COMSERVA: Jurnal Penelitian dan Pengabdian Masyarakat

E-ISSN: 2798-5210
Vol. 6, No. 5, June 2026
pp. 423-439
DOI: 10.59141/comserva.v6i4.3620

Interfacial association, hydration and polarization in PLA/PCL/PEG/nanozeolite membranes: a DFT framework

Muhammad Satya Putra Gantada*, Agung Mataram
Universitas Sriwijaya, Indonesia
Corresponding Author:amataram@unsri.ac.id*

Keywords:
Density functional theory; PLA/PCL/PEG; Nanozeolite; Many-body interactions; Interfacial hydration; Electronic polarization.

This is an open access article under the CC BY-SA license.

Copyright © 2026 by Author. Published by Publikasi Indonesia

ABSTRACT

Background: Interfaces between polylactic acid (PLA), polycaprolactone (PCL), poly (ethylene glycol) (PEG) and nanozeolite in composite membranes couple interfacial stability with competition for water-binding sites, yet no consistent electronic-structure framework separates polymer association, hydration and polarization effects.
Objectives: This study aims to propose a density functional theory (DFT) protocol that links polymer association, water-site accessibility and electronic polarization within one energetic reference.
Method: A protocol-development design was applied. Counterpoise-corrected many-body decomposition, electrostatic and density-topology descriptors, frontier response, hydration thermochemistry, vibrational shifts and finite-field polarization were defined, and their workflow was demonstrated with an internally consistent numerical illustration built from author-assigned values (not computed) using Python/NumPy arithmetic. r²SCAN-3c geometries and PBE0-D4/def2-TZVPD single points are specified for subsequent validation.
Findings and Implications: Within the assigned illustration, the four-component binding energy of −2.340 eV arises mainly from pair contacts and PEG–zeolite coupling (−0.818 eV), whereas the strict four-body term is weak (−0.032 eV). Water association reaches −0.812 eV, but a positive three-body hydration term (+0.097 eV) represents competition for cationic sites, and fields of $\pm 2\times10^{-4}$ a.u. produce modest directional energy changes of approximately 5.5 meV. These values are illustrative hypotheses rather than computed findings.
Conclusion: The framework yields a testable design criterion, namely preserving accessible oxygen sites while limiting deformation and competition for cationic sites, and defines the DFT calculations required before application to specific membrane compositions.

INTRODUCTION

The molecular basis of polymer–zeolite association depends on how oxygen-containing groups share interfacial binding sites with water. Poly(lactic acid) (PLA) and polycaprolactone (PCL) provide ester groups, whereas poly (ethylene glycol) (PEG) introduces ether oxygens and, for hydroxyl-terminated chains, hydrogen-bond donors. PLA has been widely examined as a renewable membrane material (Vatanpour et al., 2022), whereas the comparatively hydrophobic character of PCL has motivated its blending with PEG and other hydrophilic

components (Kayan & Kayan, 2023). A charge-compensated aluminosilicate adds framework oxygens, surface hydroxyls and cationic coordination sites; in polymeric nanocomposite membranes, the contribution of such zeolite fillers depends on a well-formed polymer–filler interphase (Sahu et al., 2023). Within this heterogeneous environment, favourable polymer association and accessible hydration sites must be considered together. Density functional theory (DFT) offers a route to resolving the local interactions underlying this design problem.

Recent studies establish useful precedents for this analysis. Li, (2021) used dispersion-corrected DFT to examine selected PLA–attapulgite complexes, providing a computational example of polyester–silicate association. In a related polymer system, Lu et al., (2025) examined PEG-mediated interactions in PCL-based nanocrystalline membranes through binding energies, electrostatic potentials, charge-density differences and reduced density gradients. Their PCL/PEG/water model exhibited stronger association than the corresponding PCL/water model. These findings motivate treating PEG as an active participant in the interfacial interaction network. Extending this reasoning to PLA/PCL/PEG/nanozeolite requires accounting for the additional coordination environment introduced by the inorganic component.

Zeolite hydration illustrates why this extension requires explicit consideration of site occupancy. Randrianandraina et al., (2023) showed that water coverage regulates access to Na^+ sites in Na-LTA and affects competition with other adsorbates. Fischer, (2023) found that protonation enhanced triclosan binding in high-silica zeolites while increasing water affinity even more. More generally, the adsorption behaviour of zeolites, including their affinity for water, is governed by framework composition and extra-framework cations (Pérez-Botella et al., 2022), and DFT modelling of cation exchange in faujasites reproduced the experimental site preference only when explicit water molecules were combined with an implicit solvent (Ta et al., 2024). Although these systems differ from a polymer–nanozeolite interface, their results identify site accessibility and competing coordination as relevant variables. For the four-component formulation, this motivates examining whether PEG reinforces polymer–zeolite association while preserving sites for water, and whether stronger total hydration is accompanied by favourable or unfavourable nonadditive contributions.

A consistent DFT description must distinguish these effects at the same structural and energetic reference. Binding energies combine frozen-fragment attraction with the cost of deforming individual components; an increase in total attraction alone does not establish a specifically four-body cooperative mechanism. Nonadditive contributions can arise even when the underlying interactions are pairwise in form (Heindel et al., 2023), and in heteromolecular trimers the three-body term is predominantly inductive (Ochieng & Patkowski, 2023). Pair, three-body and four-body terms therefore need separate evaluation, together with incremental water-binding energies. Density-based descriptors can then locate the contacts associated with these changes. The Hirshfeld-based independent gradient model introduced by Lu & Chen, (2022) and the wavefunction-analysis framework described by Lu, (2024) provide tools for connecting energy changes with interfragment density topology. Dispersion, basis-set effects, conformational variation and thermochemical references also require control, as emphasized by(Bursch et al., 2022).

Here, we formulate a DFT framework for interfacial association and hydration in PLA/PCL/PEG/nanozeolite models. The framework links interaction-energy decomposition

with electrostatic complementarity, charge redistribution, local density topology, frontier electronic response and vibrational signatures. Explicit hydration states and clamped-nuclei finite-field response address competition for polar sites and directional electronic polarization. An internally consistent synthetic numerical illustration demonstrates the relationships among these descriptors, and a proposed electronic-structure protocol defines their subsequent validation. The objective is to establish testable local mechanisms connecting polymer association, water-site accessibility and field response within one clearly specified model.

METHOD

Research design

This study is designed as a methodological (protocol-development) study in computational materials chemistry, rather than as a report of completed electronic-structure calculations. Its research object is a defined local interaction model of a PLA/PCL/PEG/nanozeolite membrane interface. The study proceeds in three stages: (i) definition of the fragment model and of the energetic, electrostatic, topological, electronic-response, hydration, vibrational and field-response descriptors; (ii) construction of an internally consistent numerical illustration in which every scalar quantity is an author-assigned illustrative value (not computed); and (iii) specification of the DFT protocol by which each assigned quantity is to be replaced by a computed value.

The only instrument used was a Python/NumPy environment for deterministic arithmetic; no quantum-chemistry program, experimental apparatus or measured dataset was employed. Accordingly, no primary data were collected, and the arithmetic checks reported below verify internal consistency only, not physical accuracy. The Results and Discussion section follows the same sequence as this Method: interfacial association and many-body decomposition, electrostatics and charge redistribution, density topology, frontier response, hydration thermochemistry, vibrational and finite-field response, and conformer sensitivity.

Each numerical value in that section is either an assigned input defined here or a quantity derived arithmetically from it. Statements about which interactions dominate, compete or cooperate therefore describe the consequences of the assigned inputs and are reported as testable hypotheses for the proposed validation, not as computed findings. Because no atomic coordinates or wavefunctions were generated, electrostatic-potential maps, RDG/IGMH isosurfaces, simulated infrared spectra and structural figures cannot be produced at this stage; these outputs are specified as deliverables of the validation protocol.

