THE JOURNAL OF CHEMICAL PHYSICS **122**, 164902 (2005)

van der Waals interaction of simple, parallel polymers

Jesper Kleis[a] and Elsebeth Schröder
Department of Applied Physics, Chalmers University of Technology and Göteborg University, SE-412 96 Göteborg, Sweden

(Received 11 November 2004; accepted 10 February 2005; published online 22 April 2005)

We study the mutual interactions of simple parallel polymers within the framework of density-functional theory (DFT). As the conventional implementations of DFT do not treat the long-range dispersion [van der Waals (vdW)] interactions, we develop a systematic correction scheme for the nonlocal energy contribution of the polymer interaction at the intermediate to the asymptotic separations. We primarily focus on the three polymers, polyethylene, isotactic polypropylene, and isotactic polyvinylchloride, but the scheme presented applies also more generally to other simple polymers. From first-principle calculations we extract the geometrical and electronic structures of the polymers and the local part of their interaction energy, as well as the static electric response. The dynamic electrodynamic response is modeled on the basis of these static calculations, from which the nonlocal vdW interaction of the polymers is extracted. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1884987]

I. INTRODUCTION

Density-functional theory (DFT) has proven successful in describing the interaction of dense matter systems, e.g., the covalent atomic binding in molecules. However, for sparse matter systems with regions of small or no density overlap, the nonlocal van der Waals (vdW) correlations are important. The vdW interaction is an attractive correlation force due to instantaneous dipole and multipole interactions that are mediated by the electric field. The vdW interaction is presently not included in the traditional DFT implementations, and has to be corrected for.[1–5]

The crystals of polyethylene and isotactic polypropylene, where the polymers are aligned in parallel, represent an important class of sparse materials. The intramolecular bindings of the polymers are well described with the aid of traditional DFT, but the intermolecular bindings that keep the crystals together are dominated by the long-range vdW interaction.[1,6–8] Hence, a systematic correction scheme for the nonlocal interaction of parallel polymers, consistent with the DFT framework, is of great importance. Several successful schemes dealing with the interaction of extended objects, e.g., for the interlayer interaction in graphite[9,10] and the nanotube-nanotube interaction,[11,12] have already been developed; some of them applicable both to objects sufficiently separated that the electron densities do not overlap and to objects separated less than the binding distance with electron-density overlap. This article generalizes the scheme used for nanotubes[11,12] to deal with the long-range interaction of parallel polymers.

As a first step towards eventually treating polymer-polymer interactions at the typical binding distances of parallel polymers, the scheme presented here deals with the vdW interaction in the intermediate to the asymptotic region, where the polymers have a negligible electron-density overlap.

We use traditional DFT calculations to obtain the equilibrium internal (geometrical and electronic) structures of the three polymers: polyethylene (PE), isotactic polyvinylchloride (PVC), and isotactic polypropylene (PP). PE and PP are widely used in the industry and have well-described crystal structures.[6,7] These polymers are examples of what we refer to as *simple polymers*: polymers that can be treated as linear chains of relatively small repeated subunits and are computationally feasible within the framework of DFT. The calculated geometric structures of these polymers and a comparison with other calculation as well as experimental results will be presented in Sec. II A.

The valence electron density of the polymers is the key quantity for the calculation of the dispersive polymer-polymer interaction, with the *electrodynamic* response of the polymer modeled on the basis of static DFT calculations of the valence electron density and the electrostatic response. This part is described in Secs. III–V.

Finally, the numerical results of the vdW interaction are presented for the three polymers, and the interaction dependence on the orientations of the polymers will be further elucidated in terms of simple orientation-dependent expansions.

II. DFT RESULTS AND METHOD

A. Structure determination

The internal geometrical and electronic structures of the polymers are determined by traditional DFT calculations. Our subsequent calculations of the van der Waals interaction are based on this DFT-determined electronic structure. The DFT implementation used in this article is a plane-wave code[13] with ultrasoft pseudopotentials, and all DFT calculations are carried out within the generalized gradient approxi-

