Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Supplementary material

We present here the extended methodology for the DFT and Lanczos models and additional figures.

Figure S1 shows the values of the average values of the correlation parameter $r = \left\langle \Psi \middle| \Psi^*_{Lanczos} \right\rangle$ the wavefunction Ψ predicted by all four DFT orbitals with the Lanczos ground state (GS) for the five different configurations of bulk amorphous polyethylene cubes made with four rings of 20 carbon atoms. The DFT orbitals are the LUMO of the neutral *N* system with DFT using plane waves, and the LUMO of the neutral *N* system and the HOMO of the charged *N*+1 system using linear combination of atomic orbitals with (LCAOG) and without (LCAO) ghost atoms. This correlation parameter gives a quantitative estimation of how well the DFT wavefunctions correlate with Lanczos' that is taken as reference because yields negative excess energies that in good agreement with experimental data of alkanes.[1] Error bars indicate two standard deviations.

Figure S2 plots the exponential fits to the decay of the electron charge density taken from Lanczos and DFT in amorphous polyethylene/vacuum interfaces with a gap of 3.0 nm.

Figure S3 illustrates the averaged Hartree potential in the x-direction in neutral and charged systems to display the effects of the positive background potential in the latter that compensating the excess electron charge.

S.I. FULL METHODOLOGY

S.I.1. Preparation of polyethylene systems

To build the lamellar chains we first place four chains of 20 carbons ($-CH_2$) inside the central cell. Then, we bond two neighbouring chains with four $-CH_2-$ groups in the y-direction at each of the two chain endings. At the y axis periodic boundaries we also add two 4 $-CH_2-$ groups to create a semi-infinite lamella. The lateral dimensions of the systems are set to 0.986 and 0.74 nm in the y and z directions[2], respectively, with a length of 2.68 nm in the x direction. Surfaces are created by separating both (100) faces with a vacuum with thicknesses of 0.1, 0.5, 1.0, 1.5, 2.0, and 3.0 nm. Amorphous polyethylene slabs are built with four lamellar chains of 20 (or 40) carbons each with no terminal methyl groups. These slabs are prepared with Materials Studio using the COMPASS2[3] force field with no periodic boundaries in the x direction to avoid splitting the chains when the vacuum is imposed. The cubic simulation cell has with a side length of 1.29 nm and a density of 0.86 g/cm^3 to match the value used in Ref. 4 for amorphous low-density polyethylene.

S.I.2. DFT methods

The geometry of all systems is optimised with the ab-initio package CP2k[5] in its QUICKSTEP[6] implementation. These optimisations employ the local-density approximation

(LDA) exchange-correlation functional, GTH pseudopotentials[7,8], and double-ζ basis sets with polarisation functions (DZVP).[9] We use a threshold of $1x10^{-5}$ Ha, a cut-off of 500 Ry for the plane wave basis set, and the DRSLL non-local scheme[10] to include long-range forces. In principle, an extra electron might produce a change in the position of the nuclei, forming a polaron. However, polaron energies are -0.06 ± 0.03 eV in polyethylene with a lifetime on the time scale of a few tens of picoseconds.[11] As a first approximation, we can then assume that the distortion exerted by the excess electron on the nuclei can be neglected.

We have decided to optimise the geometries with CP2k because this task is much faster with this code than with Quantum Espresso or CRYSTAL14. When comparing CP2k with Quantum Espresso, the former is a hybrid pseudopotential code that expands the atomic orbitals with plane waves to solve the Poisson equation and with a linear combination of Gaussians to calculate the nuclear-electronic, correlation, and exchange interactions of the Schrodinger equation. This feature, called Quickstep in CP2k, is ideal for our systems with vacuum because their geometries are optimised much faster than with Quantum Espresso as we do not need to solve the Schrodinger equation more precisely in the vacuum at the expense of using a more expensive orbital expansion with full plane waves.

In the case of CRYSTAL14, relaxing the geometry is almost prohibitive as this code expands all atomic bands as a linear combination of Gaussian orbitals, which increases the computational cost exponentially even for a small number of atoms. Note that, as the name of this program suggests, this code is more suitable for crystalline systems where the users can exploit CRYSTAL14's symmetry operators, which drops the computational cost as they just need to compute the properties of interest in the primitive cell.