Model definition

The illustration represents hydroxyl-containing PLA, PCL and PEG trimers as fragments A, B and C, respectively, and a hydroxylated aluminosilicate environment as Z. The Z composition has Si/Al = 4, one framework Al and one compensating Na^{+}; neutral hydroxyl termination gives zero total charge. AB, ABC, ABZ and ABCZ provide the comparison series. Water is denoted W. Contact distances, angles and bond lengths are assigned structural descriptors. Atomic coordinates, crystallographic zeolite topology and electronic wavefunctions were not generated. Consequently, the model specifies a local interaction environment rather than a nanoparticle or a particular membrane formulation.

Construction of the assigned illustrative data (not computed)

Python and NumPy were used for deterministic arithmetic, without random sampling or an electronic-structure engine. Isolated-fragment reference energies were set to zero. Six pair contributions, four three-body contributions and one four-body contribution were assigned, and every subset energy was reconstructed from its contained terms: The resulting energies are therefore illustrative inputs selected by the authors; their relative magnitudes reflect that selection rather than an electronic-structure result.

$$\begin{aligned} U_X &= \sum_{\substack{K\subseteq X \\ 2\le|K|\le4}} \kappa_K\,, \qquad U_A = U_B = U_C = U_Z = 0, \\ (\kappa_{AB}, \kappa_{AC}, \kappa_{AZ}) &= (-0.168, -0.234, -0.512)\ \text{eV}, \\ (\kappa_{BC}, \kappa_{BZ}, \kappa_{CZ}) &= (-0.206, -0.476, -0.628)\ \text{eV}, \\ (\kappa_{ABC}, \kappa_{ABZ}, \kappa_{ACZ}, \kappa_{BCZ}) &= (-0.026, -0.051, -0.087, -0.071)\ \text{eV}, \\ \kappa_{ABCZ} &= -0.032\ \text{eV}, \\ \Delta E_{\text{bind}}(X) &= U_X + D_X, \\ (D_{AB}, D_{ABC}, D_{ABZ}, D_{ABCZ}) &= (0.052, 0.102, 0.080, 0.151)\ \text{eV}. \end{aligned} \tag{1}$$

The values implement the reference conventions of the subsequent DFT equations; no basis-set superposition correction was actually evaluated. ESP extrema, orbital energies, charge changes and density-topology quantities were assigned scalar inputs. QTAIM energy densities were closed algebraically through $V = \nabla^2 n/4 - 2G$ and $H = G + V$. For the donor–acceptor illustration, occupations of 1.97, 1.96 and 1.95 and orbital separations of 0.45, 0.48 and 0.42 Hartree were combined with the specified stabilization magnitudes to determine $|F_{ij}|$. Charge conservation, unit-integrated Fukui responses, many-body reconstruction and local virial closure were checked to a numerical tolerance of 10^{-12} in their reported units. These checks establish arithmetic consistency only; they do not constitute physical validation of the assigned values.

Proposed electronic-structure validation

The following protocol is proposed for replacing the assigned quantities with DFT outputs. Independent starting arrangements would sample carbonyl, ether, hydroxyl and Na^+ coordination sites, since the preferred Na^+ position in aluminosilicates depends on framework Al siting (Saeed & Fischer, 2025). Neutral assemblies and fragments would use singlet states. Gas-phase optimization and harmonic Hessians would employ r²SCAN-3c, including its defined basis, dispersion and geometric counterpoise terms, following (Grimme et al., 2021). Single-point energies would use PBE0-D4/def2-TZVPD. The proposed targets are an SCF energy change below 10^{-8} Hartree and a maximum optimization gradient below 3×10^{-4} Hartree a_0^{-1}; minima would require no imaginary internal modes.

Full counterpoise interaction energies would be evaluated at the single-point level, with ghost centres carrying basis functions only. All 15 nonempty ABCZ subsets would share the frozen supersystem geometry and basis. Deformation energies would use the same functional and fragment basis for associated and isolated geometries. The composite-method gCP correction would not be added to these single-point energies. Basis enlargement and comparison with a range-separated functional would test sensitivity, as absolute adsorption

energies in zeolites vary widely among dispersion-corrected functionals even when qualitative trends are preserved (Fischer & Brauer, 2024). This multilevel design follows (Bursch et al., 2022). ORCA provides a possible implementation, as described by Neese, (2022) and updated for version 6.0 by Neese, (2025); it was not invoked to generate this illustration. Upon validation, optimized Cartesian coordinates, input files and output summaries for all assemblies and subsets would be provided as Supporting Information to permit independent reproduction.

Electrostatic, topological and orbital descriptors

For validation, wavefunctions would be analysed with the framework described by Lu, (2024). ESP extrema would be extracted on the $n = 0.001$ e a_0^{-3} surface using the common -0.100 to +0.140 a.u. range. Frozen-fragment density differences and charge changes would use identical atom-based Hirshfeld weights. RDG and IGMH surfaces would use isovalues of 0.5 and 0.005 a.u., respectively; the latter follows Lu & Chen, (2022). QTAIM critical points would be located from the density gradient and classified by the Hessian eigenvalues. Grid refinement would check numerical stability.

Vertical ionization and electron attachment would use N-1 and N+1 doublet calculations at the neutral geometry, with the same diffuse basis and unrestricted-state stability checks. The excess-electron distribution would be examined before accepting an electron affinity. Frontier orbital populations and fragment Fukui responses would use one consistent partition. Donor–acceptor stabilization would require a compatible localized-orbital analysis. These operations are the validation route for the assigned scalar descriptors.

Hydration and vibrational treatment

The hydration illustration contains zero to four waters. Incremental adsorption energies were assigned and cumulatively summed; mean energies were obtained by division by occupancy. Thermochemical components were specified separately at 298.15 K. The standard-state conversion uses 1 bar and 1 mol L^{-1}, and pocket populations were normalized at a chemical-potential offset of -0.200 eV relative to that same reference. In the validation protocol, differential aqueous solvation would be evaluated with SMD for each assembly and its references, while zero-point and thermal terms would come from harmonic calculations. A modified rigid-rotor/harmonic-oscillator entropy treatment with a 100 cm^{-1} crossover would address low-frequency modes, consistent with the guidance of (Bursch et al., 2022).

The four reported vibrational positions are assigned after application of the common illustrative scale factor 0.965. Lorentzian broadening uses an 8 cm^{-1} half-width. These plotting conventions do not generate Hessians or thermochemical corrections; the latter are separate inputs in the current example. Water coverage and contact placement would be varied during validation, following the mechanistic considerations of (Fischer, 2023; Randrianandraina et al., 2023).

Finite-field response and conformer averaging

The assigned z-directed response was evaluated from a cubic energy expansion at fields of 0, $\pm 10^{-4}$ and $\pm 2 \times 10^{-4}$ a.u., holding the structural reference fixed. With F expressed in atomic units, the interaction energy and dipole were constructed as

$$\begin{aligned}\frac{\Delta E_{\mathrm{int}}(F)}{\mathrm{eV}} = \quad & -2.491 - 27.211386245988\frac{11.360 - 8.790}{2.541746473}F \\ & -\frac{27.211386245988 \times 48.5}{2}F^2 - \frac{27.211386245988 \times 1200}{6}F^3, \qquad (2) \\ \frac{\mu_z(F)}{\mathrm{D}} = \quad & 11.360 + 2.541746473\left[635.2F + \frac{2180}{2}F^2\right].\end{aligned}$$

Central differences checked dipole and polarizability consistency. Six conformer free-energy offsets, all with unit degeneracy, were Boltzmann-weighted at 298.15 K. For this illustrative construction, each conformer binding energy equals -2.340 eV plus its assigned free-energy offset. Population-weighted spreads therefore describe the chosen state set, rather than a sampling error. Trimer, pentamer, heptamer, surface, basis and functional variants are assigned sensitivity scenarios. In actual validation, these quantities would be independently recalculated, and the conformer search would be extended until the relevant populations and observables converge, for example by using the automated conformer–rotamer sampling implemented in CREST (Pracht et al., 2024).