---

[a] Electronic mail: kleis@fy.chalmers.se

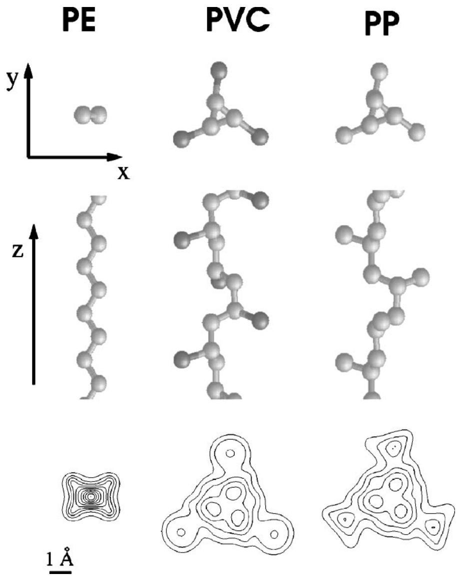

FIG. 1. The three polymers shown from the top and from the side. The hydrogen atoms are not shown in order to make the helical structure more apparent. the gray spheres are carbon atoms and the dark gray spheres are chlorine atoms. The bottom figures show the corresponding contour plots of the valence electron density averaged along the chain. The contour lines are equally spaced by 0.15 e/Å^3.

mation (GGA) in flavors PW91 (Ref. 14) or revPBE.[15] We use a 400-eV cutoff of the plane-wave basis set and a $1\times1\times12(1\times1\times4)$ Monkhorst–Pack sampling[16] of the Brillouin zone of our PE (PVC and PP) unit cell. The length l of the unit cell corresponds to the length of the repeated polymer segment. The calculations of the structures of the isolated polymers are carried out in unit cells chosen such that the polymers are surrounded by at least 10 Å of vacuum in any direction.

The geometrical structures of both PE and PP have previously been determined within the DFT framework and our results agree well with the previous DFT calculations[17,18] as well as experimental data,[8,19,20] while to our knowledge isotactic PVC has not previously been treated in first-principles calculations and the isotactic variant is not observed experimentally.

PE is a linear polymer with a repeated segment consisting of two C and four H atoms. PP and PVC, respectively, have a CH_3 group or a Cl atom substituting one quarter of the H atoms in the PE chain. This asymmetry in PP and in PVC makes each such substituted PE segment rotates 120° with respect to the neighboring segments, by which PP and PVC obtain a 3:1 helical structure. This is shown in Fig. 1. Thus each unit cell consists of three CH_3- or Cl-substituted PE segments.

The structures are determined by varying the unit-cell length l and at the same time relaxing the atomic positions by minimizing the local Hellmann–Feynman forces on the atoms such that the sum of all forces within the unit cell is less than 0.05 eV/Å. Data characterizing the calculated and experimentally observed geometrical structure of the polymers are given in Table I and the polymers are shown in Fig. 1.

B. Electron density

The DFT calculations of the equilibrium structure also provide the valence electron density. We use the density to determine the van der Waals interaction between the polymers at the intermediate to the asymptotic separations of the polymers. For simplifications in the following we use a valence electron density that is averaged along the polymer (Fig. 1), but there is no general problem in retaining the full three-dimensional density, besides an increased computational cost and the absence of the symmetry-related simplifications discussed later.

This approach of averaging the electron density along the polymer is reasonable when the polymers have a center-to-center separation d much larger than a length representing the typical variation of the polarization along the polymer. It

TABLE I. Geometric data characterizing the polymers: the repetition length l (unit-cell length), the average separation d_{AB} of atoms A and B, and the angle ψ formed by the carbon atoms in the main chain. C^* denotes a carbon atom with an attached subgroup CH_3 or Cl, R stands for CH_3 or Cl.

	d_{CC} (Å)	d_{CH} (Å)	d_{CR} (Å)	$\psi_{C^*CC^*}$ (deg)	ψ_{CC^*C} (deg)	l (Å)
PE (PW91)	1.52	1.10	1.10	113.7	113.7	2.55
PE (revPBE)	1.53	1.10	1.10	113.9	113.9	2.57
PE (PBE[a])	1.52	1.11	1.11	113.0	113.0	2.57
PE (LDA[a])	1.51	1.11	1.11	114.3	114.3	2.52
PE (x ray[b])	1.53	1.09	1.09	112±0.8	112±0.8	2.54
PVC (PW91)	1.52	1.10	1.81	115.4	113.3	6.50
PVC (revPBE)	1.53	1.10	1.81	115.5	113.5	6.54
PP (PW91)	1.53	1.10	1.52	117.4	111.5	6.53
PP (revPBE)	1.54	1.10	1.54	118.3	111.7	6.57
PP (LDA[c])	1.52	1.11	1.52	117.5	111.5	6.37
PP (GC[c])	1.53	1.10	1.53	117.9	111.8	6.50
PP (experimental)				116.9[d]	112.4[d]	6.50[e]

