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Integral equation study of particle confinement effects in a polymer/particle mixture

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Abstract

Integral equation theory techniques are applied to evaluate the structuring of the polymer when large solid particles are embedded into a bulk polymer melt. The formalism presented here is applied to obtain an insight into the filler particle aggregation tendency. We find that with the employed polymer-particle interaction model it is very unlikely that the particles will aggregate. We believe that in such a system aggregation and clustering can occur when the filler particles are dressed by tightly bound polymer layers.

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I. INTRODUCTION

The authors are pleased to dedicate this paper to Keith Gubbins on the occasion of his birthday at the midpoint of his career.

One of the most pronounced features of polymer melts (for instance, various silicones such as polydimethysiloxane or PDMS) is its ability to dramatically change its mechanical properties with the addition of an inorganic filler to the pure polymer phase. In particular, the strength of the polymer/particle system increases as the filler concentration increases. This reinforcing mechanism is poorly understood and consequently, the rational control of the resulting mechanical properties is difficult and usually is based on empirical assumptions. Currently, it is believed that the primary reinforcing mechanism in this polymer/particle system has its origin in some peculiar features of particle-polymer interactions. At the same time, there are arguments indicating that taking into account particle-polymer interaction alone is not enough to explain the reinforcement. In particular, the interaction between a single particle surface and polymer molecules does not depend how many particles are embedded into a polymer melt. But, on the other hand, the properties of polymer strongly depend on the fraction of filler particles[1,2]. The latter observation suggests that, besides the polymer-filler interaction, geometrical restrictions imposed on the polymer by the presence of particles has a major impact on the resulting polymer properties.

Computer simulations are the most efficient tool to deal with system with complex chemical structures using a full atomistic level of modelling. Computer simulations for the particular polymer/particle system experience problems that involve the consideration of the simultaneous presence of a large number of filler particles. In fact, the length scale (diameter) of filler particles usually is much larger than the equivalent polymer length scale (diameter of a polymer bead or radius of gyration or transverse diameter of the polymer chains). Therefore, simulations of polymer/particle system with an experimental volume fraction of the particles will require an extremely large number of polymer molecules. In contrast, an integral equation theory study of a system of complex chemical structures requires the involvement of some approximations and the effect of these approximation often is not known in advance. However, integral equation theory techniques do allow one to deal with the system comprising realistic numbers (densities) of both the filler particles and the surrounding polymer melt.

The purpose of the present note is to apply the integral equation theory (IET) to deal with the polymer/particle system with the aim of obtaining a deeper insight into the nature of the reinforcement. By performing atomistic (or if necessary even *ab initio*) computer simulation for bulk polymer solution and for polymer with a single particle surface we can obtain the necessary information concerning the nature of the polymer-particle interactions and then incorporate this information into integral equation calculations by means of effective parameters of the surface-polymer interaction. In such a case, the level of the modelling within the framework of IET can be simplified. For instance, we will not need to include explicitly the presence of the water on the silica surface since the effect of water is incorpo-

rated already into the parameters of the surface-polymer interaction. The outcome of our IET calculations will be in a form that will show the sensitivity of the physical properties of the polymer to variations in the interfacial region.

II. INTEGRAL EQUATION APPROACH AND ITS IMPLICATION TO POLYMER/PARTICLE SYSTEM

Typically the integral equation technique is based on the Ornstein-Zernike (OZ) equation[3]

$$h_{\lambda\mu}(r_{12}) = c_{\lambda\mu}(r_{12}) + \sum_{\nu=\mathrm{s,p}} \rho_\nu \int h_{\lambda\nu}(r_{13}) c_{\nu\mu}(r_{32}) d\mathbf{r}_3 \,, \tag{1}$$

where the Greek subscripts range over all the system components, i.e. polymer (p) as well as particles (s), and $\mathbf{r}_\alpha$ is the position of particle α. Finally, $r_{\lambda\mu} = |\mathbf{r}_\lambda - \mathbf{r}_\mu|$. The function $h_{\lambda\mu}(r) = g_{\lambda\mu}(r) - 1$ is the total correlation functions for a pair of particles of component λ and μ that are separated by the distance r. The function $g_{\lambda\mu}(r)$ is the pair or radial distribution functions (RDF). The function $c_{\lambda\mu}(r)$ is the direct correlation function.

One of the important features of this polymer/particle system is the simultaneous presence of the different length scales that characterize the polymer species and filler particles. Two different approaches developed within the IET can be employed to deal with the issue of different length scales. The first approach relates to the reduction of the initial polymer/particle system to an effective one-component particle system with an effective particle-particle interaction that incorporates the properties of polymer. The second approach assumes that different length scales result in a different mobilities of the filler particles and polymer. This suggests treating the filler particles as the immobile species, while the polymer is considered as being adsorbed into a disordered particle environment. However, this approach is beyond the scope of the present study.

To proceed with the first approach let us assume in equation (1) that there are only one or two particles in the mixture. Thus, the particles are present at infinite dilution with zero concentration, $\rho_\mathrm{s} = 0$. Further, we assume that the product of the particle density and the particle size D, which is large, vanishes, i.e., $\rho_\mathrm{s} D^3 = 0$; otherwise, the particle would affect the entire polymer matrix. In other words, the particles are part of the bulk polymer at vanishingly small density, i.e. $\rho_\mathrm{s} \to 0$. Using this fact, equation (1) results in a system of three equations

$$h_\mathrm{pp} = c_\mathrm{pp} + \rho_\mathrm{p} c_\mathrm{pp} \otimes h_\mathrm{pp} \,, \tag{2}$$

$$h_\mathrm{ps} = c_\mathrm{ps} + \rho_\mathrm{p} c_\mathrm{sp} \otimes h_\mathrm{pp} \,, \tag{3}$$

and

$$h^o_\mathrm{ss} = c^o_\mathrm{ss} + \rho_\mathrm{p} c_\mathrm{sp} \otimes h_\mathrm{ps} \,. \tag{4}$$

This limiting procedure is called the Henderson-Abraham-Barker approach. For notational convenience, in all the equations above we have omitted the dependence on r; the symbol

$\otimes$ denotes a convolution in r-space. The first equation, (2), is just the OZ equation for the homogeneous polymer melt. Equations (3) and (4) involve the filler particles and, due to this, play an important role in the statistical mechanics of inhomogeneous systems, i.e., systems involving diluted mesoscopic objects. Namely, equation (3) describes the polymer inhomogeneity by means of the local density profiles $\rho_{\rm p}(r) = \rho_{\rm p} g_{\rm ps}(r)$ of the polymer species near the particle or surface. In turn, equation (4) describes the correlations between only two filler particles mediated by the polymer, and consequently yields information that can be used to evaluate the effective pair interaction between a pair of silica particles. Because the particles are large, the region between pair can be approximated as a slit.