The optimised configurations are then used as input for the CRYSTAL14 code[12] to perform DFT calculations with periodic boundary conditions at the B3LYP[13] theory level. This exchange-correlation functional has given excellent estimates of band gaps[14] and optical gaps[15] of extended systems. A standard all-electron 6-31G**[16,17] basis set is used to represent the local atomic orbitals as primitive Gaussian functions. The polarisation functions of this basis set ensure that orbitals can distort from their original atomic symmetry to better adapt to the molecular surroundings, which leads to a more precise prediction of the total energy of systems with high hydrogen content. Reciprocal space integrations are restricted to the Γ-point of the Brillouin zone and a ground-state energy convergence is enforced at $1x10^{-6}$ Ha. Standard parameters for two-electron integral calculations are used. The calculations are made for systems with N and N+1 electrons using the same simulation cell parameters and nuclei configuration. For the N+1 electron systems a positive homogeneous charge background is added to avoid divergences in the total energy originating from the periodic boundary conditions.

We also make these calculations CRYSTAL14 on lamellar slabs to compare those made with the plane wave code Quantum Espresso[18] with ultrasoft pseudopotentials. The well-documented difficulty of converging wavefunctions for charged interfaces restricts our study to neutral systems[19]. The level of theory is local-density approximation supplemented with Becke88 for the exchange and Perdew86 for the correlation (LDA+BP). We use this level of theory, plane waves, and this specific geometry to compare our results with those published

by Righi et al. [20]. The kinetic energy cutoff for the wavefunctions is set at 200 Ry after several tests in which the total energy of the system varies less than 0.1 Ry. The kinetic energy cutoff for charge density and potential cutoff are set to 800 Ry. Calculations are restricted to the Gamma point. The self-consistency iteration is stopped when the variation between two consecutive cycles is less than 1.0 x 10^{-6} Ry.

S.I.3. Building of lattices with ghost atoms

We note that basis sets expanded with Gaussian type orbitals limit the space to be occupied by the electrons to a small region in the vicinity of the nuclear centres. This limitation represents a problem when studying interfaces of amorphous polyethylene and vacuum, where the negative electron affinity of the former repels an injected electron whose charge density extends into the gap space. Therefore, we build a lattice of ghost hydrogen atoms in the simulation domain for bulk and interfacial systems. This lattice is built replicating a simple cubic unit cell with a side length d_g, i.e. the distance between two ghosts, in the x, y, and z directions. This distance is obtained by slicing the domain's length in the y or z directions in a number of equal layers. For instance, in amorphous systems slabs made with four rings of 20 carbons, whose domain's side length is 1.294 nm, d_g is equal to 0.185 nm for seven layers and 0.162 nm for eight layers. Once this number of layers is set, we replicate the unit cells in the x-direction. For the bulk cubic systems, the number of replicas is the same in all three directions which makes the simulation domain uniformly occupied by ghost atoms. When vacuum gaps are imposed, the separation between the first and the last layers is sometimes slightly longer than d_g as the empty space, e.g. 0.1, 0.5, or 1.0 nm, is not a multiple of such distance. Furthermore, with or without vacuum the distance d_g is also taken as the cutoff radius to decide if a ghost is finally placed in the region occupied by a polyethylene atom. If the distance between a ghost and carbon or hydrogen is larger or equal than itself, then the ghost atom is placed. Otherwise, no ghost is placed to avoid wavefunction overlapping which will lead to numerical instabilities in the self-consistent solution and hence divergence in the total energy minimisation. Overlapping is also taken care of by the choice of the basis set of these massless particles. These particles use the same basis set 6-31G** as real hydrogens with the option GHOSTS available in CRYSTAL14. This option removes the charge and mass of the nuclei and charges in the electrons of these atoms, but keeps the basis set centred on the ghost nuclei.