[a] Reference 18.
[b] Reference 19, x ray.
[c] Reference 17.
[d] Reference 20, x ray.
[e] Reference 8, x ray.

is applicable to the vdW-interaction calculations at separations in the intermediate to the asymptotic regime, defined as the regime where we have no electron-density overlap of the polymers, neither for the averaged electron density nor for the full three-dimensional electron density (discussed in Sec. V B). This regime corresponds to separations larger than 8 Å for PE and 10 Å for PP and PVC, which will be the scope of this article. As shown in Sec. IV, this greatly simplifies the computational problem of evaluating the interaction integral and will prove useful in finding the polarizability properties along the polymer, as discussed in Sec. III.

III. THE POLYMER ELECTRODYNAMIC RESPONSE

The origin of the vdW interaction is the interaction, mediated by electric fields, of local dipoles and multipoles spontaneously appearing in the electron density of the polymers. Thus the electrodynamic response of the polymers is essential for the calculation of their vdW interaction. The dipole-dipole interaction dominates the long-range interaction and we will here neglect the more complex multipole interactions. The dynamic response is modeled on the basis of DFT calculations, from which the static polarization as well as the electron density is obtained. The model contains a single tunable parameter, which is chosen such as to reproduce the static polarizability. From the dynamic response, in particular, from the polarizabilities, we are able to extract the attractive vdW interaction.

We model the local dynamic electron response to a local field by a simple local plasmon-pole model[11,21] with the bare susceptibility

$$\chi_0(\mathbf{r},\mathbf{r}';u) = \delta(\mathbf{r}-\mathbf{r}')\frac{n(\mathbf{r})}{u^2+u_c^2}, \tag{1}$$

where $n(\mathbf{r})$ is the electron density at position $\mathbf{r}$ obtained from DFT and u is related to the frequency ω of the electric field by $u \equiv -i\omega$. All quantities are in hartree atomic units.

In order to remove the divergence at zero frequency and instead reproduce the static polarization obtained from DFT calculations we introduce a cut-off frequency u_c. However, since the model is only an approximation of the response for nonzero frequencies, the cut-off frequency thus determined varies with the orientation of the applied field relative to the polymer. For simplicity we only consider a single cut-off value, which is chosen such that the angular average of the model polarizabilities reproduces the average of the DFT-calculated static polarizabilities. The model of the response (1) used here may be replaced by a more complicated functional form, but preliminary calculations with more realistic response models[4,22] show that our results are not more sensitive to this choice than to the averaging of the electron density.[23]

For convenience we describe all quantities in a Cartesian coordinate system local to the polymer. The repeated polymer segments are oriented along the z direction, and the origin in the (x,y)-coordinate system is located at the center-of-mass line of the polymer.

The local effective susceptibility tensor χ, which describes the locally induced polarization due to an external applied electric field, is a key quantity for the vdW interaction. The local field and, in turn, the local effective susceptibility are found by requiring that the charge is conserved under the action of an applied electric field when modeling the local response by Eq. (1). This defines a three-dimensional electrodynamical problem which is to be solved.

Since the electron density is averaged along the polymer, the electrodynamic problem is effectively reduced to a two-dimensional one. The translational invariance in the z direction, along the polymer, leads to the requirement that no local charge can be induced in the x-y direction due to a field in the z direction or vice versa. Thus the corresponding components of the susceptibility vanish, $\chi^{xz}=\chi^{yz}=\chi^{zx}=\chi^{zy}=0$. Furthermore, the electrodynamic solution requires that the potential is linear along the z direction, and thus we find the susceptibility component $\chi^{zz}(\mathbf{r};u)=\chi_0(\mathbf{r};u)$.

The components of the effective local susceptibility in the x-y plane are given by the relation

$$\chi^{ab}(x,y;u)E_{\text{app}}^{(a)} = -\frac{\partial\Phi^{(a)}(x,y;u)}{\partial b}\chi_0[n(\mathbf{r});u], \tag{2}$$

with indices $a,b=x,y$. $\Phi^{(a)}(x,y;u)$ is the electrodynamic potential due to an applied field of magnitude $E_{\text{app}}^{(a)}$ over the polymer in the a direction and is given by the charge conservation

$$\nabla\{(1+4\pi\chi_0[n(x,y);u])\,\nabla\,\Phi(x,y;u)\} = 0, \tag{3}$$

with appropriate boundary conditions.