III. BRIEF REVIEW OF THE INTEGRAL EQUATION THEORIES FOR A PURE POLYMER SYSTEMS

The integral equation technique that is to be applied to deal with polymer molecules differs from the ordinary IET approach that deals with simple molecular liquids. Currently several integral equation theories that enable one to predict the structure and thermodynamical properties of the fluid of chain molecules in a bulk phase are available. Among those, the most promising are the theories, that are based either on *the reference interaction site model* (RISM) approach[4] or on *the multi-density* approach for associating fluids[5,6]. The theories of the first type are known under the general name polymer RISM (PRISM). Originally PRISM has been developed by Curro and Shweizer[7,8] as a simple application of the RISM approach of Chandler and Andersen[4] to a fluid of flexible ring molecules. Since then several modifications have been proposed and used in a large number of applications. Two review papers[9,10] give a reasonable insight into the older developments of PRISM. Later developments have been reviewed recently[11].

Originally, the PRISM approach appeared not to be a self-contained theory, i.e. certain input information other than the intramolecular distribution functions, was needed. Several different approximations for the intramolecular correlations have been proposed. Later, a self-consistent version of the theory was developed with the intramolecular distribution function obtained from a one-chain computer simulation, i.e. the simulation of one molecule with an effective potential between the monomers of the chain that is obtained from the solution of the PRISM equation during the previous iteration cycle. Other self-contained versions of the theory are also available; however, they appear to be less successful. In general PRISM provides reasonable qualitative, and sometimes quantitative, predictions for the structure of dense polymer systems (melts and alloys), polymer-colloidal mixtures. It is not utilized extensively that in the prediction of thermodynamical properties.

The version of the multi-density theory that is represented by thermodynamic perturbation theory (TPT)[6,12] and its modifications, i.e. statistical associating fluid theory (SAFT), proves to be very successful in predicting thermodynamical properties of a fluid of chain molecules and its mixtures. An integral equation version of Wertheim's multi-

density theory for associating fluids[5,6] has been also developed and applied to study the properties of the chain molecule fluids[13,14]. This extension of the Wertheim's theory is known as a product-reactant Ornstein-Zernike approach (PROZA). The PROZA is a general statistical-mechanical theory of reacting mixtures in which the product molecules and reacting molecules are treated on the same footing. When applied to polymerizing monomers, PROZA yields the mean monomer-monomer pair correlation function, from which the thermodynamics of a fluid of polymerizing molecules can be obtained directly. In the complete-association limit, the PROZA becomes a theory for the structure and thermodynamics of a fluid of fully polymerized chain. Several different approximations (PY-like, MSA-like and HNC-like) have been proposed and applied to a different macromolecular systems which include hard-sphere chain fluids[15–17], hard-sphere ring fluids[18] and star molecule fluids[19,20], chain fluids with Yukawa[21,22] and Coulomb[23] interactions between monomers, etc.

Unlike the PRISM approach, PROZA is a self-contained theory and provides predictions for both intermolecular and intramolecular correlation simultaneously. While PRISM requires the application of numerical methods of solution, analytical solution of the Percus-Yevick (PY) and mean spherical approximation (MSA) versions of PROZA are available for most of the cases. Thus, within PROZA one can have analytical expressions for both thermodynamics and structural properties. However, PRISM has an advantage of being applicable to a fluid of long chain molecules, while so far PROZA-based theories have been used mostly for fluids of relatively short chain molecules. The application of the latter approach is restricted by the increasing dimensionality of the matrices involved into the corresponding multidensity Ornstein-Zernike (OZ) equation, which appears to be proportional to the length of the chain molecules. We will attempt to remove this obstacle and reduce the dimensionality of the matrices by neglecting the chain end effects, i.e. assuming that all intermolecular site-site distribution functions are equal regardless of their position in the chain. This allows us to treat the molecules of any length using corresponding OZ equation of the same dimensionality.

In the present study PROZA integral equation approach is applied to study the effect of the hydration level of the silica surface on the interaction between filler particles. We start from PROZA approach for the bulk structure of PDMS and extend it on the inhomogeneous PDMS melts including the presence of a single confining surface and a pair of surfaces, i.e. slit pore of a variable thickness.

IV. PROZA MULTI-DENSITY FORMALISM FOR POLYMER MELTS

A. Fluid of linear homo-nuclear chain molecules

We start with the simplest case of chain molecule fluids – a melt of linear homo-nuclear chain molecules. Each homo-nuclear chain molecule consists of m identical repeated monomer units. Each monomer units is composed of a single atom modelled by a hard

sphere with two interacting sites, A and B. Each of these sites bond one site of two different atoms from two neighboring monomers to form the monomer chain. The number m of repeated monomer units serves as a measure of the length of the chain.

The multi-density OZ equation for such a model chain fluid reads,

$$\hat{\mathbf{h}}_{\alpha\beta}(k) = \hat{\mathbf{c}}_{\alpha\beta}(k) + \rho \sum_{\gamma} \left(\hat{\mathbf{c}}_{\alpha\gamma}(k) + \hat{\boldsymbol{\Delta}}_{\alpha\gamma}(k) \right) \boldsymbol{\alpha} \left(\hat{\mathbf{h}}_{\gamma\beta}(k) + \hat{\boldsymbol{\Delta}}_{\gamma\beta}(k) \right) , \tag{5}$$

where ρ is the number density of chain molecules, subscripts α, β, γ stand for the monomers in the system. The notation $\hat{\mathbf{h}}_{\alpha\beta}(k)$ and $\hat{\mathbf{c}}_{\alpha\beta}(k)$ is used for the matrices whose elements are the Fourier transforms of the elements of the matrices $\mathbf{h}_{\alpha\beta}(r)$ and $\mathbf{c}_{\alpha\beta}(r)$, respectively. In particular,

$$\mathbf{c}_{\alpha\beta}(r) = \begin{pmatrix} c_{\alpha_0\beta_0}(r) & c_{\alpha_0\beta_A}(r) & c_{\alpha_0\beta_B}(r) \\ c_{\alpha_A\beta_0}(r) & c_{\alpha_A\beta_A}(r) & c_{\alpha_A\beta_B}(r) \\ c_{\alpha_B\beta_0}(r) & c_{\alpha_B\beta_A}(r) & c_{\alpha_B\beta_B}(r) \end{pmatrix} ,$$

and similarly for $\mathbf{h}_{\alpha\beta}(r)$. The functions $h_{\alpha_m\beta_n}(r)$ and $c_{\alpha_i\beta_j}(r)$ are the partial pair and direct correlation functions. The subscripts i, j characterize the bonding state of the site of the monomer α, namely, 0 means unbonded site, A – site A is bonded, B – site B is bonded.

