profiles from the positive- and negative-field calculations after subtracting the zero-field reference. The linear-response density used below is the half-difference

$$\rho_{\text{ind}}(z; E) = \frac{1}{2} [\rho_{+E}(z) - \rho_{-E}(z)], \quad (\text{B.1})$$

so it corresponds to the response to one field amplitude E , not to the full separation between the $+E$ and $-E$ calculations. The slab-normal polarization accumulated up to position z is then

$$P(z) = \frac{e}{a_0^2} \int_0^z \rho_{\text{ind}}(z'; E) dz', \quad (\text{B.2})$$

where e is the elementary charge and a_0 the Bohr radius. The prefactor converts the integral of the atomic-unit charge density into C m^{-2} . With displacement field $D = \varepsilon_0 E$, the corresponding local field is

$$E_{\text{loc}}(z) = E - \frac{P(z)}{\varepsilon_0}, \quad (\text{B.3})$$

and the reconstructed local dielectric response is

$$\varepsilon(z) = \frac{D}{\varepsilon_0 E_{\text{loc}}(z)} = \frac{\varepsilon_0 E}{\varepsilon_0 E - P(z)}, \quad (\text{B.4})$$

where E is the applied macroscopic field in SI units and ε_0 is the vacuum permittivity. This form makes the sign convention explicit: positive induced polarization reduces the local field inside the polymer and therefore increases the reconstructed $\varepsilon(z)$.

Because $\varepsilon(z)$ depends on E through the denominator of Eq. B.4, the reconstruction is meaningful only if the induced density scales linearly with the applied field. This was tested by repeating the calculation at six amplitudes between 2×10^{-4} and 10^{-2} a.u. and comparing both the plateau value of ε and the field-scaled induced density (Fig. B.1).

Over the five amplitudes from 2×10^{-4} to 2×10^{-3} a.u. the plateau dielectric constant moves only from 2.6826 to 2.6835, a variation of 0.001 or 0.03%, and the field-scaled induced density agrees with the low-field limit to better than 0.03%. The largest tested amplitude, 10^{-2} a.u., raises the plateau value to 2.6852 and increases the scaled-density root-mean-square error from 0.011% to 0.163%, which is the onset of a measurable nonlinear contribution. Every production calculation in this thesis therefore uses an amplitude inside the low-field plateau.

The defect series of Appendix C was run at 10^{-3} a.u. That choice is well inside the plateau: the values at 10^{-3} and 1.5×10^{-3} a.u. are 2.68335 and 2.68339, differing by 4×10^{-5} , so the two amplitudes are numerically indistinguishable at the precision reported anywhere in this thesis.

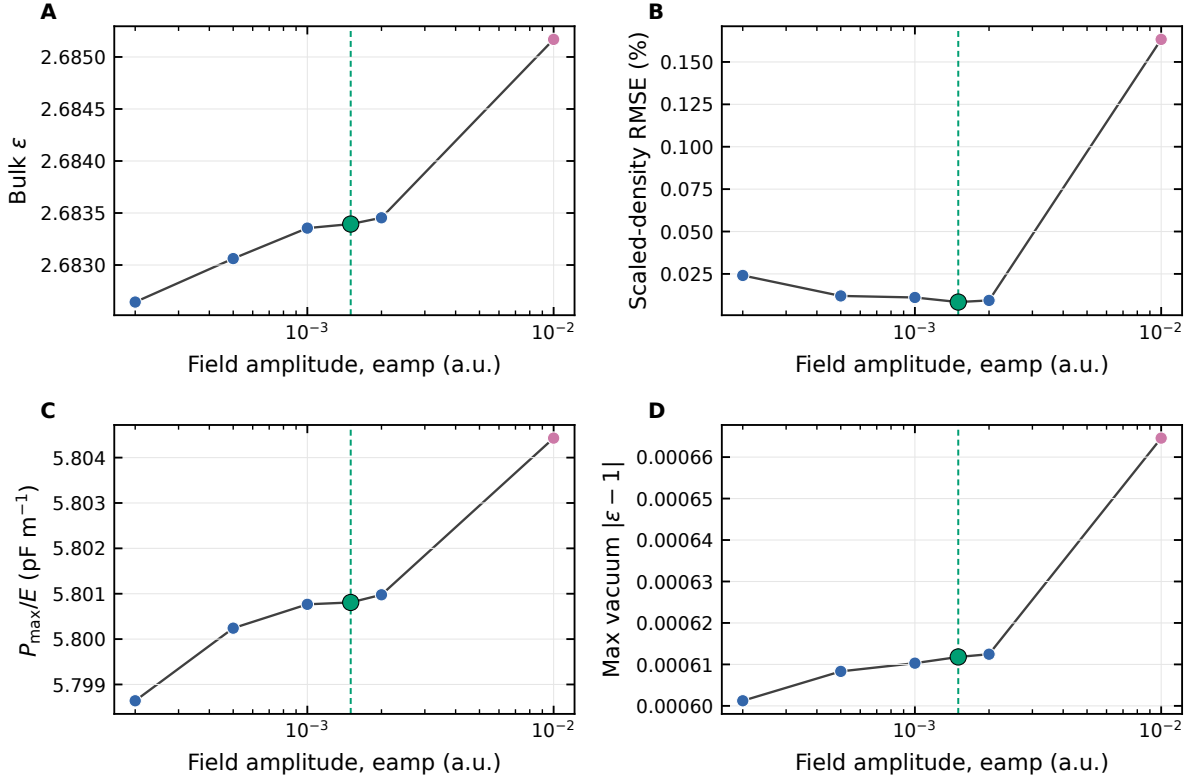


Figure B.1: Finite-field convergence metrics for the pristine folded polyethylene slab, plotted against the applied amplitude. **(A)** plateau dielectric constant, spanning a total range of 0.003 over the whole set; **(B)** root-mean-square departure of the field-scaled induced density from the low-field limit; **(C)** maximum polarization divided by the field; **(D)** maximum deviation of the reconstructed ϵ from unity in the vacuum region. In every panel the green marker and the vertical guide identify the amplitude used for the checks reported in this appendix. The vertical scale in (A) is strongly expanded: the low-field points form a plateau in the sense that the variation is below the reporting precision, not that the curve is flat by eye. Only the largest amplitude departs measurably in (B).

B.2. Macroscopic-Averaging Window

The macroscopic averaging length was selected by balancing two requirements. The window must be long enough to suppress the microscopic oscillations of the planar-averaged density inside the polyethylene slab, but short enough that the reconstructed dielectric response does not spread into the vacuum region. The selection rule was applied in that order: windows whose maximum vacuum deviation $|\varepsilon - 1|$ exceeded 0.02 were rejected, and among the remainder the window with the smallest standard deviation of ε over a fixed bulk window (10.12–17.13 Å) was chosen. The 4.34 bohr (2.30 Å) window satisfies both requirements (Table B.1).

Table B.1: Macroscopic averaging-window metrics for the pristine folded polyethylene dielectric profile. Two averaging conventions are listed. The bulk mean and bulk standard deviation are taken over the fixed window 10.12–17.13 Å and are the quantities the selection rule minimizes; ε_{p70} is the mean over the region where the macroscopic polarization exceeds 70% of its maximum, which is the convention carried forward to Appendix C. The threshold sensitivity is the spread of that plateau mean when the 70% criterion is varied between 60% and 80%.

Averaging window (bohr)	Bulk mean (Å)	Bulk mean ε	Bulk SD ε	Plateau ε_{p70}	Threshold sensitivity	Max vacuum deviation
2.170	1.148	2.7647	0.1430	2.7270	0.0626	0.0091
3.250	1.720	2.7654	0.0809	2.7010	0.0677	0.0124
4.340	2.297	2.7683	0.0316	2.6834	0.0790	0.0177
5.420	2.868	2.7721	0.0375	2.6696	0.0930	0.0259
6.515	3.448	2.7749	0.0511	2.6600	0.1049	0.0378

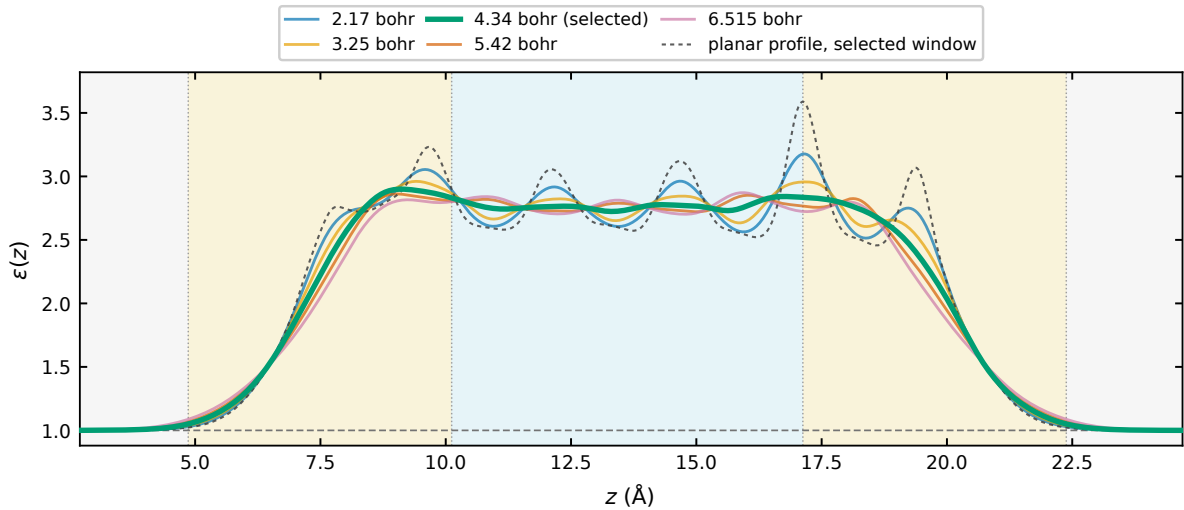


Figure B.2: Position-dependent dielectric profiles reconstructed with different macroscopic averaging windows. The dotted curve is the planar-averaged profile for the selected window, shown for reference. Shading separates the vacuum region (gray), the fold-surface region (yellow), and the fixed bulk window used for the selection metric (blue). The selected window suppresses the bulk oscillations while keeping the vacuum response within 0.02 of unity.

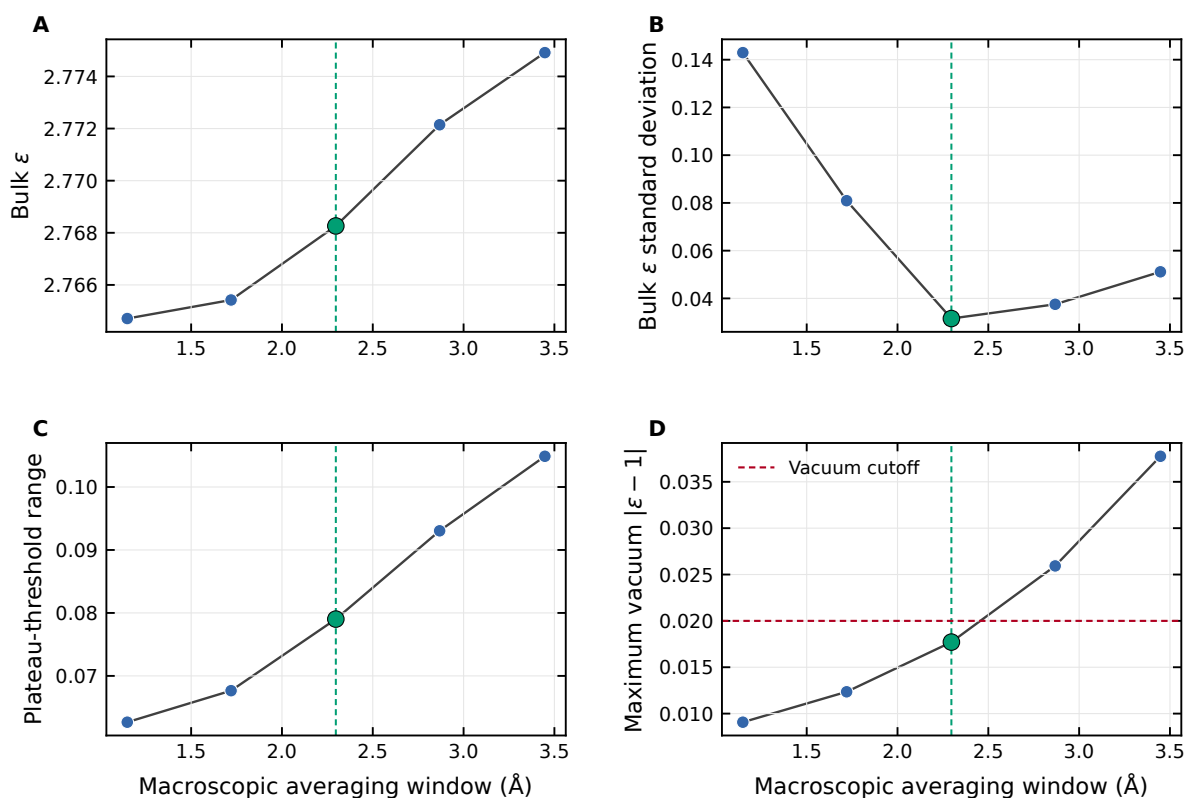


Figure B.3: Macroscopic-averaging metrics against window length. **(A)** bulk mean ϵ ; **(B)** bulk standard deviation, the quantity minimized by the selection rule; **(C)** plateau threshold sensitivity; **(D)** maximum vacuum deviation, with the acceptance cutoff of 0.02 marked. The green marker and vertical guide identify the selected window; the selected-window marker is described here rather than repeated in the legend. The selected window is the smoothest profile that stays inside that cutoff.