S.I.4. Lanczos method

The optimised configurations with CP2k are also used as an input to run the Lanczos method calculations. These calculations are based on a semi-empirical pseudopotential describing the interaction between the excess electron and the atoms. The Lanczos algorithm is a numerical method used to diagonalise matrices. In our work, the matrix is the Hamiltonian that describes the interactions between one excess electron with the methylene groups of the polyethylene chains. These interactions are calculated using a pseudopotential that contains two parts: a short-range repulsive potential, which accounts for Coulomb, exchange and orthogonality of the excess electron with the methylene group; and a second long-range, attractive part, representing the polarization interaction between the excess electron and the atoms. The latter uses atomic polarisabilities, calculated using fully ab-initio methods. The

short-range potential has an assumed exponential form, with parameters obtained from fitting to experiments, measuring the onset of conduction in fluids made of small alkanes (ethane and propane). Further details are given in Ref. 21 and references therein.

In order to compute the polarization interaction, the local electric field at each methylene unit is required. This field has contributions from the induced dipoles at the surrounding methylene groups, and thus, it has to be computed self-consistently using an iterative approach, see Ref. 21. Moreover, the long-range polarisation potential is truncated beyond a given cutoff r_c from the excess electron. The correction to this approximation is estimated by assuming, for the polarization energy, the functional form A/r_c, where A is a constant to be determined from simulations of the same atomic configuration with different cutoffs r_c, here taken as r_c = 0.8, 0.9, 1.0, and 1.2 nm. This procedure allows both the validation of the assumed form (which can be derived using perturbation-theory) in a particular setup, and the calculation of the parameter A, and hence the estimation of the total energy for the infinite system. The above functional form for the long-range correction has been numerically confirmed in all the interfacial configurations considered in this paper, with typical Pearson correlation coefficients of 0.9998.

Once the Hamiltonian for a given atomic configuration is obtained, the Schrodinger equation is then solved for the ground and low lying excited states of the extra electron. This calculation directly provides the information required to estimate the density of excess electron states of our system, which can then be used to calculate transport properties, such as excess electron mobilities due to extended states.

FIGURES

Figure S1

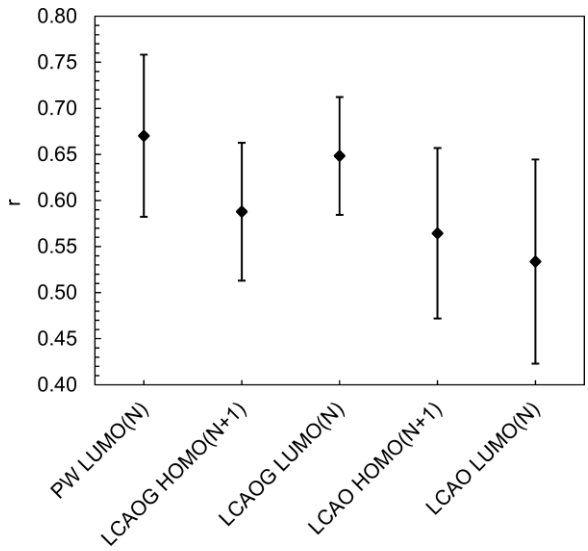

Figure S1. Average values of the correlation parameter $r = \left\langle \Psi \middle| \Psi^*_{Lanczos} \right\rangle$ between the wavefunction Ψ predicted by any method and that given by the Lanczos ground state (GS) for five configurations of bulk amorphous polyethylene. The correlation is calculated for the LUMO of the neutral *N* system with DFT using plane waves and the LUMO and HOMO of the neutral N and charged N+1 systems of DFT using linear combination of atomic orbitals with (LCAOG) and without (LCAO) ghost atoms. Error bars indicate two standard deviations.