In contrast, matrices $\boldsymbol{\alpha}$ and $\hat{\boldsymbol{\Delta}}_{\alpha\beta}(k)$ are defined as follow,

$$\alpha_{ij} = 1 - \delta_{ij} + \delta_{0i}\delta_{0j} ,$$

and

$$\hat{\boldsymbol{\Delta}}_{\alpha\beta}(k) = \delta_{\alpha,\beta+1} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \hat{\Delta}(k) \\ 0 & 0 & 0 \end{pmatrix} + \delta_{\alpha,\beta-1} \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & \hat{\Delta}(k) & 0 \end{pmatrix} , \tag{6}$$

where $\delta_{\alpha\beta}$ is the Kronnekker symbol,

$$\hat{\Delta}(k) = \frac{1}{\rho} \frac{\sin(kL)}{kL} ,$$

with L being the bond length.

Taking the sum over α and β from both sides of the OZ equation (5) and assuming, that both the direct and total correlation functions are independent of the indices α and β, we have

$$\hat{\mathbf{h}}(k) = \hat{\mathbf{c}}(k) + \rho \left(\hat{\mathbf{c}}(k) + \hat{\boldsymbol{\Delta}}(k) \right) \boldsymbol{\alpha} \left(\hat{\mathbf{h}}(k) + \hat{\boldsymbol{\Delta}}(k) \right) , \tag{7}$$

where

$$\hat{\mathbf{h}}(k) = \frac{1}{m^2} \sum_{\alpha\beta} \hat{\mathbf{h}}_{\alpha\beta}(k), \qquad \hat{\mathbf{c}}(k) = \frac{1}{m^2} \sum_{\alpha\beta} \hat{\mathbf{c}}_{\alpha\beta}(k),$$

$$\hat{\mathbf{\Delta}}(k) = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \hat{\Delta}(k) \\ 0 & \hat{\Delta}(k) & 0 \end{pmatrix} \tag{8}$$

with

$$\hat{\Delta}(k) = \frac{1}{m\rho}\left(\frac{m-1}{m}\right)\frac{\sin(kL)}{kL}\,.$$

The dimensionality of the set of OZ equations (7) is 3×3 regardless of the chain length m.

B. Application to the bulk PDMS melts

All calculations that will be reported here have been performed for a model polymer system that mimics polydimethylsiloxane (PDMS) melt. As for filler prototype we consider silica particles.

1. *United atom model*

The chemical formula of polydimethylsiloxane is $(C_2H_6OSi)_n$. This means that the molecules of this melt are modelled by the chain composed of the repeated monomer units composed of four species: two of them are associated with O and Si atoms while another two are CH_3 groups. This model is the united atom (UA) approach since the methyl group CH_3 is treated as a single atom while O and Si atoms are treated explicitly. The parameters of the model have been given[24,25].

To keep the theory treatable, we simplify the UA model in the following way: (i) removing bending and torsional interaction, (ii) adding one more oxygen atom, so that the chain from one end starts with, say, a Si atom and ends up with ,say, a O atom (for symmetry), (iii) on both ends of the chain we have two CH_3 groups, instead of three as in the original model.

2. *OZ equation*

The modified version of the multidensity OZ equation for such a model has the following form,

$$\hat{\mathbf{h}}^{ab}_{\alpha\beta}(k) = \hat{\mathbf{c}}^{ab}_{\alpha\beta}(k) + \rho\sum_{c=1}^{4}\sum_{\gamma}\left(\hat{\mathbf{c}}^{ac}_{\alpha\gamma}(k) + \hat{\mathbf{\Delta}}^{ac}_{\alpha\gamma}(k)\right)\boldsymbol{\alpha}_c\left(\hat{\mathbf{h}}^{cb}_{\gamma\beta}(k) + \hat{\mathbf{\Delta}}^{cb}_{\gamma\beta}(k)\right)\,. \tag{9}$$

Now all the functions additionally have superscripts a, b and c that denote the type of atoms comprising the chain monomer unit. Because of this, in contrast to equation (5) there is an extra summation over the species of monomer units where 1 stands for the O atom, 2 – for the Si atom, and 3 and 4 – for both the CH_3 groups treated as a single atom.

The chain length is m, which equals the a number of either oxygen or silicon atoms. For the sake of convenience this set of equations can be rewritten as follows,

$$\hat{\mathbf{h}}(k) = \hat{\mathbf{c}}(k) + \rho \left(\hat{\mathbf{c}}(k) + \hat{\mathbf{\Delta}}(k) \right) \boldsymbol{\alpha} \left(\hat{\mathbf{h}}(k) + \hat{\mathbf{\Delta}}(k) \right) , \tag{10}$$