C – Position-Dependent Dielectric Profiles

This appendix gives the position-dependent dielectric-profile analysis for the defective folded-polyethylene lamella used in Chapter 3. This is the larger finite-field slab used for the production defect profiles, not the smaller pristine check cell of Appendix B. The finite-field calculations use an electric-field intensity of 10^{-3} a.u., the 4.34 bohr macroscopic averaging window, and the 70% polarization-plateau definition of ε established in Appendix B. The residual net induced charge was removed before integration in every profile. The polymer slab occupies $z = 10.71\text{--}36.32$ Å of the cell, the pristine reference gives a plateau value of $\varepsilon = 2.619$, and 35 defect profiles were analyzed: seven defect families at five sampled positions each.

Because the slab contains folded surfaces, crystalline chain segments, and an amorphous chain, the profile is not flat across the cell. The analysis below therefore separates the average shift in ε from the local, spatially resolved perturbation $\Delta\varepsilon(z)$, and reports both against the sampled morphology.

C.1. Pristine Reference

The pristine profile defines both the baseline value and the background spatial structure that must be subtracted before a defect-induced change can be interpreted. The induced response rises from the vacuum value to the polymer plateau and returns to vacuum at the opposite cell boundary; the vacuum regions remain close to $\varepsilon = 1$, which is the same acceptance check applied in Appendix B.2.

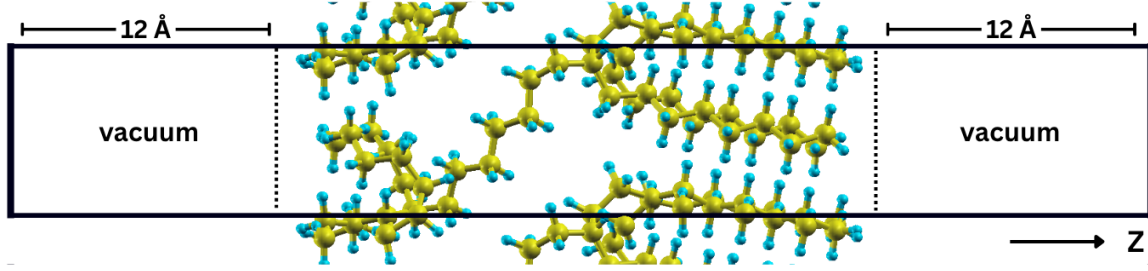
Table C.1 and Fig. C.2 give the average dielectric response for each defect types. Two quantities are reported for each defect type: the mean shift $\Delta\varepsilon$ of the plateau value, and the root-mean-square of the local perturbation $\Delta\varepsilon(z)$ across the polymer region.

Table C.1: Summary for the position-dependent dielectric profiles for different defects. Each defect group was sampled at $n = 5$ positions: two on the lower- z crystalline side, two in the amorphous, and one on the upper- z crystalline side. SD is the sample standard deviation over those five positions.

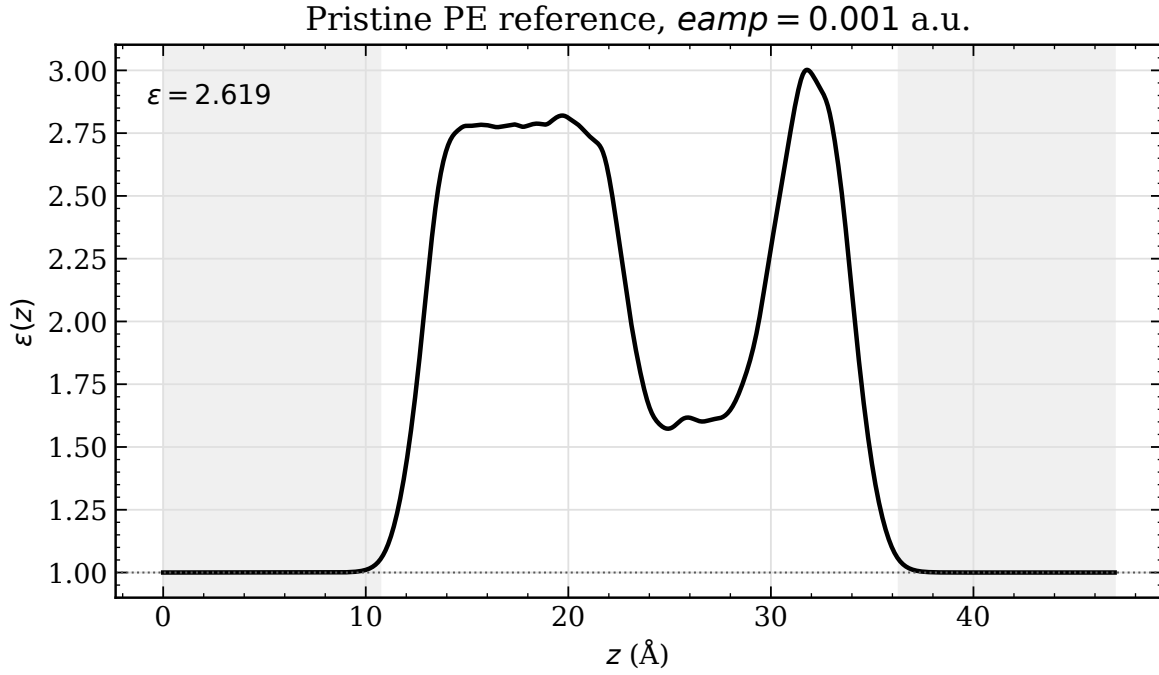
Defect family	n	Mean ε	SD	Min	Max	Mean $\Delta\varepsilon$	RMS $\Delta\varepsilon(z)$
Ketone	5	2.624	0.008	2.612	2.630	+0.005	0.015
Alcohol	5	2.621	0.018	2.598	2.639	+0.002	0.038
Ester	5	2.628	0.014	2.614	2.645	+0.009	0.027
Carboxyl	5	2.639	0.031	2.605	2.675	+0.021	0.052
Aldehyde	5	2.630	0.013	2.611	2.647	+0.011	0.034
Enone	5	2.677	0.089	2.574	2.797	+0.058	0.101
Vinylene	5	2.675	0.068	2.613	2.775	+0.057	0.092

On the mean-shift measure, enone (+0.058) and vinylene (+0.057) are the largest and the five oxygenated defect families all lie between +0.002 and +0.021. That ordering should be quoted with its uncertainty attached. With $n = 5$ and sample standard deviations of 0.089 and 0.068, the enone and vinylene means correspond to standard errors of 0.040 and 0.030, so neither is separated from zero at any conventional level, and the error bars in Fig. C.2 straddle it. The mean shift is best read as a trend within a small sample rather than as a resolved ranking.

The profile-RMS measure in Fig. C.3 is considerably better resolved, because it does not allow positive and negative regions of $\Delta\varepsilon(z)$ to cancel. On that measure enone (0.101) and vinylene (0.092) separate clearly from carboxyl (0.052), alcohol (0.038), aldehyde (0.034), ester (0.027) and ketone (0.015). This contrast between the two measures is itself the main result of the section: a defect can produce



(a) Production folded-polyethylene slab and vacuum regions.



(b) Pristine dielectric reference profile.

Figure C.1: Production folded-polyethylene slab used for the position-dependent dielectric-profile calculations, together with the pristine reference profile. The structural panel shows the polymer slab, vacuum regions and the z direction. The profile was obtained with an electric-field intensity of 10^{-3} a.u. and the averaging convention of Appendix B.

a clear local response around the insertion site while leaving the plateau average nearly unchanged, whenever positive and negative regions of $\Delta\epsilon(z)$ compensate over the slab.

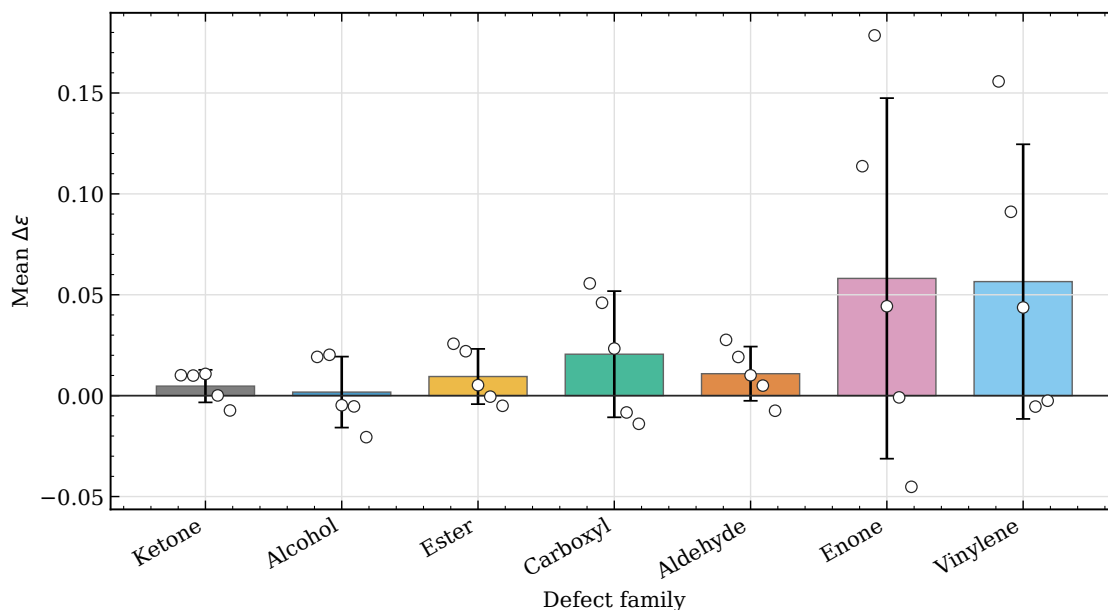


Figure C.2: Average $\Delta\epsilon$ of the plateau value for the position-dependent profile calculations at an electric-field intensity of 10^{-3} a.u. Open circles are the five sampled morphology locations within each group; error bars span $-\sigma$ to $+\sigma$, where σ is the sample standard deviation over those five values.

C.2. Morphology and Local-Profile Sensitivity

Grouping the sampled sites by morphology sharpens the comparison. The semicrystalline model contains crystalline chain segments on both sides of an amorphous chain, and the sites were classified accordingly into a lower- z crystalline side, an amorphous, and an upper- z crystalline side (Table C.2).

Table C.2: Morphology-region summary for the position-dependent dielectric profiles. The three regions contain 14, 14 and 7 sampled sites, corresponding to two, two and one position per defect group.

Morphology region	n	$z_{\min}$	$z_{\max}$	Mean ϵ	Mean $\Delta\epsilon$
(Å)					
Lower- z crystalline side	14	15.71	19.20	2.676	+0.057
Amorphous middle	14	21.43	25.57	2.627	+0.008
Upper- z crystalline side	7	27.00	28.10	2.604	-0.015

The result is asymmetric, and the asymmetry matters more than the mean values. The lower- z crystalline placements give the largest positive average shift (+0.057), the amorphous is close to the pristine reference (+0.008), and the upper- z crystalline placements are slightly *negative* (-0.015). Two nominally equivalent crystalline regions therefore produce shifts of opposite sign.