RESULTS AND DISCUSSION

All numerical values in this section are author-assigned illustrative values (not computed), constructed as described in the Method. They are reported to demonstrate how the proposed descriptors would be derived, cross-checked and interpreted once DFT outputs become available. Consequently, expressions such as “dominates”, “competes” or “indicates” refer to relationships within the assigned dataset and constitute hypotheses to be tested rather than empirical findings. Figures such as ESP maps, RDG/IGMH isosurfaces, IR spectra and optimized structures are not presented because no electronic-structure calculation was performed; they are specified outputs of the validation protocol.

Interfacial association and cooperative stabilization

The illustrative numerical model combines hydroxyl-containing PLA, PCL and PEG trimers, denoted A, B and C, with a representative hydroxylated aluminosilicate fragment Z. Its Si/Al ratio is 4, with one Na^+ per framework Al and no uncompensated boundary charge. S = ABCZ denotes the complete assembly. Charge balance follows

$$\begin{aligned}\frac{Q_Z}{e} &= -N_{\mathrm{Al}} + N_{\mathrm{H,comp}} + \sum_{j=1}^{N_{\mathrm{cat.types}}} z_j\, N_j + q_{\mathrm{termination}}, \\ \frac{Q_Z}{e} &= 0 \quad \text{for a neutral, charge-balanced fragment,} \\ N_{\mathrm{Al}} &= \text{number of framework Al substitutions,} \\ z_j &= \text{formal charge of compensating cation type } j.\end{aligned} \qquad (1)$$

The model uses $N_{\mathrm{Al}} = N_{\mathrm{Na}} = 1$, $N_{\mathrm{H,comp}} = 0$ and $q_{\mathrm{termination}} = 0$. Its assigned contact geometry contains a zeolite O–H···O(PLA) linkage with an H···O distance of 1.86 Å and an angle of 168.4°, and a PEG O–H···O(PCL) linkage of 2.01 Å and 160.7°. PEG ether–Na and PLA carbonyl–Na distances are 2.36 and 2.51 Å. Carbonyl bond lengths change from 1.211 to

1.218 Å for PLA and from 1.213 to 1.219 Å for PCL. The electronic-energy framework includes extended dispersive contacts:

$$
\begin{aligned}
E_X[n,\mathbf{R}] = \quad & -\frac{1}{2}\sum_i f_i \int \psi_i^*(\mathbf{r})\nabla^2\psi_i(\mathbf{r})\, d\mathbf{r} \\
& -\sum_a Z_a \int \frac{n(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_a|}\, d\mathbf{r} + \frac{1}{2}\iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \\
& +E_{\mathrm{xc}}[n] + \sum_{a<b}\frac{Z_a Z_b}{R_{ab}} \\
& -\sum_{a<b}\sum_{p\in\{6,8\}} \frac{s_p C_p^{ab}}{R_{ab}^p} f_{\mathrm{damp}}^{(p)}(R_{ab}) + E_{\mathrm{disp}}^{(3)}, \\
n(\mathbf{r}) = \quad & \sum_i f_i\, |\psi_i(\mathbf{r})|^2, \qquad E_X^{\mathrm{opt}} = \min_{\mathbf{R}} \min_{n\to N} E_X[n,\mathbf{R}].
\end{aligned}
\tag{2}
$$

Dispersion treatment and basis-error control follow the considerations discussed by (Bursch et al., 2022; Grimme et al., 2021). The numerical energies below use isolated-fragment reference zeros and the counterpoise/deformation conventions

$$
\begin{aligned}
\Delta E_{\mathrm{int}}^{\mathrm{CP}}(ABCZ) = \quad & E_{ABCZ}^{\mathcal{B}_{ABCZ}}(\mathbf{R}_{ABCZ}^*) \\
& -E_A^{\mathcal{B}_{ABCZ}}(\mathbf{R}_A^*; \text{ghost } B,C,Z) - E_B^{\mathcal{B}_{ABCZ}}(\mathbf{R}_B^*; \text{ghost } A,C,Z) \\
& -E_C^{\mathcal{B}_{ABCZ}}(\mathbf{R}_C^*; \text{ghost } A,B,Z) - E_Z^{\mathcal{B}_{ABCZ}}(\mathbf{R}_Z^*; \text{ghost } A,B,C), \\
\Delta E_{\mathrm{int}}^{\mathrm{CP}}(ABCZ) \quad & < 0 \quad \Rightarrow \quad \text{attraction relative to the specified frozen fragments.}
\end{aligned}
\tag{3}
$$

$$
\begin{aligned}
\Delta E_{\mathrm{def}} = \quad & \left[E_A^{\mathcal{B}_A}(\mathbf{R}_A^*) - E_A^{\mathcal{B}_A}(\mathbf{R}_A^0)\right] + \left[E_B^{\mathcal{B}_B}(\mathbf{R}_B^*) - E_B^{\mathcal{B}_B}(\mathbf{R}_B^0)\right] \\
& +\left[E_C^{\mathcal{B}_C}(\mathbf{R}_C^*) - E_C^{\mathcal{B}_C}(\mathbf{R}_C^0)\right] + \left[E_Z^{\mathcal{B}_Z}(\mathbf{R}_Z^*) - E_Z^{\mathcal{B}_Z}(\mathbf{R}_Z^0)\right], \\
\Delta E_{\mathrm{bind}}^{\mathrm{CP}} = \quad & \Delta E_{\mathrm{int}}^{\mathrm{CP}} + \Delta E_{\mathrm{def}}.
\end{aligned}
\tag{4}
$$

Here, $\mathbf{R}^*$ denotes the assembled geometry and $\mathbf{R}^0$ the isolated reference. The assigned four-component interaction energy is -2.491 eV; deformation costs of 0.047, 0.031, 0.060 and 0.013 eV for A, B, C and Z sum to 0.151 eV, giving a binding energy of -2.340 eV. In this assigned set, PEG carries the largest deformation cost, while the overall attraction remains favourable. Surface-dependent PLA association has also been examined by Li, (2021), whose attapulgite results provide a mechanistic comparison rather than transferable zeolite energies.

That study combined reactive molecular dynamics with dispersion-corrected DFT, demonstrating that polyester–silicate association can be resolved at the DFT level. The present assigned contacts likewise place PLA carbonyl and silicate hydroxyl groups at the interface; however, because the present energies are not computed, this correspondence is structural and qualitative rather than quantitative.

Table 1. Assigned illustrative energetic values within the numerical model (not computed)**.** Energies are author-assigned illustrative values (not computed), expressed in eV per assembly relative to its isolated constituents.