where

$$\hat{\mathbf{h}}(k) = \begin{pmatrix}
h^{11}_{00} & h^{11}_{0A} & h^{11}_{0B} & h^{12}_{00} & h^{12}_{0A} & h^{12}_{0B} & h^{12}_{0C} & h^{12}_{0D} & h^{13}_{00} & h^{13}_{0A} & h^{14}_{00} & h^{14}_{0A} \\
h^{11}_{A0} & h^{11}_{AA} & h^{11}_{AB} & h^{12}_{A0} & h^{12}_{AA} & h^{12}_{AB} & h^{12}_{AC} & h^{12}_{AD} & h^{13}_{A0} & h^{13}_{AA} & h^{14}_{A0} & h^{14}_{AA} \\
h^{11}_{B0} & h^{11}_{BA} & h^{11}_{BB} & h^{12}_{B0} & h^{12}_{BA} & h^{12}_{BB} & h^{12}_{BC} & h^{12}_{BD} & h^{13}_{B0} & h^{13}_{BA} & h^{14}_{B0} & h^{14}_{BA} \\
h^{21}_{00} & h^{21}_{0A} & h^{21}_{0B} & h^{22}_{00} & h^{22}_{0A} & h^{22}_{0B} & h^{22}_{0C} & h^{22}_{0D} & h^{23}_{00} & h^{23}_{0A} & h^{24}_{00} & h^{24}_{0A} \\
h^{21}_{A0} & h^{21}_{AA} & h^{21}_{AB} & h^{22}_{A0} & h^{22}_{AA} & h^{22}_{AB} & h^{22}_{AC} & h^{22}_{AD} & h^{23}_{A0} & h^{23}_{AA} & h^{24}_{A0} & h^{24}_{AA} \\
h^{21}_{B0} & h^{21}_{BA} & h^{21}_{BB} & h^{22}_{B0} & h^{22}_{BA} & h^{22}_{BB} & h^{22}_{BC} & h^{22}_{BD} & h^{23}_{B0} & h^{23}_{BA} & h^{24}_{B0} & h^{24}_{BA} \\
h^{21}_{C0} & h^{21}_{CA} & h^{21}_{CB} & h^{22}_{C0} & h^{22}_{CA} & h^{22}_{CB} & h^{22}_{CC} & h^{22}_{CD} & h^{23}_{C0} & h^{23}_{CA} & h^{24}_{C0} & h^{24}_{CA} \\
h^{21}_{D0} & h^{21}_{DA} & h^{21}_{DB} & h^{22}_{D0} & h^{22}_{DA} & h^{22}_{DB} & h^{22}_{DC} & h^{22}_{DD} & h^{23}_{D0} & h^{23}_{DA} & h^{24}_{D0} & h^{24}_{DA} \\
h^{31}_{00} & h^{31}_{0A} & h^{31}_{0B} & h^{32}_{00} & h^{32}_{0A} & h^{32}_{0B} & h^{32}_{0C} & h^{32}_{0D} & h^{33}_{00} & h^{33}_{0A} & h^{34}_{00} & h^{34}_{0A} \\
h^{31}_{A0} & h^{31}_{AA} & h^{31}_{AB} & h^{32}_{A0} & h^{32}_{AA} & h^{32}_{AB} & h^{32}_{AC} & h^{32}_{AD} & h^{33}_{A0} & h^{33}_{AA} & h^{34}_{A0} & h^{34}_{AA} \\
h^{41}_{00} & h^{41}_{0A} & h^{41}_{0B} & h^{42}_{00} & h^{42}_{0A} & h^{42}_{0B} & h^{42}_{0C} & h^{42}_{0D} & h^{43}_{00} & h^{43}_{0A} & h^{44}_{00} & h^{44}_{0A} \\
h^{41}_{A0} & h^{41}_{AA} & h^{41}_{AB} & h^{42}_{A0} & h^{42}_{AA} & h^{42}_{AB} & h^{42}_{AC} & h^{42}_{AD} & h^{43}_{A0} & h^{43}_{AA} & h^{44}_{A0} & h^{44}_{AA}
\end{pmatrix} \tag{11}$$

The matrix for $\hat{\mathbf{\Delta}}(k)$ has the same 12×12 dimensionality with all elements equal zero except,

$$\hat{\mathbf{\Delta}}^{12}_{AB}(k) = \hat{\mathbf{\Delta}}^{21}_{BA}(k) = \hat{\mathbf{\Delta}}^{12}_{BA}(k) = \hat{\mathbf{\Delta}}^{21}_{AB}(k) = \frac{m-1}{m} \frac{\sin(kL_{12})}{m\rho k L_{12}}, \tag{12}$$

$$\hat{\mathbf{\Delta}}^{23}_{CA}(k) = \hat{\mathbf{\Delta}}^{32}_{AC}(k) = \frac{\sin(kL_{23})}{m\rho k L_{23}}, \tag{13}$$

and

$$\hat{\mathbf{\Delta}}^{24}_{DA}(k) = \hat{\mathbf{\Delta}}^{42}_{AD}(k) = \frac{\sin(kL_{24})}{m\rho k L_{24}} . \tag{14}$$

Here superscript 1 stands for the O monomers, 2 – for the Si monomers and 3 and 4 – for both CH_3 monomers. The chain length is m, which equals to the number of either oxygen or silicon atoms.

The partial pair correlation functions $h_{\alpha\beta}(r)$ that result from the solution of equation (7), do not have an immediate physical meaning. The usual physical meaning has the atom-atom (the same in the case of homo-nuclear chain) total pair correlation function or atom-atom total radial distribution function,

$$g^{total}_{ab}(r) = \sum_{ij} h^{ab}_{ij}(r) + 1 , \tag{15}$$

where the sum is over the bonding states of the sites of the atoms a and b.

3. Closure conditions

To solve OZ equation (9) we have used polymer PY (PPY) and polymer HNC (PHNC) closures. The PPY closure reads,

$$c_{00}^{ab}(r) = f_{ab}(r)\left(t_{00}^{ab}(r)+1\right) \tag{16}$$

$$c_{0K}^{ab}(r) = f_{ab}(r)t_{0K}^{ab}(r), \quad c_{K0}^{ab}(r) = f_{ab}(r)t_{K0}^{ab}(r), \quad c_{MK}^{ab}(r) = f_{ab}(r)t_{MK}^{ab}(r) \tag{17}$$

and the PHNC closure

$$c_{00}^{ab}(r) = g_{00}^{ab}(r) - t_{00}^{ab}(r) - 1, \tag{18}$$

$$c_{0K}^{ab}(r) = \left(g_{00}^{ab}(r)-1\right)t_{0K}^{ab}, \;\; c_{K0}^{ab}(r) = \left(g_{00}^{ab}(r)-1\right)t_{K0}^{ab}, \tag{19}$$

$$c_{MK}^{ab}(r) = g_{00}^{ab}(r)\left(t_{M0}^{ab}(r)t_{0K}^{ab}(r) - t_{MK}^{ab}(r)\right) - t_{MK}^{ab}(r), \tag{20}$$

where

$$t_{\alpha\beta}^{ab}(r) = h_{\alpha\beta}^{ab}(r) - c_{\alpha\beta}^{ab}(r), \quad f_{ab}(r) = \exp\left(-U_{LJ}(r)/kT\right) - 1, \tag{21}$$

$$g_{00}^{ab}(r) = \exp\left(-U_{LJ}(r)/kT + t_{00}^{ab}(r)\right), \tag{22}$$

$U_{LJ}(r)$ is the nonbonded Lennard-Jones potential of the UA model of the PDMS.