This asymmetry should be interpreted as a limitation of the finite model rather than as a resolved difference between two equivalent crystalline regions. The cell contains two ordered chain-segment regions on either side of an amorphous chain, so the production profiles sample both lower- and upper- z environments within one periodically repeated slab. The sampled defect positions are not uniformly distributed about the slab midpoint at $z = 23.5$ Å: the lower- z sites lie 4.3–7.8 Å below it,

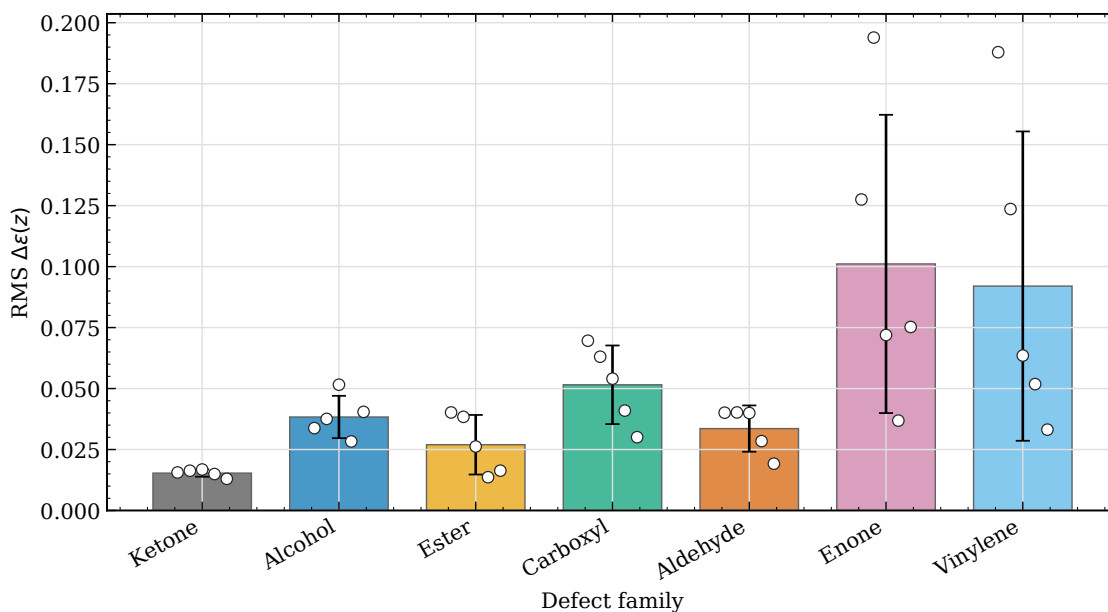


Figure C.3: Average of local profile perturbations for each defect type, measured by the root-mean-square value of $\Delta\epsilon(z)$ across the polymer region. Open circles and error bars as in Fig. C.2.

whereas the upper- z sites lie only 3.5–4.6 Å above it and are closer to the amorphous region. No defect site was sampled between 28.1 and 36.3 Å, and the upper- z group contains only seven sites, one per defect type. The region labels therefore identify the intended structural environment of each defect site in this cell; they should not be read as a statistical crystallinity classification of the full lamella. A future crystallinity-based, per-atom assignment would be needed to make that classification quantitative.

C.3. Scope of the Profile Analysis

The conclusion of this appendix is that the electronic profile response is not determined by chemical identity alone: the same defect type produces different local perturbations depending on whether it sits on a crystalline side or in the amorphous region, and the plateau average can stay small even where the local profile shows a clear perturbation.

Three limits should be carried with that conclusion. The calculation is one-dimensional along the applied field direction; it uses a finite slab geometry with vacuum boundaries; and ϵ depends on the chosen plateau region, whose threshold sensitivity is 0.08 (Table B.1) — larger than most of the mean shifts in Table C.1. The values here are therefore comparative local dielectric indicators evaluated under one fixed convention, not converged macroscopic dielectric constants. Differences between defects and between positions are meaningful; the absolute numbers are not directly comparable with experiment.

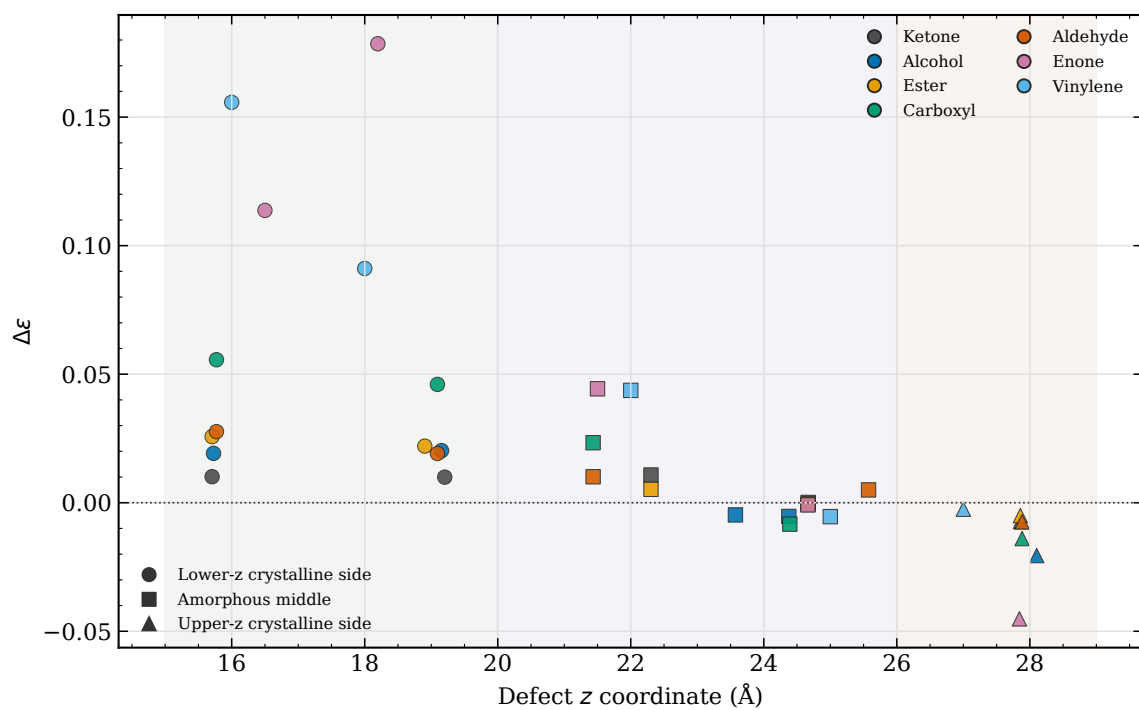


Figure C.4: $\Delta\epsilon$ as a function of the defect z coordinate. Marker shape distinguishes the three morphology regions and color distinguishes the defect groups.

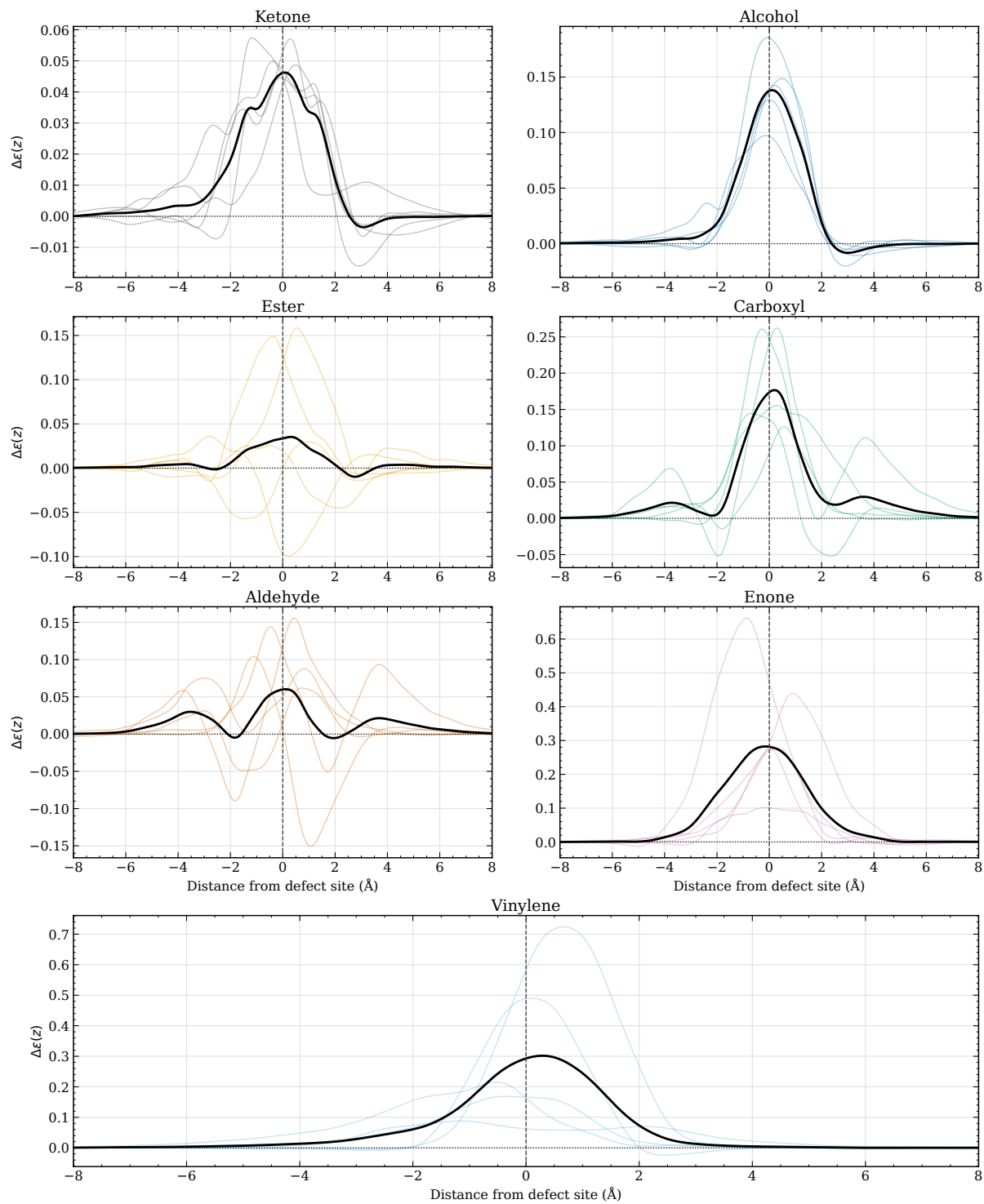


Figure C.5: Mean dielectric-profile perturbation after centring each profile on its defect position, which shows whether the response is localized at the defect or spread across the surrounding polyethylene segment.

D – Car-Parrinello Dielectric-Loss Spectra

This appendix documents the dielectric-loss spectra obtained from the Car-Parrinello molecular-dynamics trajectories. These trajectories carry explicit electronic degrees of freedom through maximally localized Wannier functions and therefore give access to high-frequency vibrational dielectric-loss features. They do not replace the long-time orientational response of the classical trajectories analyzed in Chapter 4; they supplement it by showing how defect identity affects the loss spectrum on the much shorter Car-Parrinello time scale. Six systems are reported: pristine polyethylene and five defect types (alcohol, aldehyde, ester, enone and vinylene).

D.1. Systems and Trajectories

All six cells share the same orthorhombic box, $18.36 \times 13.14 \times 37.72$ bohr, and, except for pristine polyethylene, each carries a single defect in the 151-atom $C_{51}H_{100}$ polyethylene framework, corresponding to approximately 2 mol %. The compositions are $C_{51}H_{100}$ for pristine polyethylene, $C_{51}H_{100}O$ for alcohol, $C_{51}H_{96}O$ for enone and $C_{51}H_{98}$ for vinylene; the two chain-scission defect types have one carbon fewer, $C_{50}H_{98}O$ for aldehyde and $C_{50}H_{96}O_2$ for ester.

The trajectories, run for 10 ps for pristine polyethylene and 15.0 ps for each defect system, give frequency resolutions between 1.1 and 1.7 cm^{-1} . Integration used a timestep of 0.242 fs. Every run completed and held a mean ionic temperature within 0.1 K of 300 K. The fraction of frames for which Wannier functions were successfully generated is between 53% and 68% across the six systems, which is the main quality limitation of this appendix and the reason its conclusions are kept qualitative.

D.2. Dipole Reconstruction

For each trajectory the total cell dipole was reconstructed from the ionic positions and the occupied Wannier-center positions. The number of occupied centers follows from the total valence-electron count ($N_{\text{val}} = \sum_i N_i^{\text{val}}$),

$$N_{\text{WFC}}^{\text{occ}} = \frac{N_{\text{val}}}{2} = \frac{1}{2} \sum_i N_i^{\text{val}}, \quad (\text{D.1})$$

and the instantaneous dipole is

$$\mathbf{M}_{\text{tot}}(t) = \sum_i q_i \mathbf{r}_i(t) - 2e \sum_{j=1}^{N_{\text{WFC}}^{\text{occ}}} \mathbf{r}_j^{\text{WFC}}(t), \quad (\text{D.2})$$

where q_i is the positive valence charge of ionic species i , e is the elementary charge, and each occupied Wannier center carries a pair of electrons.

Tying the center count to the valence-electron count rather than to the number of atoms or to the number of bands written to disk is essential. Several runs write more Wannier centers than there are occupied states — up to 160 written against the 151 to 155 that are occupied — and including the extra centers inflates the reconstructed dipole and hence the static increment by more than an order of magnitude.

D.3. Spectrum Calculation

The dipole trajectory was reconstructed after unwrapping atomic displacements across the periodic boundaries of the orthorhombic cell. Dipole velocities were then obtained by finite differences, their autocorrelation function was transformed to the frequency domain, and the resulting classical spectrum was converted to the reported loss spectrum using a harmonic quantum correction

[3]. A common smoothing kernel was applied to all systems for presentation; both the raw and the smoothed curves are shown in Fig. D.2.

The correction accounts approximately for the quantum detailed-balance factor missing from a spectrum obtained from a classical time-correlation function. It changes the frequency-dependent intensity scale but does not by itself correct the vibrational frequencies.

Four quantities are extracted from each spectrum and quoted in the discussion below: the static increment $\Delta\epsilon_s$ taken from the low-frequency limit, the coefficient of variation of $\Delta\epsilon_s$ across four equal trajectory blocks, the time at which the dipole autocorrelation first crosses zero, and the position and height of the dominant peak. Peak positions are given to the nearest wavenumber, but the smoothed features are 48 to 90 cm^{-1} wide, so differences between systems of a few tens of cm^{-1} lie inside the linewidth and are not resolved by these data.