The long-range interaction between polymers can be related to the interaction of the spatial moments of the macroscopic susceptibility. In the asymptotic limit the vdW interaction depends only on the frequency-dependent macroscopic susceptibility

$$\alpha^{ab}(u) = L\int \mathrm{d}x\mathrm{d}y\,\chi^{ab}(x,y;u), \tag{4}$$

where $a,b=x,y,z$. An explicit expression for the vdW interaction in this limit is given in Sec. IV.

Furthermore, since the local effective susceptibility is a tensor of rank two, we can easily treat rotations of the polymer with respect to the local coordinate system and the applied field (i.e., with respect to the neighboring polymers that give rise to the electric field). Specifically, if the polymer is rotated counterclockwise by an angle θ about the center of mass, the local susceptibility transforms as $\chi' = S^{-1}\chi S$ where the rotation operator is simply given as

$$S = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{5}$$

As an illustrative example we look at the orientation-dependent polarizability of PE. We choose to orient the polymer such that $\theta=0$ corresponds to the case where the polymer is widest in the x direction, and symmetry dictates that the off-diagonal components of the polarizability vanish. Using the above transformation properties of the susceptibility we get

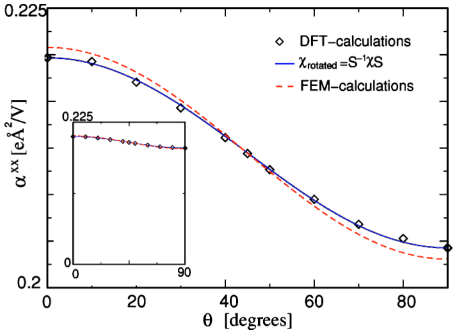

FIG. 2. The calculated static susceptibility $\alpha^{xx}(\theta)$ of a segment of PE for different angles θ. The orientation $\theta=0$ corresponds to the situation shown in Fig. 1 when the electric field is applied in the x direction. The diamonds are values obtained from DFT calculations and the full line is obtained by Eq. (6). The dashed line is found using the plasmon-pole approximation and solving the electrodynamic equations with finite element method (FEM) techniques. The inset shows the graph in full scale.

$$\alpha^{xx}(\theta) = [\alpha^{xx} + \alpha^{yy} + (\alpha^{xx} - \alpha^{yy})\cos 2\theta]/2, \tag{6}$$

in excellent agreement with DFT calculations of the susceptibility at different angles, as shown in Fig. 2.

IV. THE POLYMER-POLYMER van der Waals INTERACTION

In order to evaluate the vdW interaction for two possibly different but parallel polymers (oriented along the z direction and denoted by subscript $i=1,2$) with center-to-center separation d, we introduce two local Cartesian coordinate systems with the origin in the center of mass of polymer i and separated a distance d in the x direction.

We emphasize that the polymers are restricted to be parallel, but the formalism allows for both free rotation around the individual polymer axis as well as translation along this axis.

Now, since all quantities are averaged along the polymer, the vdW energy per unit length in the dipole approximation reads[24,25]

$$\frac{E_{\mathrm{vdW}}}{L} = -\frac{1}{L}\int_0^\infty \frac{\mathrm{d}u}{2\pi}\mathrm{trace}\{\chi_1 T_{12}\chi_2 T_{21}\}$$

$$= -\int_0^\infty \frac{\mathrm{d}u}{2\pi}\mathrm{d}x_1\mathrm{d}y_1\mathrm{d}x_2\mathrm{d}y_2\mathrm{d}(z_2 - z_1), \tag{7}$$

$$\sum_{a,b,c,d=x,y,z} \chi_1^{ab}(\mathbf{r}_1)T_{bc}(\mathbf{r}_1,\mathbf{r}_2)\chi_2^{cd}(\mathbf{r}_2)T_{da}(\mathbf{r}_2,\mathbf{r}_1), \tag{8}$$

where $T_{ij}\equiv\nabla_i\nabla_j|\mathbf{r}_i-\mathbf{r}_j|^{-1}$ and χ_i denotes the local effective susceptibility of polymer i. The integral in z_2-z_1 can be performed analytically[11] and the remaining integrals can be numerically evaluated.