C. Application to the confined PDMS melts

Within the framework of integral equation theory the equation for polymer partial density profiles has the form,

$$y_i^a(z) = \delta_{i0} + 2\pi\rho \sum_{b=1}^{4}\sum_j\sum_k \int_{z-\frac{1}{2}[\sigma_a+\sigma_b]}^{z+\frac{1}{2}[\sigma_a+\sigma_b]} \left(\int_{|z_1-z|}^{\frac{1}{2}[\sigma_a+\sigma_b]} r c_{ij}^{ab}(r)dr\right)\alpha_{jk}h_k^b(z_1)dz_1, \tag{23}$$

where $y_i^a(z)$ are the partial cavity distribution functions. The coefficients α_{jk} in equation (23) are the elements of the normalized density matrix while the subscripts i, j and k run over the bonding states of the sites of the corresponding atoms O, Si and CH_3. The most important ingredients of equation (23) are the partial direct correlation functions c_{ij}^{ab} that characterize the bulk system. These functions are the input for the inhomogeneous fluid calculations and have been obtained in previous section, together with the partial pair correlation functions.

By applying the PPY approximation to the partial polymer-surface correlations, the relation between $y_i^a(z)$ and polymer-surface correlation functions, $h_i^a(z)$, reads,

$$h_i^a(z) + \delta_{i0} = e^{-\beta U_a^{\mathrm{pW}}(z)} y_i^a(z)\,. \tag{24}$$

The functions $U_a^{\mathrm{pW}}(z)$ in equation (24) represent potentials of the polymer-surface interaction. There are a few different ways to characterize this interactions. In present calculations

we have used the polymer-surface potentials that are representative of a surface containing oxygen atoms to represent an amorphous silica surface. These potentials have the form[26]

$$U_a^{\rm pW}(z) = A_{aw}\left[\frac{2}{7}\left(\frac{\sigma_{aw}}{z}\right)^7 - \frac{3}{4}\left(\frac{\sigma_{aw}}{z}\right)^4\right] \quad \text{for } a = \text{Si, O}$$
$$= A_{aw}\left[\frac{2}{5}\left(\frac{\sigma_{aw}}{z}\right)^{10} - \left(\frac{\sigma_{aw}}{z}\right)^4\right] \quad \text{for } a = \text{CH}_3\,, \tag{25}$$

where the coefficient $A_{aw} = 2\pi\rho_{ws}\sigma_{aw}^2\epsilon_{aw}$. This potential has been obtained by integrating over the surface plane that is assumed to consist of a given density of oxygen atoms, representing the OH groups on the surface. The surface density of OH groups was taken to be $\rho_{ws} = 0.039\,\text{Å}^{-2}$. This number was obtained in an atomistic simulation of amorphous silica[27]. The parameters of the wall-atom interactions are chosen to be the same as in the hybrid/UA model for the bulk PDMS, assuming that $\sigma_{aw} = \sigma_{a\text{O}}$ and $\epsilon_{aw} = \epsilon_{a\text{O}}$.

The corresponding normalized density profiles, $g_a(z) = \rho(z)/\rho_a^{\rm bulk}$, that are the subject of interest in this section, can be written as follows,

$$g_a(z) = 1 + \sum_i h_i^a(z)\,, \tag{26}$$

where the sum is over the bonding states of the sites of the atoms a.

V. RESULTS

The solutions of integral equations were obtained at a room temperature $T = 300\ K$ and a number density of PDMS molecules $\rho = 0.0004\ \mathring{A}^{-3}$. The PPY and PHNC closures give practically the same results. Therefore, only PHNC results are presented and discussed.

A. Radial distribution functions of a bulk PDMS melt

In figure 1 the total atom-atom radial distribution functions, that consist of both intramolecular and intermolecular contributions, are displayed. The symbols correspond to the simulation data. According to the parameters of the PDMS model, the bonding distances between methyl group and silicon, L_{23} and L_{24}, and especially between oxygen and silicon, L_{12}, are rather short. This creates some problems for the PROZA theory by making the chains less flexible than they are in reality. As a result, the structural properties of a four-atom model of the PDMS, that follows from the PROZA theory seem to be not very accurate when compared against simulation data where the chain flexibility is treated properly. In contrast, the PRISM theory, that takes the intramolecular part (i.e. chain flexibility) of the radial distribution function as an input, seems to provide a better description of the PDMS structure as follows from the results reported by Curro et al[7–11].

However, the subject of our interest in the description of bulk polymer is the intermolecular correlation functions. Figure 2 shows the results for intermolecular functions that have

been calculated from PROZA theory using the simplified PDMS model when the presence of oxygen atoms was counted in an effective way. We can see, that the theoretical curves reproduce general features of the simulated radial distribution functions, but fail to reproduce the details.

B. Local density of a PDMS melt near a single surface

The normalized local density distributions of silicon and carbon atoms next to a single surface, that represents a filler particle, follow from our calculations are presented on figure 3. The similar results have been obtained from computer simulations of the full hybrid/UA model of the PDMS melt next to an atomistic silica surface. It can be seen that the pendant methyl groups of the PDMS chains seems to be closer to the silica surface than the silicon atoms on the backbone. This might be expected since the methyl group are more exposed and tend to shield the polymer backbone atoms.

We can see that interface between PDMS and silica consists of densely packed and partly ordered layers in which the polymer segments tend to run preferentially parallel to the solid surface. This perturbation of the polymer density and polymer ordering does not extend into the bulk phase more than three times the transverse diameter of the PDMS chain.

C. PDMS between two surfaces

The normalized local density distributions of silicon and carbon atoms across a slit formed by two surfaces each representing a filler particle, at different separations are shown on figure 4. The calculations have been performed in the way that the density of polymer in the slit was not fixed *a priori*, but is allowed to vary with the slit thickness in such a way that the contents of the slit is always in equilibrium with the bulk PDMS that is kept at fixed conditions.