D.4. Dielectric-Loss Spectra

Every system shows its dominant feature in the C-H stretching region between 2740 and 2820 cm^{-1} (Fig. D.1). These positions lie below the experimental C-H stretching range of polyethylene, near 2850–2960 cm^{-1} . In Car-Parrinello dynamics the fictitious electronic mass can shift dynamical quantities away from the Born-Oppenheimer limit, and the effect is most relevant for high-frequency vibrational modes [4]. For this reason, the peak positions are used only to compare the six systems with one another and not to locate the C-H stretching band in absolute terms. The peak positions span 80 cm^{-1} , which is of the order of the smoothed linewidth, so the systems are not distinguished by peak position in these data. They are distinguished instead by peak intensity and by the strength of the lower-frequency structure below 1600 cm^{-1} , where the oxygenated defect types differ most visibly from pristine polyethylene and from vinylene.

All panels in Fig. D.2 use the same intensity normalization and the same vertical scale; no per-system rescaling was applied. Peak heights can therefore be compared directly within this processing convention. Enone gives the tallest feature ($\epsilon''_{\text{max}} = 4.08$ at 2774 cm^{-1}), followed by ester (3.12 at 2762 cm^{-1}), alcohol (3.05 at 2741 cm^{-1}) and aldehyde (2.27 at 2741 cm^{-1}); pristine polyethylene sits at 2.40 (2820 cm^{-1}) and vinylene lowest at 1.60 (2762 cm^{-1}).

Carboxyl and ketone are not included in the main CP-loss comparison because the selected runs do not provide sufficiently reliable Wannier-center data for the same dipole-reconstruction protocol. They should be treated, if mentioned at all, as diagnostic cases rather than as main CP conclusions.

The static increments follow a different order from the peak heights: 0.289 for aldehyde, 0.275 for enone, 0.261 for alcohol, 0.144 for ester, 0.040 for vinylene and 0.023 for pristine polyethylene. They should be read with the block variability attached, which ranges from 0.10 for vinylene to 0.37 for enone, so the separation between neighboring systems in that list is not resolved. The dipole autocorrelation likewise decays at very different rates, crossing zero after 2.77 ps for aldehyde and 1.87 ps for alcohol but after only 0.26 ps for ester, 0.065 ps for vinylene and 0.005 ps for pristine polyethylene; the last two carry correspondingly little correlation information.

D.5. Scope of the Car-Parrinello Comparison

Three limitations bound what these spectra support. The trajectories are 10 to 15.0 ps long, so the frequency resolution is 1.1–1.7 cm^{-1} but nothing slower than a few hundred GHz is sampled at all; the orientational relaxation of Chapter 4 lies entirely outside this window. The block coefficients of variation range from 0.10 to 0.37, so the static increments $\Delta\epsilon_s$ should be read as order-of-magnitude comparisons and not as converged values. And the Wannier-generation fractions are between 53% and 68%, which is the reason the comparison here is kept qualitative.

Within those limits the appendix supports one statement: on the picosecond time scale the oxygenated defects and the unsaturated defect all modify the high-frequency vibrational loss of polyethylene, and they do so mainly by changing the intensity of the C-H stretching feature and by adding

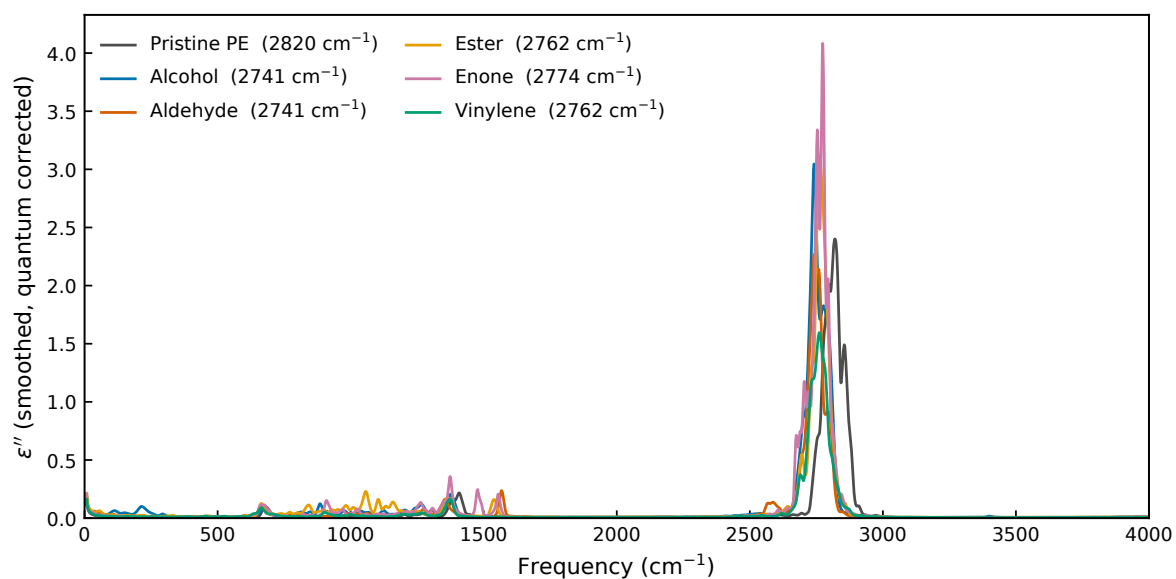


Figure D.1: Smoothed quantum-corrected Car-Parrinello dielectric-loss spectra for pristine polyethylene and the five retained defect systems. Legend entries give the dominant peak position.

lower-frequency structure, not by shifting the dominant band.

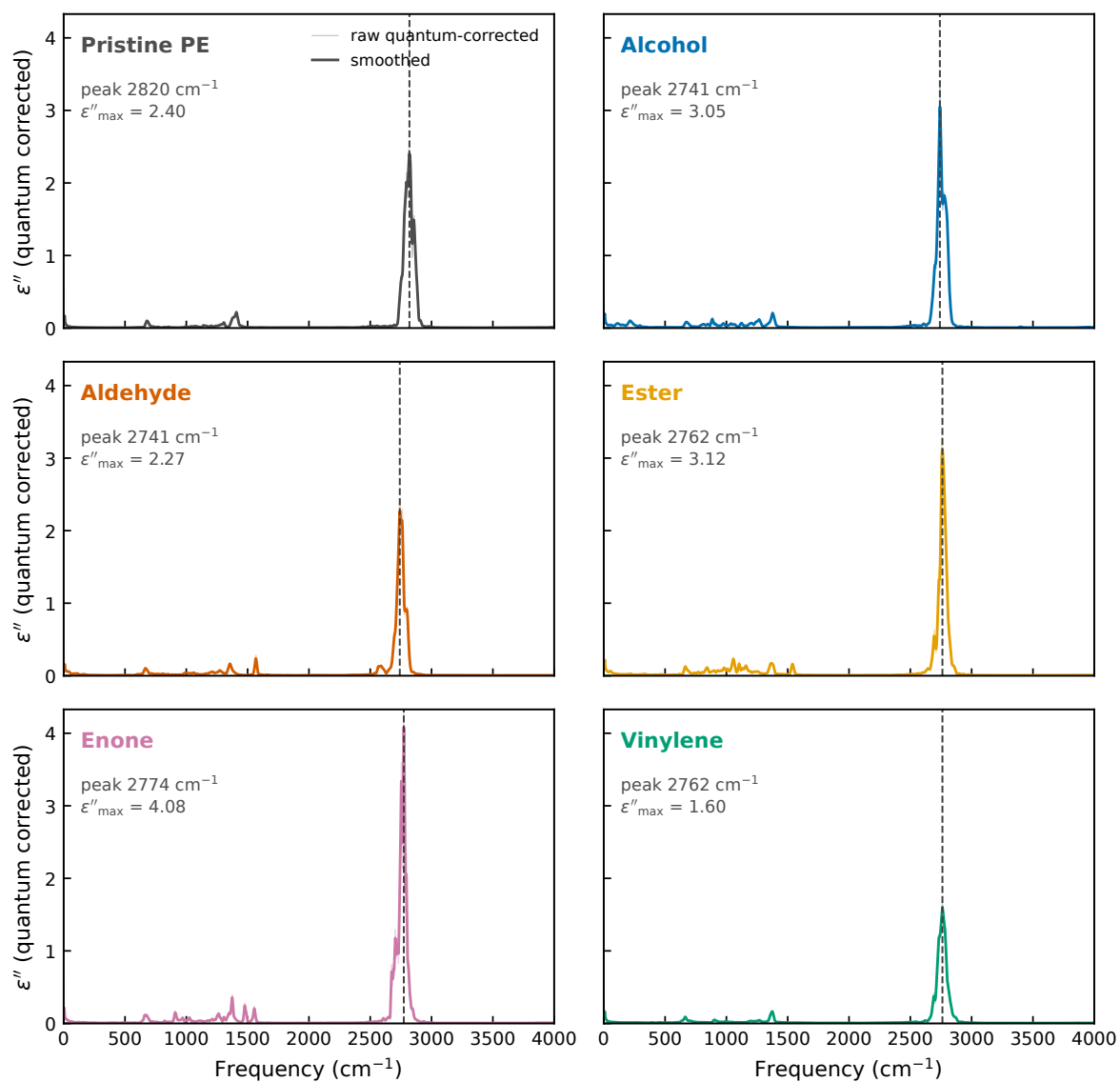


Figure D.2: Individual Car-Parrinello dielectric-loss spectra. The faint curve in each panel is the raw quantum-corrected spectrum and the solid curve is the smoothed spectrum; the dashed vertical line marks the dominant smoothed peak. All panels use the same intensity normalization and vertical scale; no per-system rescaling was applied.

E – Relaxation-Fit and Loss-Model Sensitivity

This appendix supports the Chapter 4 dielectric-loss analysis by showing how the reported relaxation behavior depends on the assumed fitting function. It covers the eight 300 K fixed-defect state points — alcohol, aldehyde, ester and ketone, each at 2 and 4 mol % — for which long classical trajectories and matching coordinate output are available.

The central issue is that polymer dipole relaxation is broad rather than single exponential. A simple analytical function can fit one part of the autocorrelation while missing the short-time drop, the long-time tail, or the frequency-domain peak shape. If a single fitted time constant is quoted without its model definition, the number appears more precise than the data support. The figures below therefore compare several representations of the same trajectories, so that the Chapter 4 conclusions can be phrased in terms of trends that survive the choice of model.

E.1. Direct-Transform Spectra and Relaxation-Time Ambiguity

The direct-transform spectra are obtained by transforming the sampled dipole autocorrelation function without imposing a Debye, KWW, or Havriliak–Negami dielectric lineshape (Fig. E.1). By construction, the low-frequency limit recovers the static orientational increment used in Chapter 4. The comparison against fitted spectra therefore tests whether a fitted lineshape preserves the integrated response while changing how that response is distributed over frequency. In the shaded region, the transform is controlled by the fitted continuation of the autocorrelation beyond the sampled lag-time window rather than by directly sampled data; that region should therefore be read as model-sensitive.

Table E.1 collects five different answers to the question “what is the relaxation time”: the integral of the normalized autocorrelation, the $1/e$ decay time, the mean relaxation time of a two-component KWW fit, the loss-peak time from a Havriliak–Negami fit, and the peak time corresponding to the direct-transform loss maximum. These definitions follow standard dielectric-relaxation practice [5], with the stretched-exponential form traced to the Kohlrausch–Williams–Watts description [6, 7] and the asymmetric-broadening lineshape to Havriliak and Negami [8]. For alcohol at 2 mol % they range from 1.36 ns ($\tau_{1/e}$) to 27 ns (Havriliak–Negami peak), a factor of twenty; for aldehyde at 2 mol % they range from 0.6 ps to 0.22 ns. This spread is the quantitative content of the appendix, and it is why Chapter 4 quotes relaxation behavior as a ranking rather than as a set of time constants.

Table E.1: Relaxation-time metrics for the eight 300 K fixed-defect state points, under five definitions: the integral of the normalized autocorrelation, its $1/e$ decay time, the mean time of a two-component KWW fit, the loss-peak time of a Havriliak–Negami fit, and the peak time corresponding to the direct-transform loss maximum.