Assembly	Interaction energy	Deformation energy	Binding energy
PLA/PCL, AB	-0.168	0.052	-0.116
PLA/PCL/PEG, ABC	-0.634	0.102	-0.532
PLA/PCL/zeolite, ABZ	-1.207	0.080	-1.127
PLA/PCL/PEG/zeolite, ABCZ	-2.491	0.151	-2.340

Nonadditivity and PEG–zeolite coupling are separated through

$$\begin{aligned} \Delta E^{(4)}_{ABCZ} = \; & E_{ABCZ} - (E_{ABC} + E_{ABZ} + E_{ACZ} + E_{BCZ}) \\ & + (E_{AB} + E_{AC} + E_{AZ} + E_{BC} + E_{BZ} + E_{CZ}) \\ & - (E_A + E_B + E_C + E_Z), \end{aligned} \tag{5}$$

$$\Delta E_S^{\mathrm{int}} = \sum_{i<j} \Delta E^{(2)}_{ij} + \sum_{i<j<k} \Delta E^{(3)}_{ijk} + \Delta E^{(4)}_{ABCZ}, \qquad i,j,k \in \{A,B,C,Z\}.$$

$$\begin{aligned} \Delta E^{\mathrm{coupling}}_{CZ|AB} = \; & [E_{ABCZ} - E_{ABZ} - E_C] - [E_{ABC} - E_{AB} - E_C] \\ = \; & E_{ABCZ} - E_{ABZ} - E_{ABC} + E_{AB}. \end{aligned} \tag{6}$$

The six pair contributions sum to -2.224 eV. The ABC, ABZ, ACZ and BCZ three-body terms are -0.026, -0.051, -0.087 and -0.071 eV, giving -0.235 eV in total. The strictly four-body term is -0.032 eV. PEG association changes from -0.466 eV in AB to -1.284 eV in ABZ, yielding a coupling term of -0.818 eV. Within the assigned inputs, stabilization therefore derives mainly from pair contacts and lower-order coupling; the small four-body term is not sufficient to support a broad claim of four-component synergy. All subset terms refer to one frozen geometry and common basis. Because these magnitudes were selected rather than computed, this ordering remains a hypothesis. Bursch et al., (2022) emphasize that interaction energies depend on the dispersion treatment, basis-set superposition and conformational choice; the hierarchy must therefore be re-evaluated from counterpoise-corrected DFT energies.

Electrostatic complementarity and charge redistribution

Electrostatic complementarity concentrates around the ether, carbonyl and charge-compensation sites. Potential extrema and association-induced redistribution are defined by

$$\begin{aligned} V^S_{\mathrm{ESP}}(\mathbf{r}) = \; & \sum_{a\in A} \frac{Z_a}{|\mathbf{r} - \mathbf{R}_a|} + \sum_{b\in B} \frac{Z_b}{|\mathbf{r} - \mathbf{R}_b|} + \sum_{c\in C} \frac{Z_c}{|\mathbf{r} - \mathbf{R}_c|} \\ & + \sum_{z\in Z} \frac{Z_z}{|\mathbf{r} - \mathbf{R}_z|} - \int \frac{n_S(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}', \\ V_{\min} = \; & \min_{\mathbf{r}\in S_{n_0}} V^S_{\mathrm{ESP}}(\mathbf{r}), \qquad V_{\max} = \max_{\mathbf{r}\in S_{n_0}} V^S_{\mathrm{ESP}}(\mathbf{r}). \end{aligned} \tag{7}$$

$$\begin{aligned} \Delta n_S(\mathbf{r}) = \; & n_{ABCZ}(\mathbf{r};\mathbf{R}_S^*) - n_A(\mathbf{r};\mathbf{R}_A^*) - n_B(\mathbf{r};\mathbf{R}_B^*) \\ & - n_C(\mathbf{r};\mathbf{R}_C^*) - n_Z(\mathbf{r};\mathbf{R}_Z^*), \\ \int \Delta n_S(\mathbf{r})\, d\mathbf{r} \; & = 0, \\ \Delta N_F \; & = \int w_F(\mathbf{r}) \Delta n_S(\mathbf{r})\, d\mathbf{r}, \qquad \Delta q_F = -e\Delta N_F, \qquad \sum_F \Delta\, q_F = 0. \end{aligned} \tag{8}$$

On a common 0.001 e a_0^{-3} density surface, the minimum/maximum potential pairs are -0.056/+0.068 a.u. for AB, -0.066/+0.073 a.u. for ABC, -0.081/+0.127 a.u. for ABZ and -0.094/+0.133 a.u. for S. In S, the minimum is assigned to a PEG ether oxygen facing Na^+ and the maximum to the exposed cation region. A common -0.100 to +0.140 a.u. scale preserves comparability.

The fragment charge changes are +0.014 e for PLA, +0.010 e for PCL, +0.029 e for PEG and -0.053 e for Z, summing to zero. In the assigned charge set, electron accumulation is placed towards the zeolite coordination environment, with depletion on the contacting polymer oxygen regions. The small net transfer is consistent with a polarization-dominated interpretation, which requires confirmation from computed Hirshfeld charges.

These local potential and charge descriptors do not represent the aqueous zeta potential of a membrane. G. Lu et al., (2025) used electrostatic potentials and charge-density differences to rationalize PEG-mediated interactions in PCL-based membranes; the present framework adopts the same descriptor types, but its assigned values cannot be compared numerically with those computed results.

Hydrogen bonding and interfacial density topology

The contact assignments are resolved with density-gradient and Hirshfeld-partitioned interfragment descriptors:

$$\begin{aligned} s(\mathbf{r}) = \; & \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla n(\mathbf{r})|}{n(\mathbf{r})^{4/3}} \\ = \; & \frac{\left[(\partial_x n)^2 + \left(\partial_y n\right)^2 + (\partial_z n)^2\right]^{1/2}}{2(3\pi^2)^{1/3} n(\mathbf{r})^{4/3}}, \\ \mathcal{H}_n \mathbf{v}_i \; & = \lambda_i \mathbf{v}_i, \qquad \lambda_1 \le \lambda_2 \le \lambda_3, \\ \xi(\mathbf{r}) \; & = \mathrm{sign}[\lambda_2(\mathbf{r})] n(\mathbf{r}). \end{aligned} \tag{9}$$

$$\begin{aligned} w_a(\mathbf{r}) \; & = \frac{n_a^0(\mathbf{r})}{\sum_b n_b^0(\mathbf{r})}, \qquad n_a^{\mathrm{H}}(\mathbf{r}) = w_a(\mathbf{r}) n_S(\mathbf{r}), \\ \delta g^{\mathrm{inter}}(\mathbf{r}) \; & = \sum_{F \in \{A,B,C,Z\}} \left| \nabla \sum_{a \in F} n_a^{\mathrm{H}}(\mathbf{r}) \right| \\ & \quad - \left| \nabla \sum_{F \in \{A,B,C,Z\}} \sum_{a \in F} n_a^{\mathrm{H}}(\mathbf{r}) \right|. \end{aligned} \tag{10}$$

At an RDG isovalue of 0.5 and an IGMH gradient-difference isovalue of 0.005 a.u., the assigned attractive regions centre on zeolite OH–PLA, PEG OH–PCL and PEG–Na contacts. Their signed-density values are -0.024, -0.018 and -0.031 a.u., respectively. The IGMH

formalism follows T. Lu & Chen, (2022). Local energy-density and donor–acceptor relationships are:

$$\begin{aligned} \nabla n(\mathbf{r}_b) &= \mathbf{0}, \qquad \lambda_1(\mathbf{r}_b) < 0, \quad \lambda_2(\mathbf{r}_b) < 0, \quad \lambda_3(\mathbf{r}_b) > 0, \\ \nabla^2 n(\mathbf{r}_b) &= \lambda_1 + \lambda_2 + \lambda_3, \\ H(\mathbf{r}_b) &= G(\mathbf{r}_b) + V(\mathbf{r}_b), \\ 2G(\mathbf{r}_b) + V(\mathbf{r}_b) &= 1/4\,\nabla^2 n(\mathbf{r}_b). \end{aligned} \tag{11}$$

$$\begin{aligned} E^{(2)}_{i\to j} &= n_i \frac{\left|F_{ij}\right|^2}{\varepsilon_j - \varepsilon_i}, \qquad \varepsilon_j > \varepsilon_i, \\ E^{(2)}_{\text{donor}\to\text{acceptor}} &= \sum_{i\in \mathrm{LP}(O_{\text{polymer}})} \sum_{j\in\sigma^*(O-H)} n_i \frac{\left|F_{ij}\right|^2}{\varepsilon_j - \varepsilon_i} \\ &\quad + \sum_{i\in\text{other declared donors}} \sum_{j\in\text{declared acceptors}} n_i \frac{\left|F_{ij}\right|^2}{\varepsilon_j - \varepsilon_i}. \end{aligned} \tag{12}$$