Figure 4a shows the case when the slit thickness allows only for one polymer layer to be accommodated in a slit. Whenever more than one layer is present, the layers are not layers of single PDMS molecules, in the sense that monomers of a given polymer molecule participate in several layers and bridge them. It is clearly seen for the slit with two and three layers where the polymer density at the middle of the slit is not zero. From these results we can see that silicon atoms are responsible for polymer stratification while carbon groups result in bridging effect.

In particular, we can see that local density distribution indicates very high probability for the polymer to be adsorbed on the silica surface by means of a single CH_3 methyl group while the second CH_3 group is placed away from the surface as it is shown schematically on figure 3. The pendant methyl groups of the PDMS chains are closer to the filler surface than the silicon atoms on the backbone. Again this seems to be physically correct result since the methyl groups are more exposed and tend to shield the polymer backbone atoms.

As follows from our calculations, in the immediate vicinity of the particle surface there is a shell around filler particles formed by an adsorbed polymer. The thickness of this shell does not exceed 1.5 nm; the shall is strongly attached to the surface of filler particle and can be associated with the immobile layer. That may result in the limiting of the mobility of adsorbed molecules. This agree well with numerous experimental evidence which suggest that the restriction of chain mobility does not extend throughout the material but affects only the chains within a few nanometers of the filler surface.

D. Solvation pressure

Once density profiles are known, some other properties of the composites can be calculated. In particular, an equilibrium property of the fluid confined by a slit-like pore is the pressure acting on the particle surfaces in the direction perpendicular to the surfaces, or local stress or normal pressure, P_N. It can be calculated from the density profiles, and as a function of gap width between filler particles by[28–30]

$$\beta P_N(H) = -\beta \sum_a \int_0^{H/2} \frac{\partial U_a^{\mathrm{pW}}(z,H)}{\partial z} \rho_a(z,H) dz \,, \tag{27}$$

where H is the separation between surfaces of two particles, while z is the distance from the center of the polymer unit from to the particle surface. The normal pressure, $P_N(H)$, measured relative to the bulk pressure, P_B, *i.e.*, pressure of a pure polymer that is at the same conditions as a composite, will define the solvation pressure, $\Pi(H)$,

$$\Pi(H) = P_N(H) - P_B. \tag{28}$$

The bulk pressure is one of the parameters that determine the thermodynamic state of the bulk polymer melt. It can be calculated independently or can be identified as a limiting value of the normal pressure acting between surfaces at infinite separation, i.e. at very low content of the filler particles. To satisfy the self-consistency of the numerical procedure, we used the second possibility *i.e.*, we assume $P_B \equiv P_N(H \to \infty)$. Particularly, to calculate bulk pressure we used suface-to-surface separation of 50 nm, that according to figure 3 provides us well defined homogeneous region.

We can see that there is large repulsive barrier at the separation between surfaces around 10Å. If we look for the density distribution at that separation we find that this gap allows for a single polymer layer.

VI. DISCUSSIONS AND CONCLUSIONS

One further aspect that should be taken into account concerns the aggregation of silica particles embedded into the PDMS melt. Quite recently[31] it has been shown experimentally that the aggregates of nanometric silica spheres have a strong influence on the mechanical

properties of the latex/silica nanocomposite. Usually it is assumed that clustering of filler particles occurs because of strong attractive van der Waals forces that are always present between particles at short distances. For this case the aggregation (vdW aggregation) will occur if the separation between filler surfaces will be smaller than 10Å when no polymer will be in the gap. Another possibility for the vdW aggregation can be expected when the polymer structuring (layering) near surface will be diminished by tuning polymer-particle interaction (25). Indeed, it was observed[31] that average aggregation number to be tuneable via the precursor solution pH that in fact may influence polymer density distribution in the particle's neighborhood[36].

On other hand, the average spacing $\langle\delta\rangle$ between silica particles as function of volume fraction,

$$\phi = \frac{\pi}{6}\frac{N_f}{V}D^3\,, \tag{29}$$

occupied by N_f filler particles can be estimated from:

$$\langle\delta\rangle = D\left[\left(\frac{1}{6}\frac{\pi\sqrt{2}}{\phi}\right)^{1/3} - 1\right]\,, \tag{30}$$

where D is the hard-core diameter of the silica sphere. It follows that at the same loading (the same volume fraction), particles with larger diameter D will be separated by larger gaps. For example, in the case of particle diameter $D = 10$nm and particle volume fraction $\phi = 0.35$, the average gap width between particles is around 30Å while in the case $D = 100$nm gap width increases up to 300Å. Interestingly, experimental studies show that smaller particles are much more effective at reinforcing polymers than large particles. Thus, the separation between particles and conditions of the geometrical confinement in the gap between them can be one of the important ingredients for reinforcement to occur.

Finally, similarly to the monatomic molecular liquids, polymer chains next to the confining surfaces form layers. The layers in molecular liquids are formed by the individual molecules, i.e. one molecule participate in the formation only one layer. In contrast, the polymer molecule usually participates in few different layers. Because of this, the part of polymer matrix that forms layered structure has very low mobility or even are immobilized; such polymer chains can be associated with tightly bound polymer. From the same reason, polymer in the region that follows layered region still does not represent bulk polymer since some of the chains from this region are parts of the immobile polymer; such polymer chains can be associated with loosely bound polymer (see figure 2 and figure 6).

The existence of these two regions in confined polymer melts has been suggested by Tsagaropoulos and Eisenberg[32] in their model to explain experimental data on two glass transitions in the polymer/particle systems. According to their measurements, a tightly bound polymer has very low spin-spin relaxation time (T_2) that does not change significantly with temperature. This has been explained that tightly bound polymer does not participate in either of two glass transition. On the other hand, a polymer beyond this layer exhibits a usual glass transition but the T_2 value was notably lower than the T_2 of the unfilled polymer. This observation was attributed to the existence of a restricted mobility layer.

The thickness of of the interfacial polymer layer reported in the literature in experimental studies of PDMS/silica systems is: 5 nm using neutron scattering[33], 0.8 nm using NMR[34], 1-25 nm using dielectric relaxation spectroscopy (DRS)[35]. If the interfacial layer will be defined as a region where local polymer density oscillates, then both our earlier simulation data[36] and present integral equation results are within the range of observations.