System	τ_{int} (ns)	$\tau_{1/e}$ (ns)	2-KWW $\langle\tau\rangle$ (ns)	HN peak (ns)	Direct peak (ns; Hz)
Alcohol 2 mol%	2.56	1.360	2.54	27	3.29 (4.84×10^7)
Alcohol 4 mol%	2.89	1.543	3.03	21.2	2.99 (5.32×10^7)
Aldehyde 2 mol%	0.22	0.004	0.21	0.000622	0.000875 (1.82×10^{11})
Aldehyde 4 mol%	0.41	0.006	0.41	1.57	0.000875 (1.82×10^{11})
Ester 2 mol%	1.52	0.115	1.41	0.0946	0.145 (1.10×10^9)
Ester 4 mol%	0.98	0.067	0.90	0.114	0.232 (6.85×10^8)
Ketone 2 mol%	1.49	0.899	1.45	18.6	2.48 (6.43×10^7)
Ketone 4 mol%	0.76	0.259	0.71	0.284	0.192 (8.28×10^8)

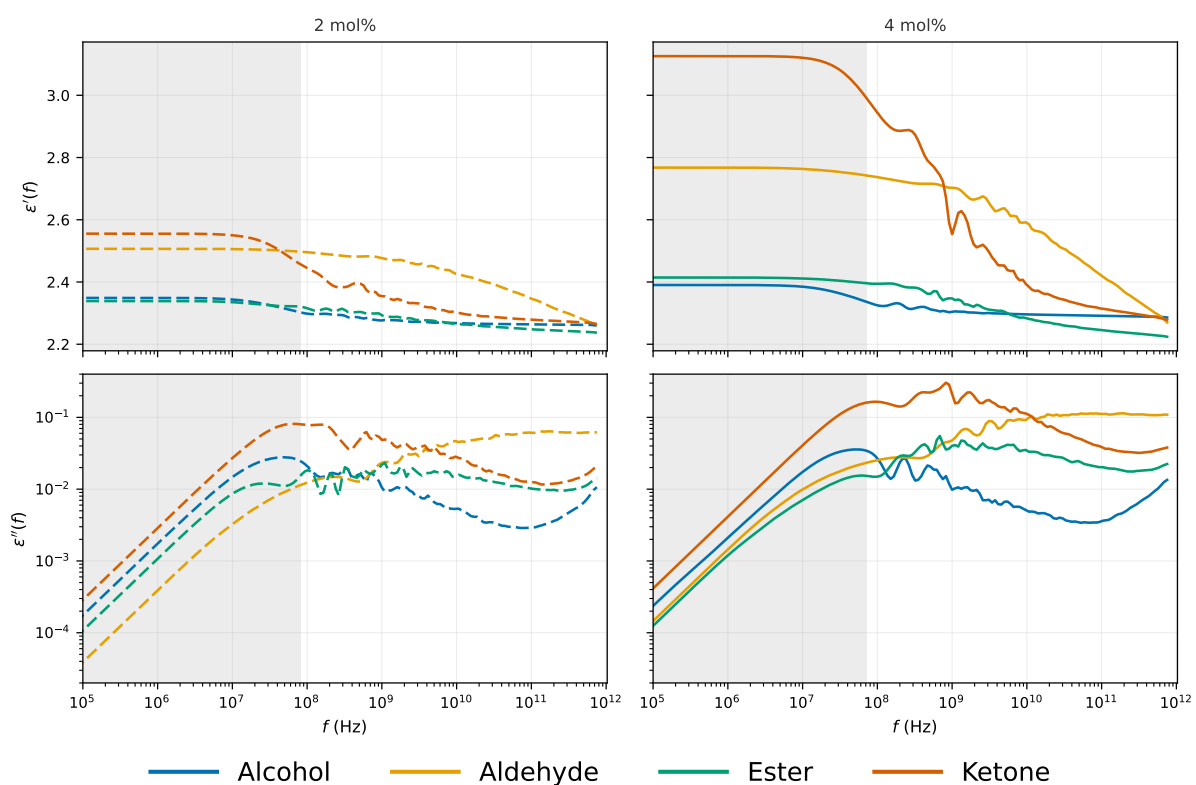


Figure E.1: Direct-transform complex permittivity from the dipole autocorrelation function. Panels in each row share the same horizontal and vertical scales, so the 2 and 4 mol% columns are directly comparable within a defect family. The shaded region is controlled by the fitted continuation of the autocorrelation beyond the sampled lag-time window rather than by directly sampled data, and is therefore model-sensitive.

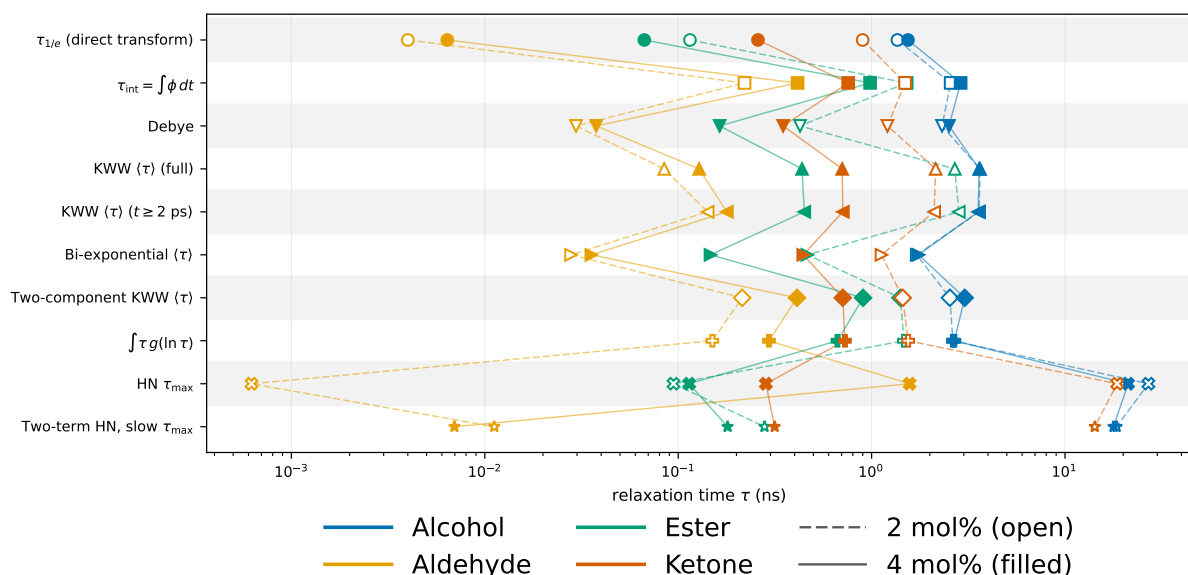


Figure E.2: Relaxation times for each state point under all ten definitions considered. The vertical spread within each state point is the ambiguity in assigning a single relaxation time to a broad polymer relaxation.

E.2. MD-Versus-Fit Loss Curves

Comparing the fitted models against the direct transform shows why a single Debye relaxation is not a defensible representation of the simulated loss. Debye fits concentrate the dispersion into too narrow a frequency range and overestimate the peak height; KWW is much better; the two-component KWW form is the best representation across the whole set.

That ordering is unanimous rather than approximate. Scored on a common $t \geq 2$ ps window, the two-component KWW form has the lowest Akaike information criterion (AIC) for all eight state points. The AIC is a penalized-likelihood model-selection criterion that balances fit quality against the number of fitted parameters [9]. The single Debye form has the highest AIC for all eight state points, with ΔAIC between the Debye and two-component KWW forms ranging from 784 for alcohol at 4 mol % to 1554 for ester at 2 mol %. The single-component KWW form comes second everywhere, trailing the two-component form by between 47 and 436 units.

The practical consequence for Chapter 4 is that no single relaxation-time definition should be treated as uniquely physical. The robust conclusions are the relative static response, the presence of broad rather than Debye relaxation, and the ranking of the stronger and weaker loss-producing systems. Peak positions and fitted shape parameters should always be quoted with the fitting convention visible.

The loss curves are likewise best used comparatively. Extrapolation to power frequencies depends on processes that the fixed-charge MD model does not represent at all, including charge transport and interfacial polarization. Within the simulated orientational response, however, the relative ordering of the defects and the presence of broad relaxation are consistent across the direct transform and the better-performing fitted models.

E.3. Dipole-Trace Quality Checks

Figures E.5 and E.6 show the total cell-dipole magnitude against time for the defect trajectories at 2 and 4 mol %, at each of the three simulated temperatures. They are included as a sampling check rather than as a quantitative result: the numbers in Chapter 4 come from the fluctuation analysis, and these traces show the time-domain signal to which the analysis is applied. The check is useful for

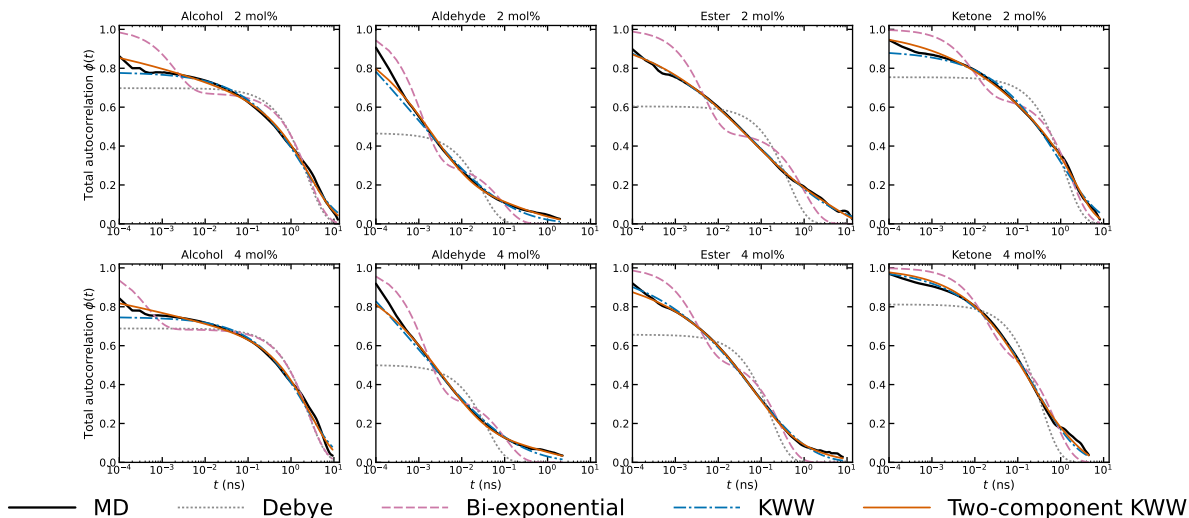


Figure E.3: Dipole autocorrelation functions from MD compared with the fitted relaxation models, for all eight 300 K fixed-defect state points.

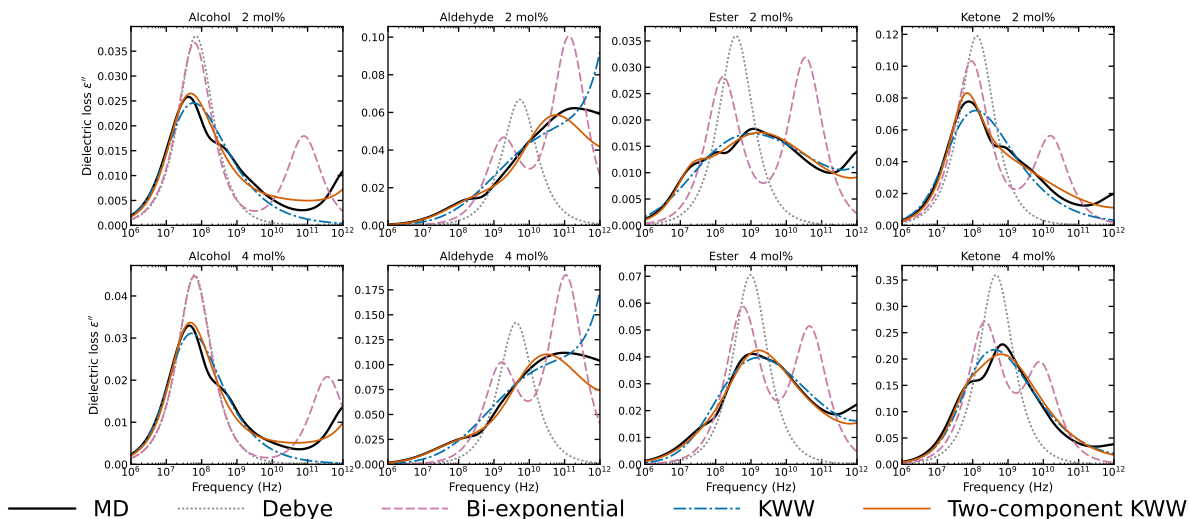


Figure E.4: Dielectric-loss spectra from the direct MD transform compared with loss curves generated from the fitted relaxation models.

identifying slow drift, a change in fluctuation amplitude partway through a run, or a persistent offset in one component of the cell dipole, any of which would invalidate a fluctuation-derived permittivity.