For physical insight and fast computation, it is useful to make analytic expansions as a function of inverse separation. This allows us to easily extract forces, find the orientation where the polymers have maximum or minimum interaction, and to compare with other calculations. The following notation is used:

$$\frac{E_{\mathrm{vdW}}^{(n)}}{L} = -\frac{B_5}{d^5} - \frac{B_6}{d^6} - \cdots - \frac{B_n}{d^n},$$

where the first term describes the polarization-polarization (α-α) interaction and can be explicitly written as

$$B_5 = \frac{3}{256L^2}\int_0^\infty \mathrm{d}u\{41\alpha_1^{xx}\alpha_2^{xx} + 16\alpha_1^{yy}\alpha_2^{yy} + 9\alpha_1^{zz}\alpha_2^{zz}$$

$$+ 15(\alpha_1^{xx}\alpha_2^{zz} + \alpha_1^{zz}\alpha_2^{xx}) - 24(\alpha_1^{xy}\alpha_2^{yx} + \alpha_1^{yx}\alpha_2^{xy})\}. \tag{9}$$

Higher-order terms involving spatial moments of the susceptibility are just as easily obtained but are cumbersome to write down. However, by assuming the molecules to possess cylindrical symmetry the terms up to the ninth order have been calculated in Ref. 24.

V. NUMERICAL RESULTS AND DISCUSSION

The interaction integrals and expansion coefficients in Sec. IV are numerically evaluated. For this we need all the components of the local frequency-dependent effective susceptibility χ. These are found by using the PW91 valence electron density $n(\mathbf{r})$ in the bare response function $\chi_0[n(\mathbf{r});u]$. For each frequency u and each independent directions x and y of the applied electric field we then solve for the electrodynamic potential in Eq. (3) by finite element methods (FEMs).

By comparing the static ($u=0$) FEM calculation and the DFT-calculated static susceptibility we determine the cut-off frequency u_c. For PE the cut-off frequency reproducing on average the DFT-calculated susceptibility is found to be $u_c^{\mathrm{PE}}=0.429$ Ha. This certainly reproduces the DFT calculations to the extent of the accuracy of the FEM,[26] as seen in Fig. 2. The method tends to slightly overestimate the difference between the maximum and minimum polarizabilities as calibrated by the DFT determination of the static susceptibility. However, the small disagreement is acceptable considering that we use a simple plasmon model for the dielectric response with a single cut-off frequency u_c.

The threefold rotational symmetry of PP and PVC makes their susceptibility almost constant under rotation. We find $\alpha^{\mathrm{PP}}=0.97$ eÅ^2/V and $\alpha^{\mathrm{PVC}}=1.01$ eÅ^2/V. The corresponding cut-off frequencies are $u_c^{\mathrm{PP}}=0.507$ Ha and $u_c^{\mathrm{PVC}}=0.482$ Ha.

These calculations permit us to evaluate the vdW interaction for the three polymers at the intermediate to the asymptotic separations. To illustrate the general interaction for all possible orientations of the polymers, we have evaluated the orientation-dependent expansion coefficients.

Of the three polymers, the PE-PE interaction is the most influenced by the relative orientation of the polymers. This is to be expected from the polarization properties of PE, which are reflected in the orientation-dependent expansion coefficients. For PE all even terms vanish due to symmetry and the nonvanishing coefficients B_5 and B_7 are shown in Fig. 3. In the asymptotic limit, described by the B_5 coefficient, the angle dependence is rather low (about 3%). Evaluating $E_{\mathrm{vdW}}^{(7)}(\theta_1,\theta_2)$ for 10-Å separation of PE with PE, we find that the variation is more pronounced (7%) and the effect grows as the separation is reduced. However, the general depen-

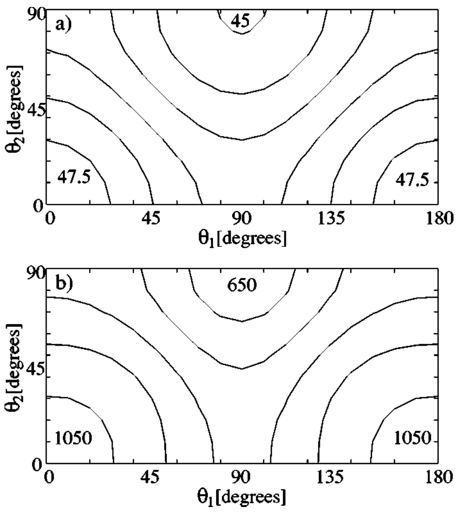

FIG. 3. The orientation-dependent expansion coefficients $B_5(\theta_1,\theta_2)$ and $B_7(\theta_1,\theta_2)$ for PE, shown as equidistant contours. θ_i is the rotation angle of polymer i about its center of mass. The initial positions of the polymers are indicated by the contours of the averaged charge densities in Fig. 1. The panels show (a) $B_5^{\text{PE-PE}}(\text{eV Å}^4)$ and (b) $B_7^{\text{PE-PE}}(\text{eV Å}^6)$, respectively.

dence of the orientations in the intermediate to the semiasymptotic regime can be concluded to be rather weak. Furthermore, we observe that the calculated expansion coefficients are nearly symmetric under the transformation $\theta_i \rightarrow 180-\theta_i$.