For the zeolite OH–PLA contact, $n = 0.024$, $\nabla^2 n = 0.079$, $G = 0.02150$, $V = -0.02325$ and $H = -0.00175$ a.u. The PEG OH–PCL contact has $n = 0.018$, $\nabla^2 n = 0.061$ and $H = -0.00155$ a.u.; PEG–Na has $n = 0.031$, $\nabla^2 n = 0.118$ and $H = -0.00470$ a.u. Each assigned set satisfies the local virial relationship algebraically. By construction of the assigned values, positive Laplacians and small negative total energy densities are consistent with polar, largely closed-shell contacts with limited orbital mixing.

The assigned donor–acceptor parameterization gives stabilization magnitudes of 9.8 kJ mol⁻¹ for PLA oxygen–OH antibonding, 6.2 kJ mol⁻¹ for PCL oxygen–OH antibonding and 15.4 kJ mol⁻¹ for PEG oxygen–Na-centred acceptance. These terms describe the contact mechanism and are not added to the total binding energy. The wavefunction-analysis methods described by T. Lu, (2024) provide the corresponding analysis framework.

Frontier electronic structure and local response

The frontier gap and vertical electron-number response remain distinct descriptors:

$$\begin{aligned} E_g^{\mathrm{KS}} &= \varepsilon_{\mathrm{LUMO}} - \varepsilon_{\mathrm{HOMO}}, \\ I_v &= E_{N-1}(\mathbf{R}_N) - E_N(\mathbf{R}_N), \\ A_v &= E_N(\mathbf{R}_N) - E_{N+1}(\mathbf{R}_N), \\ E_g^{\mathrm{fund},v} &= I_v - A_v = E_{N-1}(\mathbf{R}_N) + E_{N+1}(\mathbf{R}_N) - 2E_N(\mathbf{R}_N). \end{aligned} \tag{13}$$

$$\begin{aligned} \mu &= -\frac{I_v + A_v}{2}, \qquad \chi = \frac{I_v + A_v}{2}, \\ \eta &= \frac{I_v - A_v}{2}, \qquad S_{\mathrm{soft}} = \frac{1}{2\eta} = \frac{1}{I_v - A_v}, \\ \omega &= \frac{\mu^2}{2\eta} = \frac{(I_v + A_v)^2}{4(I_v - A_v)}. \end{aligned} \tag{14}$$

$$\begin{aligned} f^+(\mathbf{r}) &= n_{N+1}(\mathbf{r};\mathbf{R}_N) - n_N(\mathbf{r};\mathbf{R}_N), \\ f^-(\mathbf{r}) &= n_N(\mathbf{r};\mathbf{R}_N) - n_{N-1}(\mathbf{r};\mathbf{R}_N), \\ \Delta f(\mathbf{r}) &= f^+(\mathbf{r}) - f^-(\mathbf{r}) = n_{N+1}(\mathbf{r}) - 2n_N(\mathbf{r}) + n_{N-1}(\mathbf{r}), \\ \int f^+ d\mathbf{r} &= \int f^- d\mathbf{r} = 1, \qquad \int \Delta f\, d\mathbf{r} = 0. \end{aligned} \tag{15}$$

The assigned HOMO/LUMO energies change from -6.88/-0.47 eV in AB to -6.51/-0.54 eV in ABC, -6.34/-1.01 eV in ABZ and -6.12/-1.14 eV in S. Their orbital gaps are 6.41, 5.97, 5.33 and 4.98 eV. The S model assigns 54% of the HOMO weight to PEG and 63% of the LUMO weight to Z, which would place the response near the organic–inorganic interface.

For S, $I_v = 7.21$ eV and $A_v = 1.05$ eV give a vertical fundamental gap of 6.16 eV, $\mu = -4.13$ eV, $\eta = 3.08$ eV, $S_{\mathrm{soft}} = 0.1623$ eV^{-1} and $\omega = 2.769$ eV. Fragment electron-addition responses are 0.09, 0.06, 0.29 and 0.56 for A, B, C and Z; removal responses are 0.24, 0.18, 0.50 and 0.08. Each distribution integrates to one. The assigned Z dual descriptor is +0.48; if reproduced by calculation, this value would identify an enhanced electron-acceptance response in that fragment. These finite-model changes are not periodic membrane band gaps or independent measures of filtration performance.

Water binding and hydration cooperativity

Water binding distinguishes polar-site accessibility from competition for compensation sites. Average, incremental and three-body contributions are

$$\begin{aligned} \overline{\Delta E}_{\mathrm{ads}}(m) &= \frac{E^{\mathrm{opt}}_{SW_m} - E^{\mathrm{opt}}_{S} - mE^{\mathrm{opt}}_{W}}{m}, \\ \Delta E^{\mathrm{inc}}_{\mathrm{ads}}(m) &= E^{\mathrm{opt}}_{SW_m} - E^{\mathrm{opt}}_{SW_{m-1}} - E^{\mathrm{opt}}_{W}, \\ E^{\mathrm{opt}}_{SW_m} - E^{\mathrm{opt}}_{S} - mE^{\mathrm{opt}}_{W} &= \sum_{j=1}^{m} \Delta\, E^{\mathrm{inc}}_{\mathrm{ads}}(j). \end{aligned} \tag{16}$$

$$\begin{aligned} \Delta E^{(3)}_{MCW} &= E_{MCW} - E_{MC} - E_{MW} - E_{CW} + E_M + E_C + E_W, \\ \Delta E^{\mathrm{int}}_{MCW} &= \Delta E^{(2)}_{MC} + \Delta E^{(2)}_{MW} + \Delta E^{(2)}_{CW} + \Delta E^{(3)}_{MCW}. \end{aligned} \tag{17}$$

Assigned one-water association energies are -0.342 eV for AB, -0.705 eV for ABC, -0.628 eV for ABZ and -0.812 eV for S. PEG strengthens overall water association, but its three-body contribution changes from -0.082 eV without Z to +0.097 eV in the zeolite-containing environment. Within the assigned set, the latter represents coordination competition: the -0.281 eV PEG–water pair contribution is partly offset rather than cooperatively amplified. The hydrated contact geometry places water at a PEG/zeolite bridge, with an H···O(PEG) distance of 1.83 Å and an angle of 172.0°.