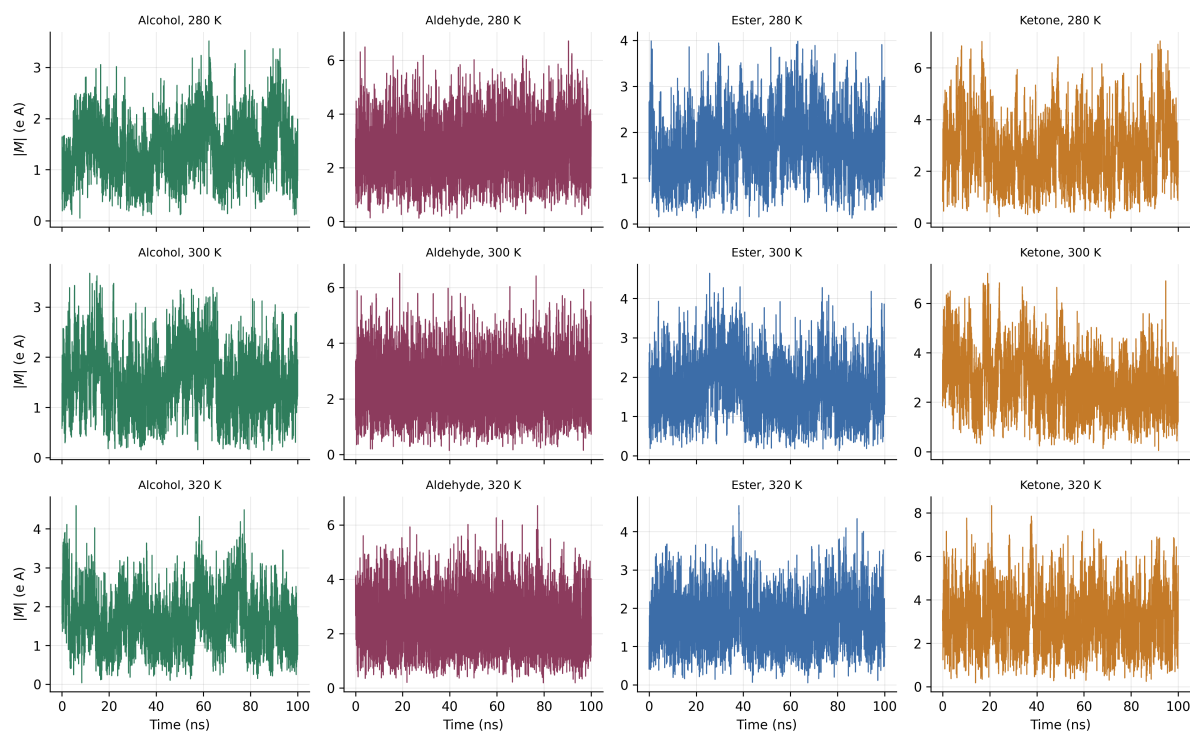


Figure E.5: Total cell-dipole magnitude against time for the 2 mol % defect systems at 280, 300 and 320 K. Each trace covers 100 ns.

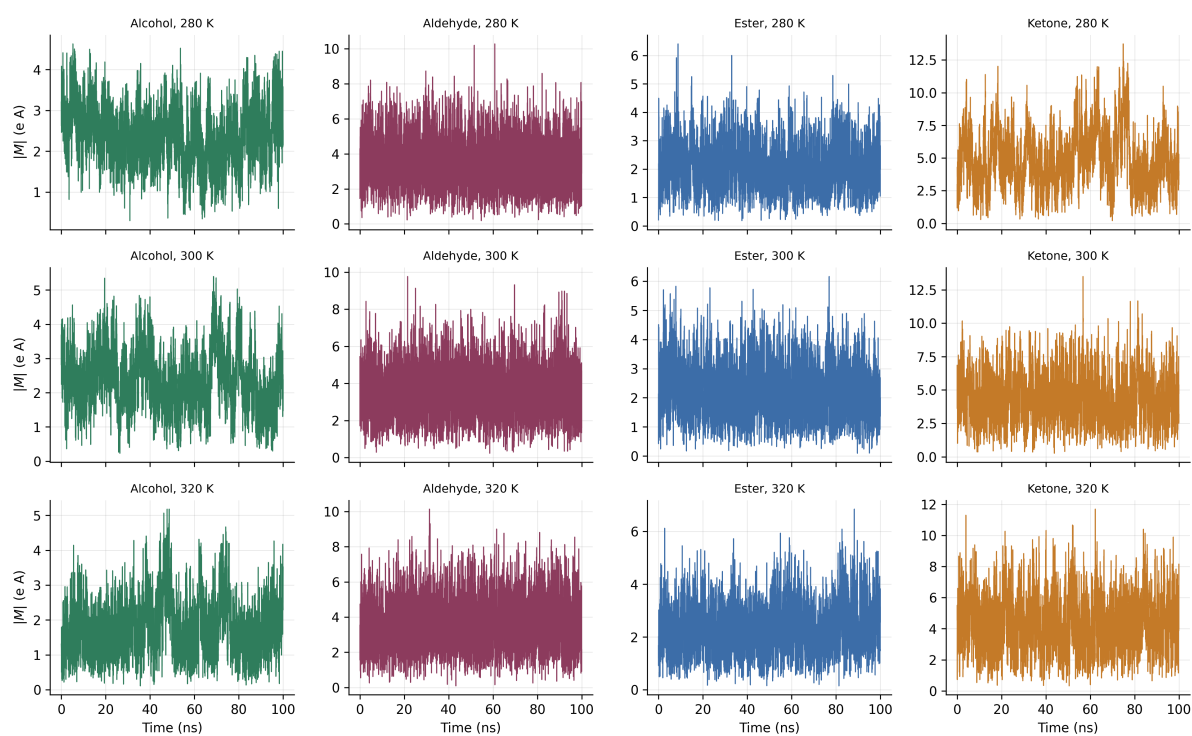


Figure E.6: Total cell-dipole magnitude against time for the 4 mol % defect systems at 280, 300 and 320 K. Each trace covers 100 ns.

F – Progressive Defect Addition and Morphology

This appendix documents the structural and dielectric checks for the progressive defect-addition simulations. In these runs the defect concentration is built stage by stage — four 50 ns stages at 300 K, taking each system from 10 to 40 defects, that is from 1 to 4 mol % — so the results represent an aging-like accumulation pathway rather than an independent fixed-defect preparation at each concentration. The distinction matters because the same trajectories supply the structural evidence used in the hydrogen-bond analysis of Appendix G.

F.1. Equilibration and Sequential Response

Averages over the last 10 ns of each stage confirm that the trajectories are thermally stationary. Across all 17 stage windows the mean temperature lies between 299.96 and 300.06 K, a total spread of 0.1 K against an instantaneous fluctuation of ± 3.2 K, so differences between stages cannot be attributed to thermostat drift. The root-mean-square displacement over the same windows falls from 4.7–5.7 Å at the first stage to 3.7–4.0 Å at the fourth, consistent with the backbone settling as defects accumulate rather than continuing to reorganize.

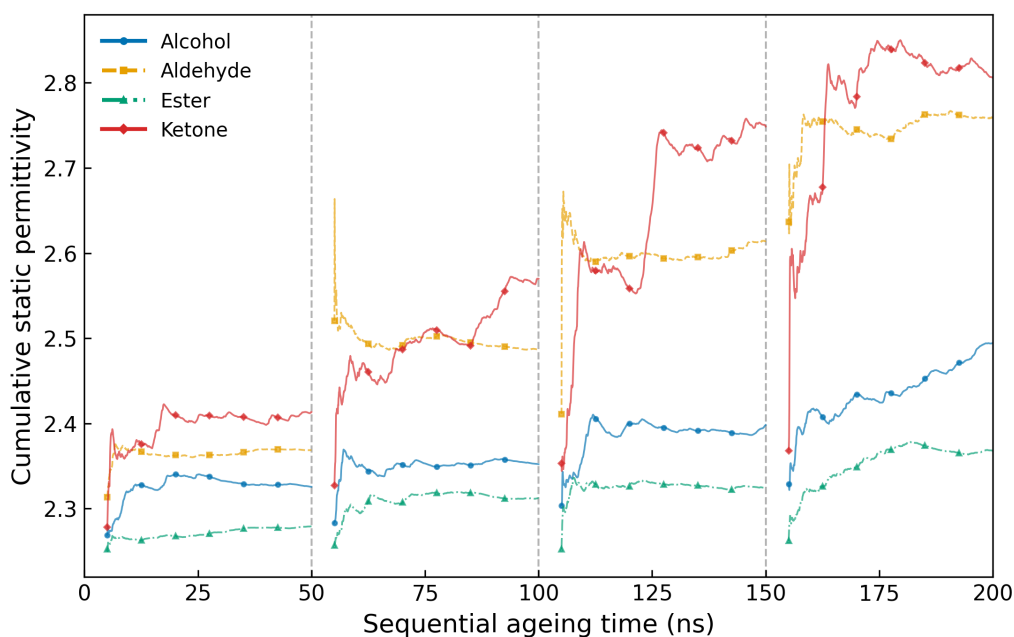


Figure F.1: Cumulative static permittivity along the 200 ns progressive-addition sequence. Dashed vertical lines mark the stage boundaries at which the next batch of defects is introduced, and the discontinuity at each boundary is the reset of the cumulative average, not a physical jump.

The radius of gyration, a measure of the compactness of the polymer morphology, shows no systematic trend for alcohol, ester or ketone, which fluctuate over bands of 0.23, 0.44 and 0.38 Å respectively. Aldehyde is the exception: it expands from 24.40 to 25.23 Å between 1 and 3 mol % and then holds that larger value (Fig. F.2).

That expansion should be interpreted with care rather than taken at face value, because the quantity itself is not strictly comparable across the set. The radius of gyration is computed over backbone atoms, and by 4 mol % the aldehyde and ester systems have 41 disconnected backbone components against one for alcohol and ketone. A radius of gyration over 41 fragments measures how those fragments fill the cell, not the conformation of a chain. That ester fragments in the same way without expanding shows that fragmentation alone does not force the increase, so the aldehyde result is not

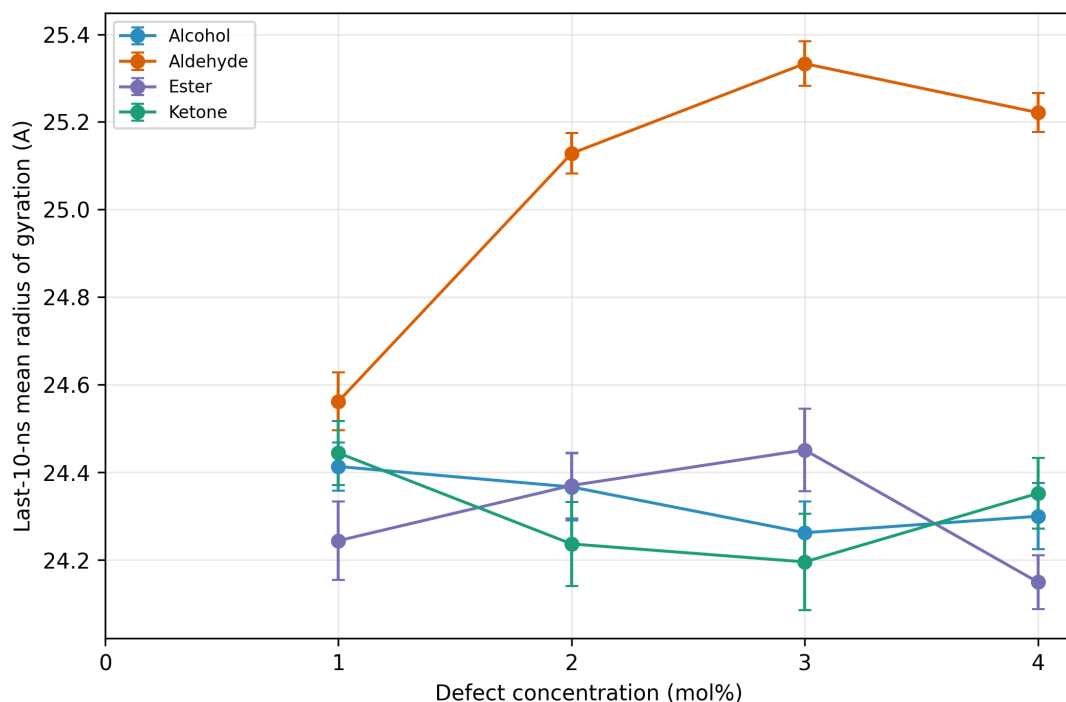


Figure F.2: Last-10-ns mean backbone radius of gyration against defect concentration. Alcohol, ester and ketone fluctuate over a 0.23–0.44 Å band with no systematic trend, whereas aldehyde rises by 0.83 Å between 1 and 3 mol % before flattening. Error bars are the standard deviation over the 10 ns averaging window.

purely an artifact; but the comparison is safest within the chain-preserving and chain-cutting groups separately rather than across them.

F.2. Morphology and Defect Contacts

The morphology analysis tracks how the defect groups are embedded in the polyethylene matrix (Table F.1). The backbone connectivity behaves differently for the two defect classes: chain-preserving defects such as alcohol and ketone keep a single backbone component at every stage, while chain-cutting defects such as aldehyde and ester produce one additional component per inserted defect. The defect-defect and defect-backbone distance metrics then show whether increasing concentration mainly adds isolated polar sites or drives local clustering: the mean nearest defect-defect distance falls from 7.9–11.9 Å at 1 mol % to 4.8–5.6 Å at 4 mol % in every defect type, and the fraction of defects lying within 5 Å of another defect rises from 0.00–0.60 to 0.40–0.72 over the same range, although not monotonically in every defect type.

These structural descriptors are needed because the same molar concentration can correspond to different microscopic arrangements. Two systems with the same number of polar groups can differ in clustering, in distance to ordered segments, and in backbone connectivity, and polar groups embedded in a constrained matrix do not reorient like polar groups in a more mobile local environment.