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TABLE I: Estimate of the average separation between filler particles in a polymer/particle mixture

particle diameter D, nm	volume fraction ϕ	weight fraction	separation, eq (30) $\langle\delta\rangle$, nm
10	6.1	9.7	13
10	9.9	15.3	10
10	15.7	23.5	6.8
10	25	-	4.4
10	35	-	2.8

Figure captions

Fig. 1 Total radial distribution functions $g_{ab}^{total}(r)$ as calculated from PROZA/PHNC theory (solid lines) and MD simulations (open circles) using united atom model.

Fig. 2 Intermolecular part of the total radial distribution functions $g_{ab}^{total}(r)$ as calculated from PROZA/PHNC theory (solid lines) and MD simulations (open circles) using united atom model.

Fig. 3 Normalized local density of silicon and united carbon atoms of the PDMS melt next to a single silica surface as calculated from the integral equation theory. The right-hand side shows a schematic interpretation of the density profiles.

Fig. 4 Normalized local density of silicon and carbon atoms of the PDMS melt in the four different slits formed by a surfaces of a pair of filler particles as calculated from the integral equation theory. The notation of lines is the same as in figure 3.

Fig. 5 The solvation pressure exerted by a model PDMS melt on filler particles as function of the separation between filler surfaces.

Fig. 6 Normalized local density of silicon and carbon atoms of the PDMS melt in a wide slit formed by a surfaces of a pair of filler particles. We can see the coexistence of tightly bound (region with density oscillations) and loosely bound (region without oscillations) polymer. The notation of lines is the same as in figure 3.

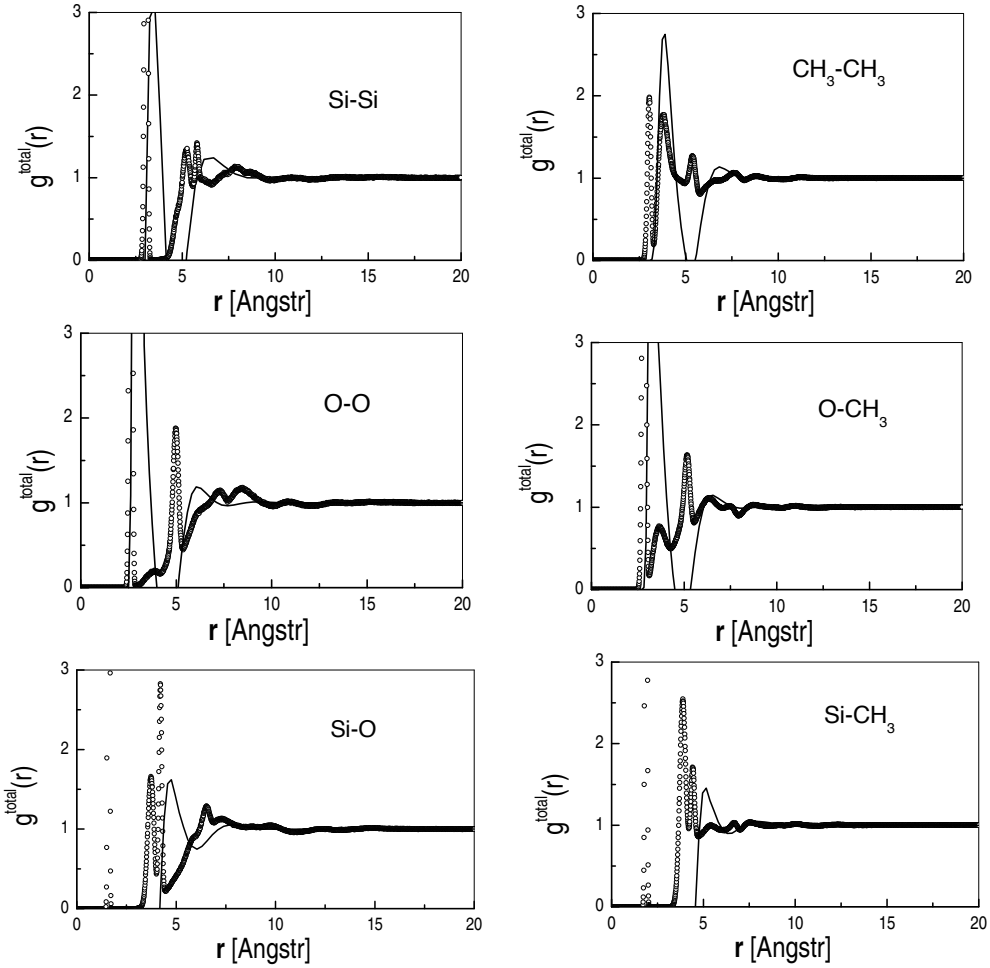

FIG. 1:

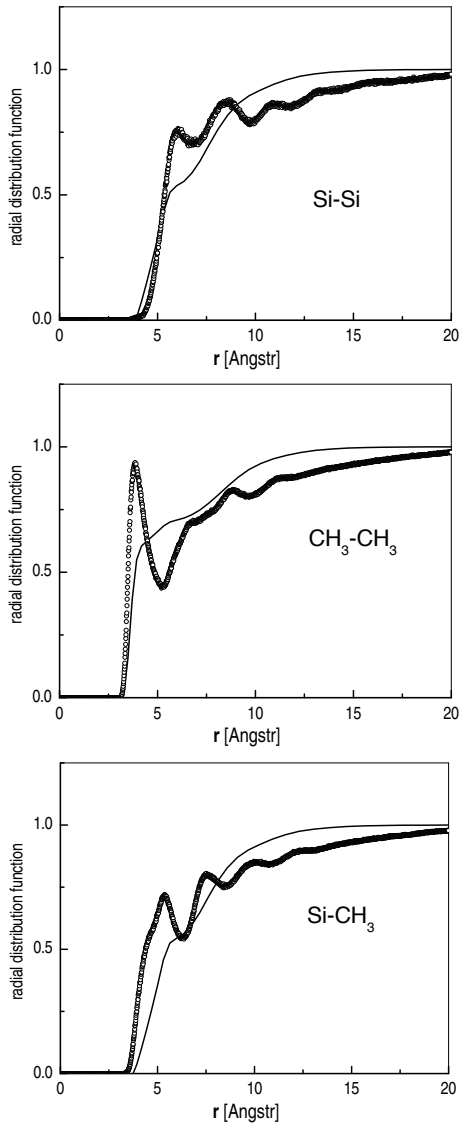
radial distribution function
1.0
0.5
0.0
0
5
10
15
20
r [Angstr]
Si-Si
CH3-CH3
Si-CH3