For S with one to four waters, incremental energies are -0.812, -0.701, -0.592 and -0.523 eV; cumulative energies are -0.812, -1.513, -2.105 and -2.628 eV. Mean energies per water consequently weaken from -0.812 to -0.757, -0.702 and -0.657 eV as the strongest sites become occupied. For context only, G. Lu et al., (2025) reported computed values of -0.386 and -0.665 eV for their PCL/H_2O and PCL/PEG/H_2O models. Because the present values are assigned and not computed, no numerical agreement is claimed; the only shared feature is the qualitative trend that PEG addition strengthens water association, which the proposed calculations would test. Thermochemical association and defined-pocket populations follow

$$
\begin{aligned}
\Delta G^{\circ}_{\mathrm{assoc}}(T) = \quad & \Delta E^{\mathrm{CP}}_{\mathrm{elec}} + \frac{1}{2}\left[\sum_{\ell\in SW_m}\hbar\,\omega_\ell - \sum_{\ell\in S}\hbar\,\omega_\ell - m\sum_{\ell\in W}\hbar\,\omega_\ell\right] \\
& + \left[\sum_{\ell\in SW_m}\frac{\hbar\omega_\ell}{\exp(\hbar\omega_\ell/k_BT)-1} - \sum_{\ell\in S}\frac{\hbar\omega_\ell}{\exp(\hbar\omega_\ell/k_BT)-1}\right. \\
& \left. - m\sum_{\ell\in W}\frac{\hbar\omega_\ell}{\exp(\hbar\omega_\ell/k_BT)-1}\right] \\
& + \Delta U_{\mathrm{trans}} + \Delta U_{\mathrm{rot}} + \Delta(pV) - T\Delta S_{\mathrm{consistent}} \\
& + [\Delta G_{\mathrm{solv}}(SW_m) - \Delta G_{\mathrm{solv}}(S) - m\Delta G_{\mathrm{solv}}(W)] + \Delta G_{\mathrm{standard\ state}},
\end{aligned}
\tag{18}
$$

$$
\Delta G_{\mathrm{standard\ state}} = \Delta\nu\, k_B T \ln\left(\frac{c^{\circ}RT}{p^{\circ}}\right), \qquad \Delta\nu = -m.
$$

$$
\begin{aligned}
P_{m,k}(T,\mu_W) &= \frac{\exp\{-\beta\left[G_{m,k}(T) - m\mu_W\right]\}}{\sum_{m'=0}^{m_{\max}}\sum_{k'}\exp\{-\beta\left[G_{m',k'}(T) - m'\mu_W\right]\}}, \\
\langle m\rangle &= \sum_{m=0}^{m_{\max}}\sum_{k} m\,P_{m,k}, \qquad \beta = (k_BT)^{-1}.
\end{aligned}
\tag{19}
$$

At 298.15 K, the one-water free-energy balance combines -0.812 eV electronic association, +0.083 eV zero-point correction, +0.028 eV vibrational thermal correction, -0.014 eV translation/rotation/pV contribution, +0.386 eV entropy penalty and +0.152 eV differential solvation. Conversion from 1 bar to 1 mol L^{-1} contributes -0.0825 eV, giving $\Delta G^{\circ}_{\mathrm{assoc}} = -0.2595$ eV. Within these assigned components, association therefore remains favourable after the thermochemical penalties. Whether this holds after computed SMD and quasi-harmonic corrections must be established through the validation protocol, given the importance of these corrections for association free energies emphasized by (Bursch et al., 2022).

For pocket states containing zero to four waters, relative standard free energies are 0, -0.2595, -0.486, -0.667 and -0.806 eV. At a water chemical-potential offset of -0.200 eV from that same standard reference, populations are 1.84%, 18.62%, 52.27%, 24.95% and 2.32%, with a mean occupancy of 2.073. These are probabilities of the specified finite state set, not a bulk adsorption isotherm. Zeolite coverage and composition effects discussed by Fischer, (2023); Randrianandraina et al., (2023) support distinguishing site accessibility from unconditional hydration cooperativity.

The former study showed that water coverage regulates access to Na^+ sites in Na-LTA, and the latter found that protonation increased water affinity more strongly than triclosan binding in high-silica zeolites. A combined diffraction, infrared and DFT study of a lithium-exchanged zeotype likewise linked cation accessibility to the arrangement of confined water and protonated water clusters (Danisi & Fischer, 2023). The positive zeolite-containing three-body hydration term assigned here represents the same class of site competition at a polymer–zeolite interface; it is therefore a physically plausible hypothesis, although its sign and magnitude remain to be determined computationally.

Vibrational signatures and finite-field polarization

Vibrational assignments connect local coordination to changes in restoring forces:

$$\begin{aligned} \mathcal{H}^{\mathrm{mw}}_{a\alpha,b\beta} &= \frac{1}{\sqrt{m_a m_b}} \frac{\partial^2 E}{\partial R_{a\alpha}\,\partial R_{b\beta}}\bigg|_{\mathbf{R}^*}, \\ \sum_{b,\beta} \mathcal{H}^{\mathrm{mw}}_{a\alpha,b\beta} L_{b\beta,\ell} &= \omega_\ell^2 L_{a\alpha,\ell}, \qquad \tilde{\nu}_\ell = \frac{\omega_\ell}{2\pi c}, \\ A^{\mathrm{IR}}_\ell &= C_{\mathrm{IR}} \sum_{\gamma\in\{x,y,z\}} \left|\frac{\partial \mu_\gamma}{\partial Q_\ell}\right|^2 . \end{aligned} \tag{20}$$

$$\begin{aligned} \mathcal{I}(\tilde{\nu}) &= \sum_{k=1}^{K} p_k \sum_{\ell=1}^{N_{\mathrm{modes},k}} A^{\mathrm{IR}}_{k\ell} \frac{\gamma/\pi}{(\tilde{\nu}-s_\nu \tilde{\nu}_{k\ell})^2+\gamma^2}, \\ \Delta\tilde{\nu}_\ell &= s_\nu\left(\tilde{\nu}_{\ell,\mathrm{associated}} - \tilde{\nu}_{\ell,\mathrm{reference}}\right). \end{aligned} \tag{21}$$

With a common frequency scale factor of 0.965 and Lorentzian half-width of 8 cm⁻¹, PLA carbonyl shifts from 1776 to 1763 cm⁻¹, PCL carbonyl from 1743 to 1731 cm⁻¹, PEG ether from 1102 to 1089 cm⁻¹ and the PEG terminal hydroxyl mode from 3640 to 3511 cm⁻¹. The respective shifts of -13, -12, -13 and -129 cm⁻¹ are assigned to illustrate how carbonyl/ether coordination and hydrogen bonding would be connected to local softening. Broadening remains a plotting parameter, and no simulated spectrum is shown because no Hessian was computed. The clamped-nuclei field response is represented by:

$$\begin{aligned} E_X(\mathcal{F}) = \;& E_X(\mathbf{0}) - \sum_i \mu_i^X \mathcal{F}_i - \frac{1}{2}\sum_{i,j} \alpha_{ij}^X \mathcal{F}_i\mathcal{F}_j \\ & - \frac{1}{6}\sum_{i,j,k} \beta_{ijk}^X \mathcal{F}_i\mathcal{F}_j\mathcal{F}_k + \mathcal{O}(|\mathcal{F}|^4), \\ \mu_i^X &= -\frac{\partial E_X}{\partial \mathcal{F}_i}\bigg|_{\mathbf{0}}, \qquad \alpha_{ij}^X = -\frac{\partial^2 E_X}{\partial \mathcal{F}_i\,\partial \mathcal{F}_j}\bigg|_{\mathbf{0}}. \end{aligned} \tag{22}$$

$$\begin{aligned} \Delta E_{\mathrm{int}}(\mathcal{F}) = \;& \Delta E_{\mathrm{int}}(\mathbf{0}) - \sum_i \left[\mu_i^S - \sum_{F\in\{A,B,C,Z\}} \mu_i^F\right]\mathcal{F}_i \\ & - \frac{1}{2}\sum_{i,j}\left[\alpha_{ij}^S - \sum_F \alpha_{ij}^F\right]\mathcal{F}_i\mathcal{F}_j \\ & - \frac{1}{6}\sum_{i,j,k}\left[\beta_{ijk}^S - \sum_F \beta_{ijk}^F\right]\mathcal{F}_i\mathcal{F}_j\mathcal{F}_k + \mathcal{O}(|\mathcal{F}|^4). \end{aligned} \tag{23}$$

$$\begin{aligned} \mu_i &\approx -\frac{E(+\delta\mathcal{F}_i) - E(-\delta\mathcal{F}_i)}{2\delta\mathcal{F}_i}, \\ \alpha_{ii} &\approx -\frac{E(+\delta\mathcal{F}_i) - 2E(\mathbf{0}) + E(-\delta\mathcal{F}_i)}{(\delta\mathcal{F}_i)^2}, \\ \alpha_{ij} &\approx -\frac{E\left(+\delta\mathcal{F}_i,+\delta\mathcal{F}_j\right) - E\left(+\delta\mathcal{F}_i,-\delta\mathcal{F}_j\right)}{4\delta\mathcal{F}_i\delta\mathcal{F}_j} \\ & \quad -\frac{-E\left(-\delta\mathcal{F}_i,+\delta\mathcal{F}_j\right) + E\left(-\delta\mathcal{F}_i,-\delta\mathcal{F}_j\right)}{4\delta\mathcal{F}_i\delta\mathcal{F}_j}, \qquad i\neq j. \end{aligned} \tag{24}$$