The success of the expansion of the energy in terms of inverse separation for PE is evident from Fig. 4 where we have compared the expansion in inverse separation to the full two-dimensional (2D) evaluation of the energy for the orientations of maximum and minimum interactions, respectively. We see that in the case of maximum interaction the agreement is excellent down to polymer separation d of 10 Å. The agreement is even better in the case of minimum interaction when the nearest distance between fragments of the two polymers is effectively largest (for a given d).

The PP-PP and PVC-PVC interactions are even less sensitive to rotations than the PE-PE interaction. We find the odd-order terms to be (independent of rotation) $B_5^{\text{PVC-PVC}} = 133$ eV Å^4, $B_7^{\text{PVC-PVC}} = 6.6$ keV Å^6, $B_5^{\text{PP-PP}} = 119$ eV Å^4, and $B_7^{\text{PP-PP}} = 5.8$ keV Å^6. Due to the trianglelike shape of PVC and PP, the even-order terms do not vanish, but in general these only give small contributions to the interaction energy (e.g., the B_6 term contributes maximum 5% of the energy at 10 Å). Thus the qualitative behavior is well described by the constant B_5 and B_7 terms. In Fig. 5 a comparison between the full numerical expansion for the PP-PP interaction and the expansion up to the seventh order is given. The curves show excellent agreement for $d > 13$ Å and fair agreement for smaller distances. We obtain similar results for the PVC-PVC interaction.[24] Thus we find that the qualitative behavior in the intermediate to the asymptotic region is well described in terms of an expansion of the energy in inverse separation.

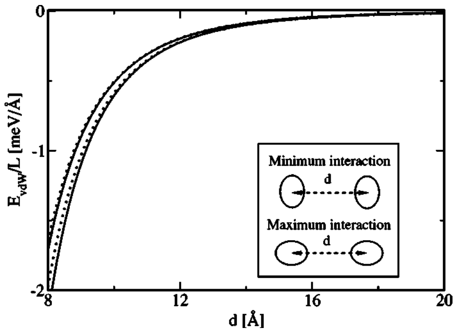

FIG. 4. The PE-PE van der Waals interaction energy as a function of separation d for the two orientations schematically shown in the inset, corresponding to the minimum and maximum interactions, respectively. The full lines are the results of the 2D numerical interaction integral, while the dotted lines show the results for the seventh order expansion in d^{-1}.

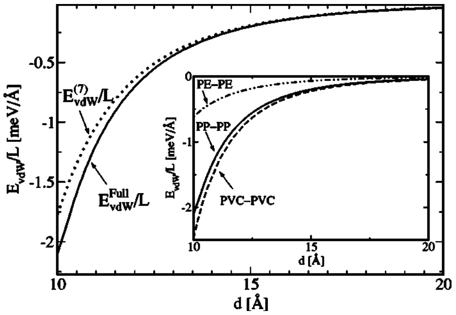

FIG. 5. The PP-PP van der Waals interaction energy as a function of separation d in different approximations. The full line corresponds to the evaluation of the 2D-interaction integral while the dotted line shows the expansion of the energy up to the seventh order in inverse distance. The inset shows the PE-PE, PP-PP, and PVC-PVC van der Waals interaction energies as a function of separation d. All the polymers are oriented as shown by the density contours in Fig. 1 and separated in the x direction.

The inset of Fig. 5 shows the evaluation of the full 2D-interaction integrals for the three polymers. We see the general tendency $E^{\text{PE}} < E^{\text{PP}} < E^{\text{PVC}}$ which is to be expected from the polarization properties of the molecules.

A. Cylindrical approximation

The small orientation dependence of the expansion coefficients for the three polymers, along with the approximate cylindrical symmetry of their length-averaged electron density (Fig. 1), suggests that their asymptotic interaction can be roughly described on the basis of the cylindrical-averaged electron density. This was utilized in Ref. 24 and a comparison between the "cylindrical" and the 2D-evaluated expansion coefficients for the three polymers is given in Table II. We see that the expansion coefficients in the cylindrical approximation typically underestimate the expansion coefficients by 15% compared to the 2D-evaluated coefficients. Much of this difference can be ascribed to the change in

TABLE II. Comparison between the expansion coefficients for the full 2D evaluation and the expansion coefficients where cylindrical symmetry is enforced.