Table F.1: Endpoint morphology metrics for the progressive-addition stages. Here an endpoint means the final configuration of each 50 ns concentration stage, after the corresponding batch of defects has been introduced and propagated.

System	mol%	R_g (Å)	Nearest defect-defect (Å)	Cluster fraction < 5 Å
Alcohol	1	24.45	7.85	0.60
	2	24.31	6.38	0.55
	3	24.46	6.02	0.50
	4	24.23	4.78	0.72
Aldehyde	1	24.40	9.48	0.20
	2	25.08	5.76	0.50
	3	25.23	5.12	0.80
	4	25.19	5.00	0.70
Ester	1	24.16	11.91	0.00
	2	24.45	7.95	0.10
	3	24.18	5.74	0.57
	4	24.02	5.55	0.40
Ketone	1	24.50	9.75	0.20
	2	24.36	7.49	0.20
	3	24.12	5.49	0.47
	4	24.39	5.23	0.45
Pristine	0	24.41	–	–

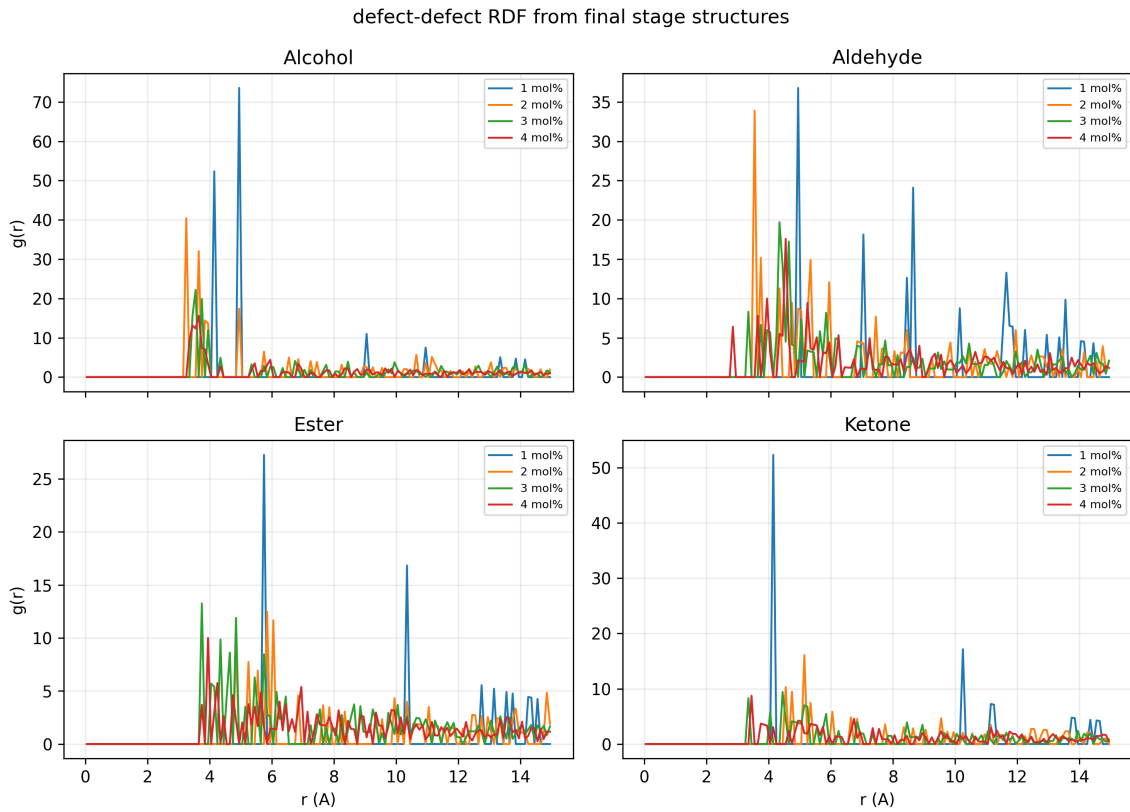


Figure F.3: Defect-defect radial distribution functions for the final progressive-addition structures.

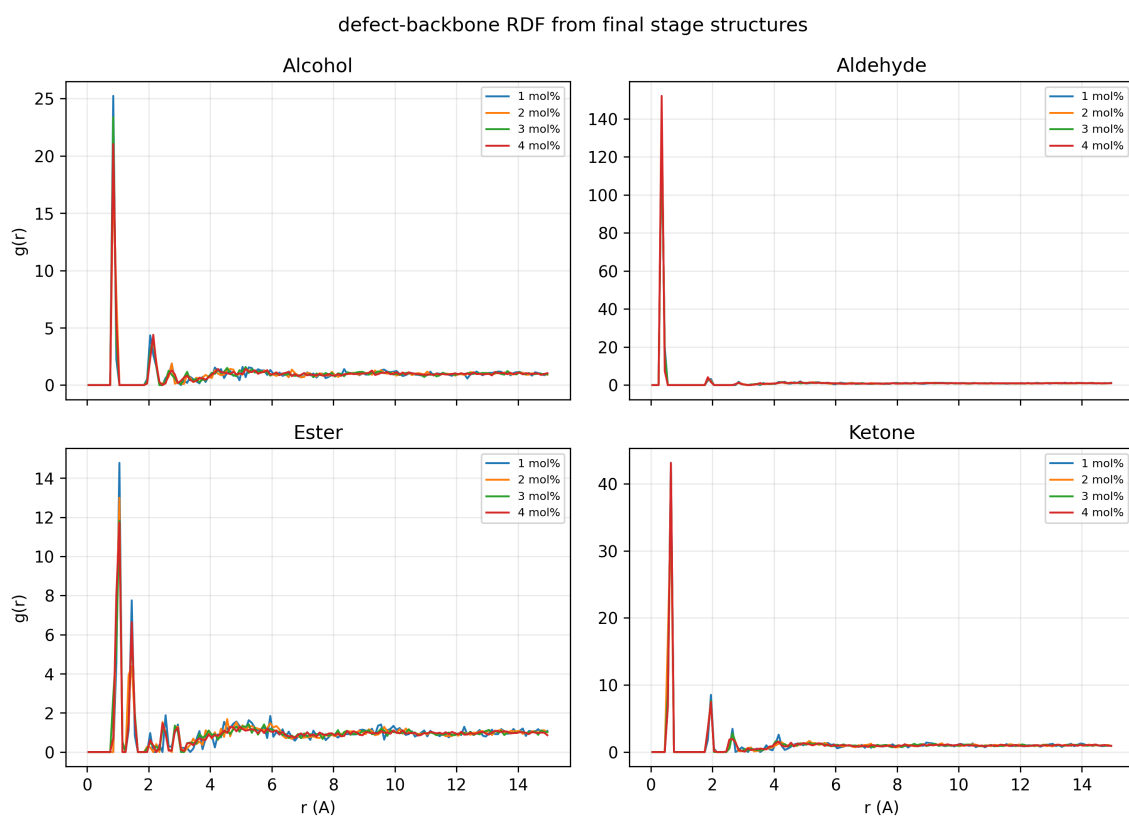


Figure F.4: Defect-backbone radial distribution functions for the final progressive-addition structures.

G – Hydrogen-Bond and Polar-Contact Mechanism

This appendix supports the interpretation of the alcohol response by analysing hydroxyl–hydroxyl hydrogen bonding, polar contacts with the polyethylene matrix, the local defect dipole, and orientational persistence. The evidence comes from the progressive-addition trajectory set of Appendix F. It provides a mechanistic interpretation of the alcohol pathway, not a numerical replacement for the fixed-defect 300 K analysis of Chapter 4.

The alcohol defect is chemically distinctive because it combines a strong local O–H bond dipole with the ability to form directional hydroxyl–hydroxyl contacts. A large local dipole would normally be expected to increase the orientational dielectric response, yet the results of Chapter 4 show the alcohol response to be modest compared with ketone and aldehyde. The question this appendix addresses is whether the hydroxyl groups remain freely reorienting or become partly constrained by recurrent contacts and coupling to the matrix.

G.1. Definitions

Contacts. Hydroxyl contacts were evaluated at three levels of geometric strictness. In the hydroxyl–hydroxyl definitions, the donor is a hydroxyl O–H group and the acceptor is the oxygen atom of another hydroxyl defect. A distance-only contact requires an oxygen–oxygen separation shorter than 3.5 Å. A loose hydrogen bond additionally requires an O–H...O angle of at least 120°, and the strict definition requires at least 150°. Matrix C–H...O contacts use a polyethylene C–H group as the donor and the hydroxyl oxygen as the acceptor, with an H...O distance cutoff of 2.7 Å and a C–H...O angle cutoff of 120°. Using several definitions prevents the analysis from depending on one threshold: the distance criterion measures how often hydroxyl oxygens are close enough to interact, the angular criteria select the subset with hydrogen-bond-like directionality, and the matrix criterion asks the different question of how often a hydroxyl oxygen sits near polyethylene C–H groups.

Local defect dipole. The local dipole measure is the mean magnitude of the defect-group dipole, $\langle |\mathbf{M}_{\text{def}}| \rangle$, computed from the time series of the dipole carried by the defect atoms alone.

Defect–matrix covariance. The coupling between the defect subsystem and the surrounding polymer is measured by the normalized cross-covariance of their dipole fluctuations,

$$\rho_{\text{def,mat}} = \frac{\langle \delta \mathbf{M}_{\text{def}} \cdot \delta \mathbf{M}_{\text{mat}} \rangle}{\sqrt{\langle |\delta \mathbf{M}_{\text{def}}|^2 \rangle \langle |\delta \mathbf{M}_{\text{mat}}|^2 \rangle}}, \quad (\text{G.1})$$

where $\delta \mathbf{M}_{\text{def}} = \mathbf{M}_{\text{def}} - \langle \mathbf{M}_{\text{def}} \rangle$ and likewise for the matrix dipole $\mathbf{M}_{\text{mat}}$. A negative value means that the matrix polarization partly cancels the defect polarization, so that the total cell dipole fluctuates less than the defect dipole alone would imply.

G.2. Hydroxyl Contacts and Local Dipole

Throughout this appendix, *endpoint* refers to the end of a concentration stage rather than to the end of the whole 200 ns run: each quantity is evaluated once its concentration has been reached, so every row below characterises one stage. The convention is not quite that of the endpoint morphology metrics of Appendix F, which are read from a single final configuration; here only the 1 mol % row is a single configuration, and the 2–4 mol % rows are averages over the retained frames of their stage.

Table G.1 collects the endpoint contact, dipole, relaxation and covariance metrics.

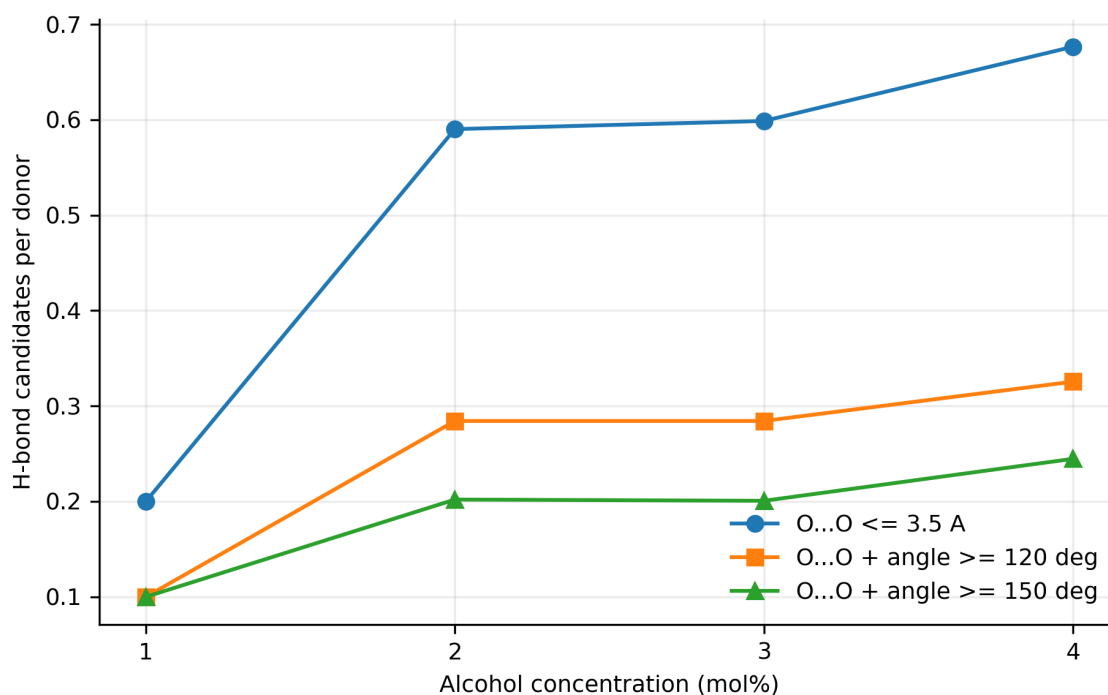


Figure G.1: Comparison of the distance-only, loose-angle and strict-angle hydroxyl contact definitions across the alcohol concentration series.