The assigned zero-field z-dipole of S is 11.360 D, compared with a signed fragment sum of 8.790 D. Its diagonal polarizability components are 502.8, 557.1 and 635.2 a_0^3, giving an isotropic mean of 565.0 a_0^3. The assembly–fragment difference in α_{zz} is 48.5 a_0^3; the corresponding β_{zzz} difference is 1200 a.u.

For $\mathcal{F} = (0{,}0{,}+2\times10^{-4})$ a.u., the interaction energy changes from -2.491000 to -2.496529 eV and the z-dipole to 11.683 D. Reversing the field gives -2.485524 eV and 11.037 D. Within the assigned expansion, the response is directional and modest, approximately 5.5 meV in either direction. Finite-difference steps of 10^{-4} and 2×10^{-4} a.u. recover $\alpha_{zz} = 635.2$ a_0^3 and dipoles within 0.00004 D of the defined zero-field value. This electronic response does not imply permanent chain alignment after removing the field.

Conformer dependence and molecular interpretation

The stability ordering is considered across conformers and local-model variations:

$$\begin{aligned} \Delta G_k &= G_k - G_{\min}, \\ p_k(T) &= \frac{g_k \exp[-\Delta G_k/(k_B T)]}{\sum_{j=1}^{K} g_j \exp\left[-\Delta G_j/(k_B T)\right]}, \\ \langle O \rangle_T &= \sum_{k=1}^{K} p_k\,(T) O_k, \\ \sigma^2_{O,\mathrm{conf}} &= \sum_{k=1}^{K} p_k\,(T)[O_k - \langle O \rangle_T]^2. \end{aligned} \tag{25}$$

$$\begin{aligned} \delta O_{\mathrm{chain}} &= O(n_A + \Delta n_A, n_B + \Delta n_B, n_C + \Delta n_C) - O(n_A, n_B, n_C), \\ \delta O_{\mathrm{surface}} &= O\left(Z_{\mathrm{expanded}}\right) - O(Z_{\mathrm{reference}}), \\ \delta O_{\mathrm{basis}} &= O\left(\mathcal{B}_{\mathrm{larger}}\right) - O(\mathcal{B}_{\mathrm{reference}}), \\ \delta O_{\mathrm{functional}} &= O(\mathrm{DFT}_2) - O(\mathrm{DFT}_1). \end{aligned} \tag{26}$$

Six conformers with unit degeneracy are assigned relative free energies of 0, 0.022, 0.039, 0.071, 0.097 and 0.146 eV at 298.15 K. Their populations are 57.69%, 24.51%, 12.64%, 3.64%, 1.32% and 0.20%. The population-weighted binding energy is -2.326 eV with a conformer spread of 0.021 eV. This spread describes the selected model set rather than experimental uncertainty. In the assigned sensitivity scenarios, extending the same local contact motif from trimers to pentamers and heptamers changes binding from -2.340 to -2.366 and -2.378 eV.

Expanded-surface, larger-basis and alternative electronic parameterizations give -2.358, -2.355 and -2.312 eV. The largest listed sensitivity is 0.038 eV, exceeding the 0.032 eV four-body contribution but far smaller than the 0.818 eV PEG–zeolite coupling. Within this illustrative set, the principal interpretation therefore rests on interfacial association and lower-order coupling, while the strict four-body contribution remains comparatively weak. Water affinity benefits from PEG, although zeolite coordination introduces a competing nonadditive hydration term.

Comparison with previous studies and implications

Comparison with earlier work must take the nature of the present data into account. The DFT studies cited here derived their energies from computed structures, whereas the present values are assigned; the comparison is therefore restricted to methodological choices and qualitative trends. Li, (2021) demonstrated that polyester silicate association can be resolved with dispersion-corrected DFT, and G. Lu et al., (2025) combined binding energies with electrostatic potentials, charge-density differences and reduced density gradients for PEG-containing PCL membranes. The present framework extends these approaches by separating interaction and deformation energies, resolving pair, three-body and four-body terms on one frozen geometry, and adding hydration thermochemistry and finite-field response. This decomposition addresses a limitation of total binding energies, which cannot by themselves distinguish cooperative many-body stabilization from accumulated pair contacts.

With respect to qualitative trends, the assigned dataset follows the direction reported by G. Lu et al., (2025), namely stronger water association in the presence of PEG, but it adds a feature that a polymer-only model cannot address: a positive three-body hydration term once

the zeolite is included. This feature is consistent with the site-competition behaviour reported for hydrated Na-LTA by Randrianandraina et al., (2023)and for protonated high-silica zeolites by Fischer, (2023), in which water occupancy or affinity modulates access to adsorption sites. The methodological choices of the protocol, namely r²SCAN-3c geometries, a dispersion-corrected hybrid single-point level, counterpoise correction and conformer averaging, follow Bursch et al., (2022); Grimme et al., (2021), whereas the density-topology analysis follows (T. Lu, 2024; T. Lu & Chen, 2022).

The practical implication of the framework is a set of testable design criteria for PLA/PCL/PEG/nanozeolite membranes: PEG should enhance polymer–zeolite association through lower-order coupling, accessible ether and carbonyl oxygens should be preserved for water binding, and competition for cationic compensation sites should be limited. The principal limitation is that none of these relationships has yet been computed. In addition, the fragment model does not represent periodic zeolite topology, polymer chain-length distributions, bulk membrane morphology or transport properties. A periodic formulation of the many-body expansion, such as that developed for ice phases by Herman & Xantheas, (2023), offers one route to extending the decomposition to extended zeolite frameworks. Future work should therefore execute the proposed protocol, report coordinates and input files, and compare computed hydration and vibrational signatures with experimental sorption and infrared data for the corresponding membranes.

CONCLUSION

This study aimed to establish a DFT protocol for resolving interfacial association, hydration and electronic polarization in PLA/PCL/PEG/nanozeolite membrane models within one consistent energetic reference. This objective was addressed by defining counterpoise-corrected many-body decomposition, density-topology, frontier-response, hydration-thermochemistry, vibrational and finite-field descriptors, and by demonstrating their combined workflow with author-assigned illustrative values that were not computed. Within this illustration, PEG-mediated pair and lower-order coupling, rather than the weak four-body term, governs association, whereas a positive zeolite-containing three-body term represents competition for hydration sites. These relationships are therefore hypotheses rather than empirical findings. The framework implies a testable design criterion: preserving accessible oxygen sites while limiting polymer deformation and competition for cationic sites. Executing the proposed r²SCAN-3c and PBE0-D4 calculations is therefore required before the framework is applied to specific membrane compositions.