	B_5^{full} (eV/Å^4)	B_5^{cyl} (eV/Å^4)	B_7^{full} (keV/Å^6)	B_7^{cyl} (keV/Å^6)
PP	119	108	5.8	4.5
PVC	133	112	6.6	5.8
PE (Max. inter.)	47.5	40	0.65	0.76
PE (Min. inter.)	45	40	1.1	0.76

dielectric model response when the electron density is further averaged around the polymer center-of-mass line.

Thus, the cylindrical approximation proves useful for simple estimates of the magnitude and behavior (even in the intermediate regime) of the effective polymer interaction, but in order to study the behavior in more details we have to resort to the 2D-evaluated interaction.

B. Length averaging approximation

The comparison of the 2D approximation and the cylindrical approximation illustrates the point that any averaging procedure in general will alter the local dielectric model response and in turn the magnitude of the interaction.

In the same manner the length averaging, leading to the 2D approximation, is expected to alter the magnitude of the interaction compared to the full three-dimensional (3D) interaction. We have investigated the effect of the length averaging by evaluating parts of the susceptibility for both the 2D- and the 3D-electron densities and estimating the difference these densities give rise to in the resulting interaction energy. We find that for our polymers the effects of the averaging procedure are of minor importance in the intermediate to the asymptotic regime. A more detailed comparison of the 2D approximation with the 3D interaction will be carried out in a forthcoming paper.[23]

VI. COMPARISON WITH OTHER METHODS

The direct comparison to other calculations and measurements of polymer binding energies is difficult because most results are from polymer crystals where the polymers are packed at their natural binding distance. The scheme presented here does not apply at the binding distances in polymer crystals and it is not possible to validate the accuracy of our approach from experimental data on such polymer crystals. However, for PE it is possible to directly compare our present calculation for the intermediate to the asymptotic separations to the asymptotic interaction parameters extracted from other calculations. This will be described below.

The asymptotic ethane-ethane interaction might be used to estimate a PE-PE asymptotic interaction by approximating PE as a long row of ethane molecules. The ethane molecules are thought of as oriented along the z axis with a repeat distance l_r that equals the length of our unit cell, and by summing up all the asymptotic ethane-ethane interactions we obtain an approximate value for the B_5 value.

The asymptotic ethane-ethane interaction is on the form $E^{\mathrm{asymp}} = -C_6/d^6$ such that

$$\frac{B_5}{d^5} \approx \int_{-\infty}^{\infty} \mathrm{d}z \frac{C_6/l_r^2}{(\sqrt{d^2+z^2})^6} = \frac{3\pi}{8}\frac{C_6}{l_r^2}\frac{1}{d^5}. \tag{10}$$

The ethane-ethane interaction parameter has previously been evaluated in an approach similar to ours[27] as well as in a more accurate time-dependent approach.[28] Table III shows the result of this comparison; we see that the asymptotic interaction estimated this way is in good agreement with our calculations.

Furthermore, if we focus on PE as being build up of CH_2 groups, we can use the parameters typically adopted in force-field calculations[29] and sum up the CH_2-CH_2 interactions. This approach gives, as shown in Table III, an asymptotic interaction parameter slightly larger (20%) than our interaction parameters. This difference is fully acceptable, considering that the force-field parameters are adapted for calculations at the crystal binding distance, and thus only provide estimates for the asymptotic interaction parameters.

TABLE III. Comparison of the B_5 coefficients for the PE-PE interaction obtained by other methods with those obtained by our method. Underlined quantities are estimated using Eq. (10).

Interacting group	C_6 (eV/Å^6)	l_r (Å)	B_5 (eV/Å^5)
CH_2 (Force-field parameter[a])	78	1.27	$\underline{57}$
C_2H_6 (Similar method[b])	210	2.55	$\underline{39}$
C_2H_6 (TDFT[c])	239	2.55	$\underline{45}$
Max. B_5 in our calculations	$\underline{264}$	2.55	47.5
Min. B_5 in our calculations	$\underline{248}$	2.55	45

[a] Reference 26.
[b] Reference 24.
[c] Reference 25.

To sum up, the relatively crude estimates of the asymptotic interaction parameters described above are in good agreement with our calculations. The vdW interaction of parallel polymers from the intermediate distance to their binding distance will be the scope of a forthcoming paper.