Figure S2

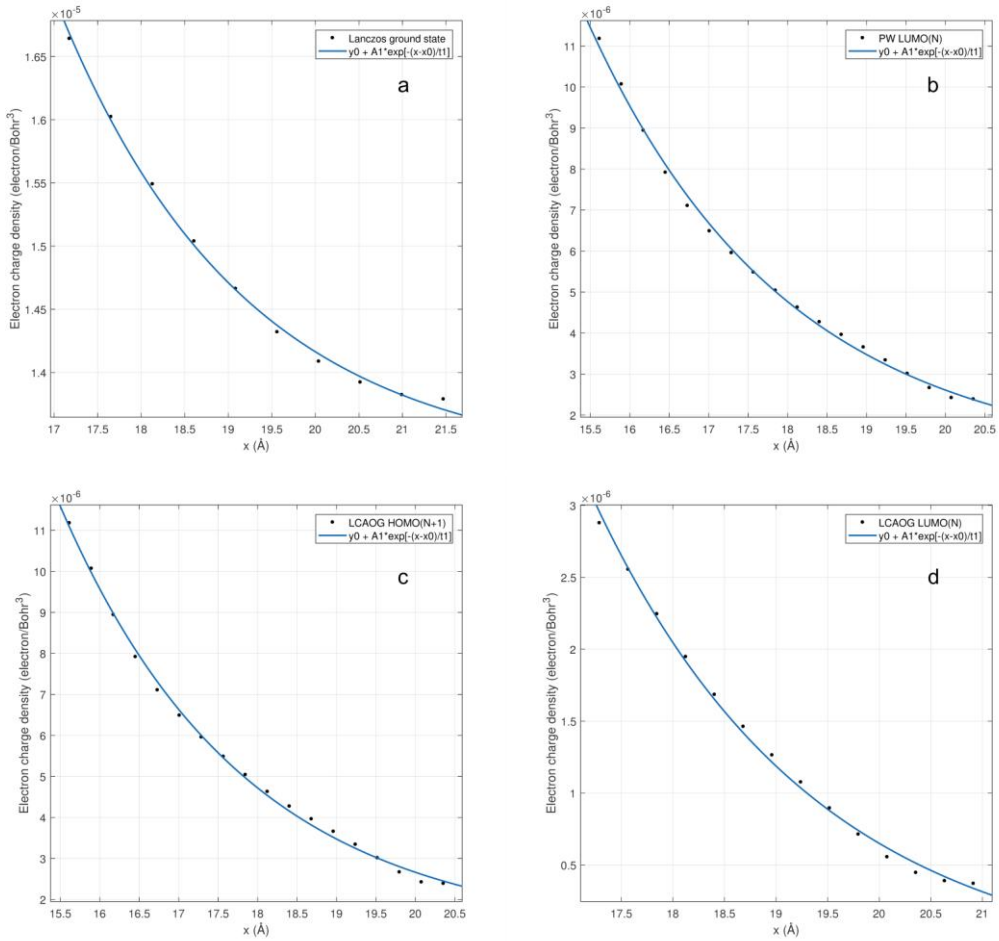

Figure S2. Exponential decays of the averaged profiles of the electron charge density shown in Fig. 6 of the ground-state level by Lanczos (a), and the LUMO(N) by plane waves PW (b), the HOMO(N+1) (c) and LUMO(N) with LCAOG with a separation of 0.185 nm between ghost atoms that fill a vacuum gap of 3.0 nm.

Figure S3

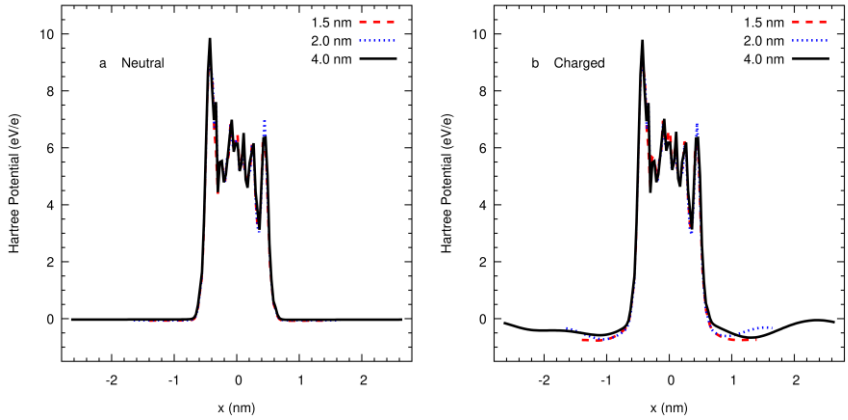

Figure S3. Averaged profiles of the Hartree potential of the neutral (a) and charged (b) systems in vacuum gaps of 1.5, 2.0, and 4.0 nm.

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