FUNDING

The authors declare that no external financial support or funding was received for the research, authorship, and publication of this article. The study was conducted independently without financial assistance from public, commercial, or nonprofit funding organizations.

CONFLICT OF INTEREST

The authors declare that there are no financial, commercial, professional, or personal relationships that could be perceived as potential conflicts of interest influencing the research, analysis, interpretation, or publication of this manuscript.

AUTHOR CONTRIBUTIONS

The study involved the conceptualization and development of a methodological framework for investigating interfacial association, hydration, and electronic polarization in PLA/PCL/PEG/nanozeolite membranes. The research activities included literature review, theoretical framework development, numerical illustration using Python/NumPy, methodological analysis, interpretation of illustrative results, and manuscript preparation. All authors contributed to the intellectual development of the study, critically reviewed the manuscript, and approved the final version for publication. All authors accept responsibility for the accuracy, integrity, and scientific content of the published work.

GENERATIVE AI STATEMENT

The authors acknowledge the use of generative artificial intelligence (AI) tools to assist in improving the linguistic clarity, grammatical accuracy, readability, and academic presentation of this manuscript. The use of generative AI was limited to language refinement and editorial assistance and did not replace the authors' intellectual contributions, methodological decisions, or scientific interpretation. The research framework, author-assigned illustrative numerical values, analytical procedures, and conclusions remain the responsibility of the authors. All AI-assisted content was reviewed and verified by the authors to ensure accuracy, transparency, and compliance with ethical standards for scholarly publication. The authors assume full responsibility for the integrity and final content of the manuscript.

REFERENCES

Bursch, M., Mewes, J., Hansen, A., & Grimme, S. (2022). Best-Practice DFT Protocols for Basic Molecular Computational Chemistry**. *Angewandte Chemie International Edition*, *61*(42). https://doi.org/10.1002/anie.202205735

Danisi, R. M., & Fischer, M. (2023). Accessibility of lithium cations in VSH-2 zeotype: Structural effects and formation of protonated water clusters. *European Journal of Inorganic Chemistry*, *26*(32), e202300343. https://doi.org/10.1002/ejic.202300343

Fischer, M. (2023). Density functional theory study of hydrophobic zeolites for the removal of triclosan from aqueous solution. *Environmental Science: Advances*, *2*(8), 1082–1098. https://doi.org/10.1039/D3VA00078H

Fischer, M., & Brauer, J. (2024). Studying the adsorption of emerging organic contaminants in zeolites with dispersion-corrected density functional theory calculations: From numbers to recommendations. *ChemistryOpen*, *13*(7), e202300273. https://doi.org/10.1002/open.202300273

Grimme, S., Hansen, A., Ehlert, S., & Mewes, J.-M. (2021). A “Swiss army knife” composite electronic-structure method. *The Journal of Chemical Physics*, *154*(6). https://doi.org/10.1063/5.0040021

Heindel, J. P., Herman, K. M., & Xantheas, S. S. (2023). Many-body effects in aqueous systems: Synergies between interaction analysis techniques and force field development. *Annual Review of Physical Chemistry*, *74*, 337–360. https://doi.org/10.1146/annurev-physchem-062422-023532

Herman, K. M., & Xantheas, S. S. (2023). A formulation of the many-body expansion (MBE) for periodic systems: Application to several ice phases. *The Journal of Physical Chemistry Letters*, *14*(4), 989–999. https://doi.org/10.1021/acs.jpclett.2c03822

Kayan, G. Ö., & Kayan, A. (2023). Polycaprolactone composites/blends and their applications

especially in water treatment. *ChemEngineering*, *7*(6), 104. https://doi.org/10.3390/chemengineering7060104

Li, L. (2021). Comprehensive investigations of interaction properties of polylactic Acid–Attapulgite composite by reactive molecular dynamics simulations and dispersion corrected DFT calculations. *Current Applied Physics*, *28*, 78–86. https://doi.org/10.1016/j.cap.2021.05.001

Lu, G., Shang, W., Ma, X., Xu, H., A, H., Sun, J., Li, X., Jia, M., Lu, S., Wu, J., Chen, X., Chen, S., Fan, J., & An, A. K. (2025). Supramolecular nanocrystalline membranes with well-aligned subnanochannels for enhanced reverse osmosis desalination. *Nature Communications*, *16*(1), 6289. https://doi.org/10.1038/s41467-025-61352-6

Lu, T. (2024). A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn. *The Journal of Chemical Physics*, *161*(8). https://doi.org/10.1063/5.0216272

Lu, T., & Chen, Q. (2022). Independent gradient model based on Hirshfeld partition: A new method for visual study of interactions in chemical systems. *Journal of Computational Chemistry*, *43*(8), 539–555. https://doi.org/10.1002/jcc.26812

Neese, F. (2022). Software update: The ORCA program system—Version 5.0. *WIREs Computational Molecular Science*, *12*(5). https://doi.org/10.1002/wcms.1606

Neese, F. (2025). Software update: The ORCA program system—Version 6.0. *WIREs Computational Molecular Science*, *15*(2), e70019. https://doi.org/10.1002/wcms.70019

Ochieng, S. A., & Patkowski, K. (2023). Accurate three-body noncovalent interactions: The insights from energy decomposition. *Physical Chemistry Chemical Physics*, *25*(42), 28621–28637. https://doi.org/10.1039/D3CP03938B

Pérez-Botella, E., Valencia, S., & Rey, F. (2022). Zeolites in adsorption processes: State of the art and future prospects. *Chemical Reviews*, *122*(24), 17647–17695. https://doi.org/10.1021/acs.chemrev.2c00140

Pracht, P., Grimme, S., Bannwarth, C., Bohle, F., Ehlert, S., Feldmann, G., Gorges, J., Müller, M., Neudecker, T., Plett, C., Spicher, S., Steinbach, P., Wesołowski, P. A., & Zeller, F. (2024). CREST—A program for the exploration of low-energy molecular chemical space. *The Journal of Chemical Physics*, *160*(11), 114110. https://doi.org/10.1063/5.0197592

Randrianandraina, J., Badawi, M., Ramseyer, C., Cardey, B., Groetz, J.-E., Perreau, N., Torrealba-Anzola, F., Chambelland, C., Ducret, D., & Grivet, M. (2023). Effect of the water coverage on the interaction of O 2 and H 2 with the Na-LTA zeolite by first-principles simulations. *Inorganic Chemistry Frontiers*, *10*(2), 383–395. https://doi.org/10.1039/D2QI01280D

Saeed, L., & Fischer, M. (2025). Computational insights into aluminum and cation placement in clinoptilolite: Optimizing DFT parameters for natural zeolites, Part I. *Applied Sciences*, *15*(7), 3955. https://doi.org/10.3390/app15073955

Sahu, A., Dosi, R., Kwiatkowski, C., Schmal, S., & Poler, J. C. (2023). Advanced polymeric nanocomposite membranes for water and wastewater treatment: A comprehensive review. *Polymers*, *15*(3), 540. https://doi.org/10.3390/polym15030540

Ta, A. T., Daouli, A., Ullberg, R. S., Fonseca, E., Proust, V., Grandjean, A., Hennig, R. G., zur Loye, H.-C., Badawi, M., & Phillpot, S. R. (2024). Incorporating solvent effects in DFT: Insights from cation exchange in faujasites. *Physical Chemistry Chemical Physics*, *26*(20), 14561–14572. https://doi.org/10.1039/D4CP00467A

Vatanpour, V., Dehqan, A., Paziresh, S., Zinadini, S., Zinatizadeh, A. A., & Koyuncu, I. (2022). Polylactic acid in the fabrication of separation membranes: A review. *Separation and Purification Technology*, *296*, 121433. https://doi.org/10.1016/j.seppur.2022.121433