VII. CONCLUSION

We have presented a general approach based on first-principles electron density calculations for computing the intermediate to long-range interactions of parallel, geometrically simple polymers.

We have applied the scheme to polyethylene, isotactic polypropylene, and isotactic polyvinylchloride, and the interaction energy for these polymers has been evaluated. Furthermore, we have found orientation-dependent expansion coefficients up to the seventh order in d^{-1}, which give a qualitative description of the orientation-dependent polymer-polymer interaction, and for PE give quantitative correct values for $d^{\mathrm{PE}} > 10$ Å ($d^{\mathrm{PP}} > 12$ Å and $d^{\mathrm{PVC}} > 12$ Å). These expansions are consistent with other studies in the asymptotic limit.

ACKNOWLEDGMENTS

This work was partly supported by the Swedish Research Council (VR), the Swedish National Graduate School in Materials Science, the EU Human potential research training network ATOMCAD under Contract No. HPRN-CT-1999-00048, and the Swedish Foundation for Strategic Research (SSF) through the consortium ATOMICS.

[1] S. Serra, S. Iarlori, E. Tosatti, S. Scandolo, and G. Santoro, Chem. Phys. Lett. **331**, 339 (2000).
[2] X. Wu, M. C. Vargas, S. Nayak, V. Lotrich, and G. Scoles, J. Chem. Phys. **115**, 8748 (2001).
[3] U. Zimmerli, M. Parrinello, and P. Koumoutsakos, J. Chem. Phys. **120**, 2693 (2004).

[4] D. C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard, and B. I. Lundqvist, Int. J. Quantum Chem. **101**, 599 (2005).
[5] J. F. Dobson and J. Wang, Phys. Rev. B **69**, 235104 (2004).
[6] J. F. Twistleton and J. W. White, Polymer **23**, 578 (1982).
[7] B. Lotz, J. C. Wittman, and A. J. Lovinger, Polymer **37**, 4979 (1996).
[8] M.-H. Kim, J. D. Londono, and A. Habenschuss, J. Polym. Sci., Part B: Polym. Phys. **38**, 2480 (2000).
[9] H. Rydberg, N. Jacobson, P. Hyldgaard, S. I. Simak, B. I. Lundqvist, and D. C. Langreth, Surf. Sci. **606**, 532 (2003).
[10] H. Rydberg, B. I. Lundqvist, D. C. Langreth, and M. Dion, Phys. Rev. B **62**, 6997 (2000).
[11] E. Schröder and P. Hyldgaard, Mater. Sci. Eng., C **23**, 721 (2003).
[12] E. Schröder and P. Hyldgaard, Surf. Sci. **532**, 880 (2003).
[13] Open-source computer code DACAPO, http://www.fysik.dtu.dk/CAMPOS
[14] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).
[15] Y. Zhang and W. Yang, Phys. Rev. Lett. **80**, 890 (1998).
[16] H. Monkhorst and J. Pack, Phys. Rev. B **13**, 5188 (1976).
[17] B. Montanari, P. Ballone, and R. O. Jones, J. Chem. Phys. **106**, 8545 (1997).
[18] B. Montanari, P. Ballone, and R. O. Jones, J. Chem. Phys. **108**, 6947 (1998).
[19] S. Kavesh and J. M. Schultz, J. Polym. Sci., Part A-2 **8**, 243 (1970).
[20] A. Immirzi and P. Iannelli, Macromolecules **21**, 768 (1988).
[21] E. Hult, H. Rydberg, B. I. Lundqvist, and D. C. Langreth, Phys. Rev. B **59**, 4708 (1999).
[22] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, Phys. Rev. Lett. **92**, 246401 (2004).
[23] J. Kleis and E. Schröder (unpublished).
[24] J. Kleis, P. Hyldgaard, and E. Schröder, Comput. Mater. Sci., **33**, 192 (2005).
[25] B. I. Lundqvist, Y. Andersson, H. Shao, S. Chan, and D. C. Langreth, Int. J. Quantum Chem. **56**, 247 (1995).
[26] The FEM calculations have converged such that the polarizability calculated with the nth refinement of the mesh, α^n, deviates no more than 0.5% from α^{n+1}.
[27] Y. Andersson and H. Rydberg, Phys. Scr. **60**, 211 (1999).
[28] S. J. A. van Gisbergen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. **103**, 9347 (1995).
[29] S. Fujiwara and T. Sato, J. Chem. Phys. **107**, 613 (1997).