Table G.1: Alcohol hydrogen-bond, local-dipole and covariance metrics across the progressive-addition series. The 1 mol % row is a single endpoint-only structure; the 2–4 mol % rows are averages over the retained trajectory frames for each concentration stage, as reported by the frame-count column. $\rho_{\text{def,mat}}$ is defined by Eq. G.1.

mol%	Defects	Frames	H-bonds per defect	$\langle M_{\text{def}} \rangle$ (D)	τ_{int} (ns)	$\tau_{1/e}$ (ns)	$\rho_{\text{def,mat}}$
1 [‡]	10	1	0.100	1.363	1.169	0.845	−0.089
2	20	51	0.202	1.751	1.629	1.144	−0.113
3	30	51	0.201	2.925	1.540	1.442	−0.102
4	40	51	0.245	2.528	4.089	5.549	−0.326

[‡] The 1 mol % contact statistics come from a single endpoint configuration, because no co-ordinate trajectory was retained for that stage. The remaining rows are averages over 51 frames. The 1 mol % row is therefore a single-configuration estimate and its contact numbers carry no sampling uncertainty estimate.

The strict hydrogen-bond count per defect rises from 0.100 at 1 mol % to 0.245 at 4 mol %, but not monotonically: the 2 and 3 mol % values are equal within rounding (0.202 and 0.201). At every concentration only 10–25% of alcohol defects are hydrogen bonded at any instant, so the correct description is a dilute population of transient inter-defect hydrogen bonds and not a percolating network. The geometry of the bonds that do form is chemically reasonable, with mean O–O separations of 2.84–2.89 Å over the trajectory-averaged stages and mean angles between 163° and 170°. The 1 mol % entry sits at 3.28 Å, but it is a single-configuration value drawn from one hydrogen bond.

The dielectrically relevant quantity is not the contact count. A contact can be frequent and still be dielectrically unimportant if it does not affect the orientation or the persistence of the local dipole. Two other columns of Table G.1 carry that information. The defect–matrix covariance is negative at every concentration and becomes markedly more negative at 4 mol % (–0.326 against –0.089 to –0.113 elsewhere), meaning that the matrix increasingly opposes the defect polarization. At the same concentration the defect-dipole autocorrelation time rises sharply.

That last number needs a caveat, because the mechanism argued here leans on it. The autocorrelation was evaluated over a maximum lag of 10 ns and integrated to its first zero crossing. At 4 mol % the resulting $\tau_{\text{int}} = 4.09$ ns is accompanied by $\tau_{1/e} = 5.55$ ns, that is the correlation function has not decayed to $1/e$ within the window over which the integral was taken. The 4 mol % value is therefore a lower bound set by the analysis window rather than a converged relaxation time, and the concentration trend rests on this single point. Repeating the analysis with a longer maximum lag would settle it.

The local defect dipole itself is not monotonic in concentration (1.36, 1.75, 2.93, 2.53 D). Since it is the mean magnitude of a vector sum over an increasing number of defects, it depends on their mutual orientation as well as on their number, and the drop between 3 and 4 mol % coincides with the most negative covariance — both consistent with increasing mutual and matrix compensation at the highest concentration.

The sign of $\rho_{\text{def,mat}}$ turns out to be the sharpest discriminator in the whole progressive-addition set, and alcohol is alone on one side of it. Applying Eq. G.1 unchanged to the other three defect types gives uniformly *positive* values at every concentration: aldehyde +0.13 to +0.24, ester +0.23 to +0.30, and ketone +0.39 to +0.65, against –0.09 to –0.33 for alcohol. In the three carbonyl systems the matrix polarization therefore reinforces the defect polarization, whereas in the hydroxyl system it opposes it. The negative alcohol values are consequently a property of the hydroxyl functional group and not an artifact of the covariance definition.

That distinction lines up with the dielectric increments of Chapter 4 at the extremes but not in detail. Alcohol has both the most negative covariance and the smallest orientational increment, and ketone has both the most positive covariance and the largest orientational increment; aldehyde and ester, whose covariances are close to each other, exchange places between the two rankings. The covariance should therefore be read as a mechanistic indicator of how the matrix responds to a polar group, not as a predictor of the increment. One further caution applies to any such comparison: the covariances here come from the progressive-addition trajectories, while the increments quoted in Chapter 4 come from the fixed-defect runs, so the two sets share a defect type but not a preparation history.

G.3. Hydrogen-Bond Residence Times

Table G.2 reports how long individual donor–hydrogen–acceptor triplets persist. Continuous residence counts uninterrupted presence on the sampled frames; intermittent residence allows the same triplet to break and reform.

Read with those limits, the table says that a given hydroxyl pair is typically in contact for one or two consecutive sampled frames, and that the same pair recurs over tens of nanoseconds. The picture is a recurrent pairing between neighboring hydroxyl groups rather than a static hydrogen-bond network:

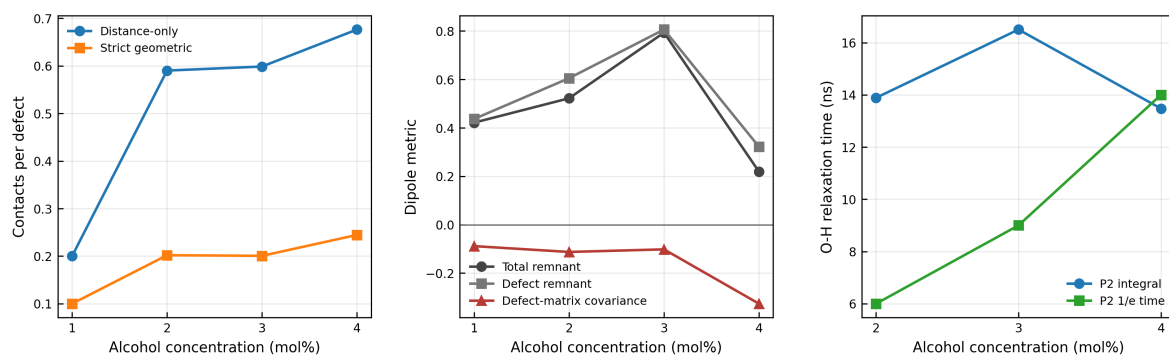


Figure G.2: Summary of the alcohol mechanism, combining hydroxyl contacts per defect, the local dipole measures, and the orientational persistence of the defect dipole.

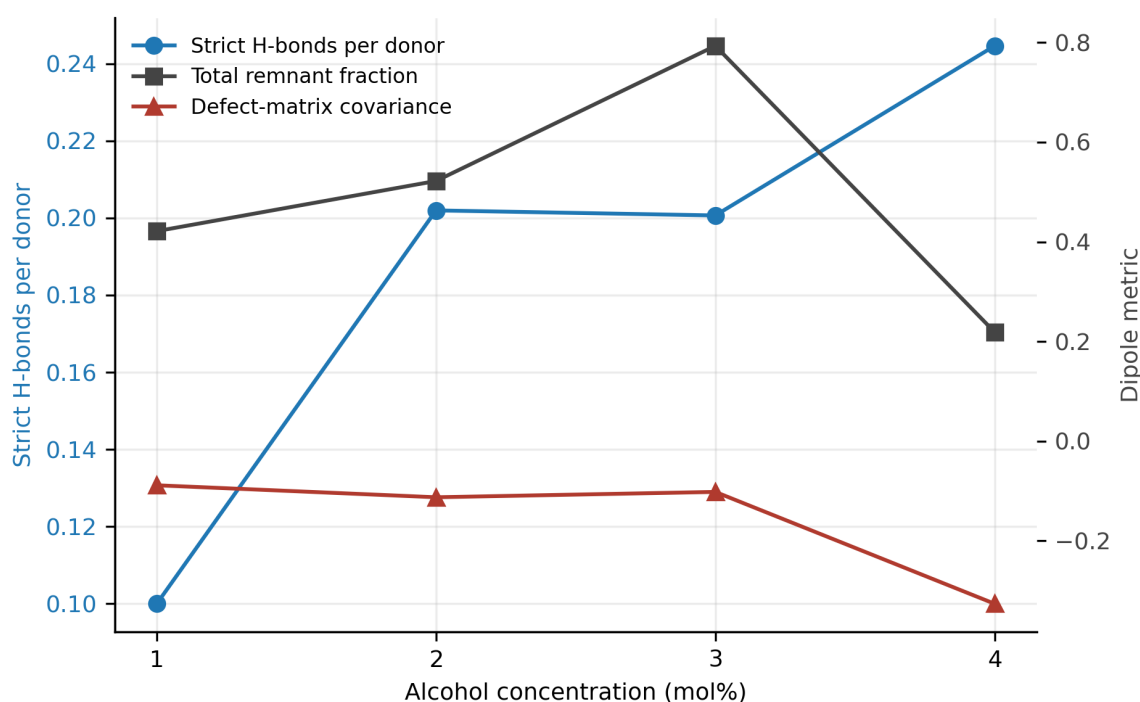


Figure G.3: Relationship between strict hydroxyl hydrogen bonding, the local dipole measures, and the defect-matrix covariance across the alcohol progressive-addition series.

Table G.2: Strict hydroxyl hydrogen-bond residence times for the alcohol progressive-addition trajectories.

mol%	Unique triplets	Mean occupancy	Continuous residence mean (ns)	Continuous residence max (ns)	Intermittent residence mean (ns)	Intermittent residence max (ns)
2	18	0.224	1.75	9	4.69	31
3	17	0.354	2.49	20	5.90	34
4	34	0.288	2.44	16	6.26	50

Coordinates were sampled every 1 ns over a 50 ns stage, so residence times are quantised in 1 ns steps and bounded above by 50 ns.

thermal motion breaks a contact, but the local environment keeps the same two groups close enough to reform it. The orientational autocorrelation of the O–H vectors (Fig. G.4) decays slowly on the same nanosecond scale, which is the dielectrically relevant consequence.

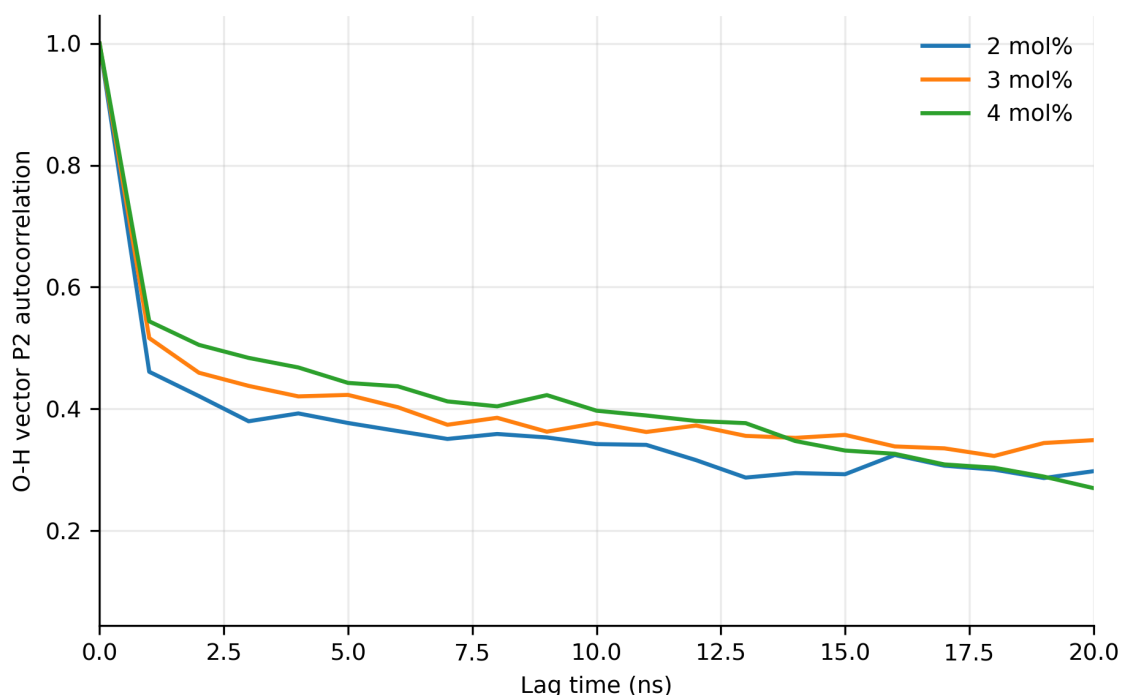


Figure G.4: Second-order orientational autocorrelation of the hydroxyl O–H vectors. The slow decay supports the interpretation that recurrent contacts constrain hydroxyl orientation over nanosecond time scales.

This appendix explains why a polar hydroxyl group can increase the local dipole strength while still producing a limited orientational dielectric increment. Hydroxyl defects add polarity, but polarity alone does not determine the macroscopic orientational response; the surrounding matrix controls how much of the local dipole can decorrelate on the simulation time scale. Recurrent hydroxyl contacts, slow O–H reorientation and increasingly negative defect–matrix covariance together provide a structural route by which alcohol defects remain locally polar while contributing less orientational permittivity than the more freely reorienting carbonyl defects.

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