FIG. 2:

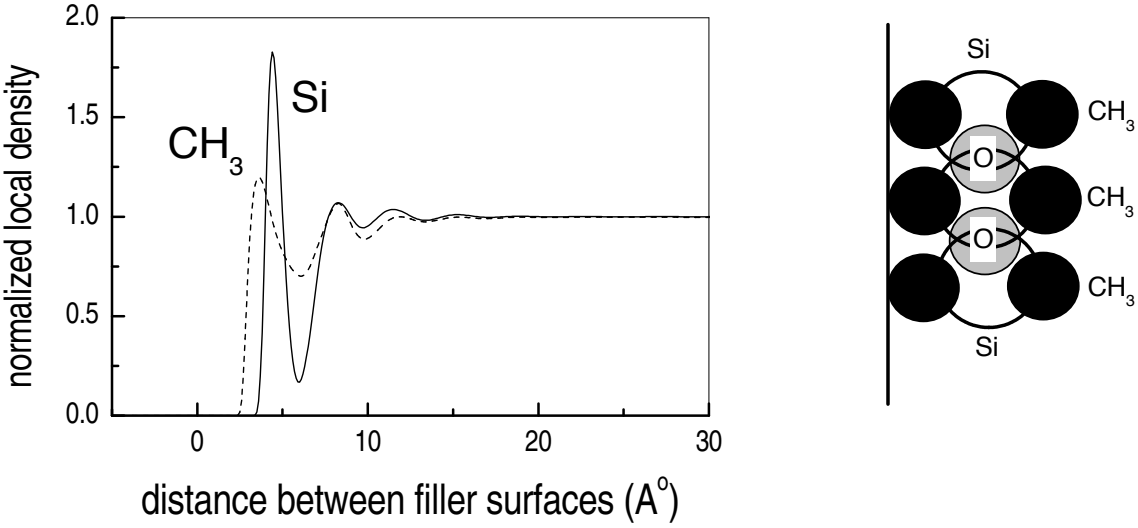
2.0
1.5
1.0
0.5
0.0
normalized local density
Si
CH3
0
10
20
30
distance between filler surfaces (A°)
Si
CH3
O
CH3
O
CH3
Si

FIG. 3:

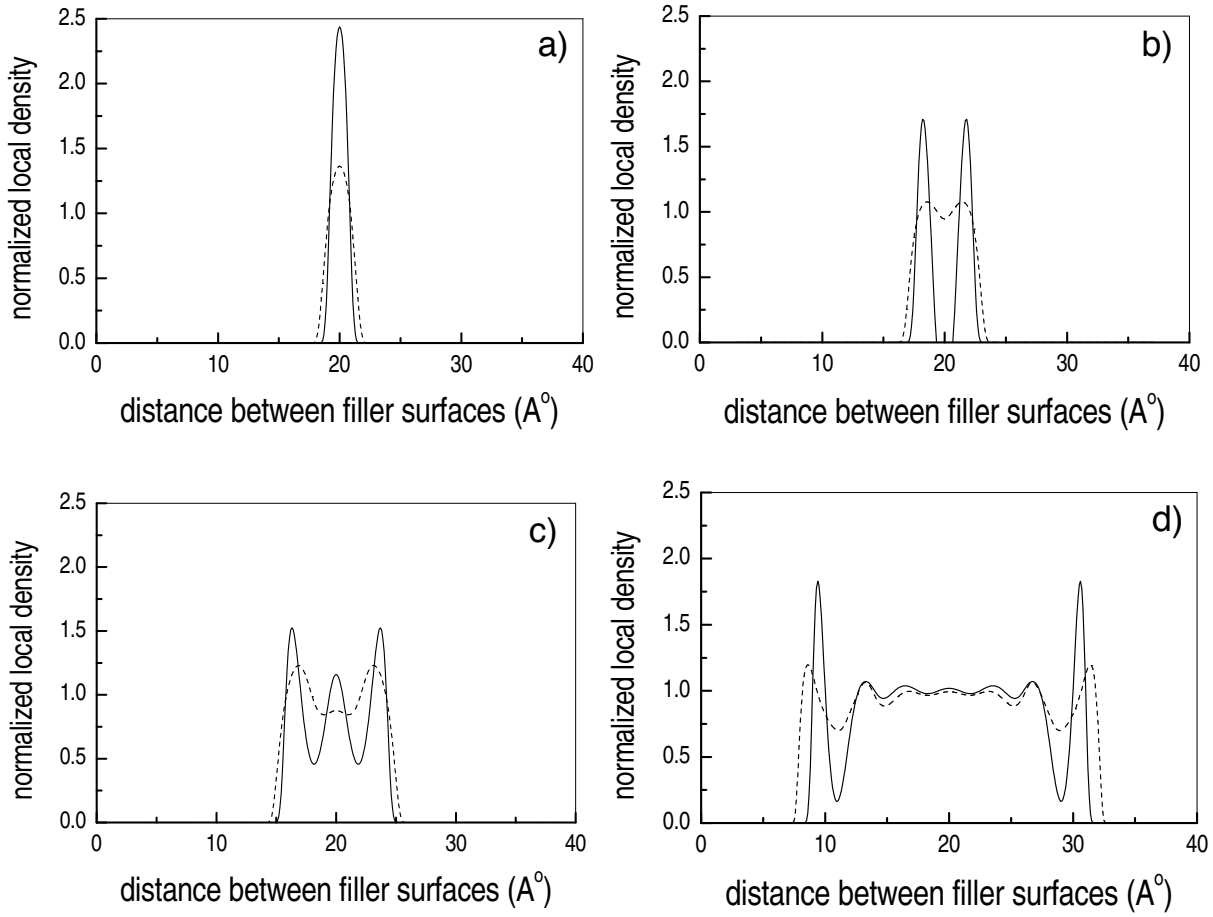
a)
b)
c)
d)
normalized local density
distance between filler surfaces (A°)
0.0
0.5
1.0
1.5
2.0
2.5
0
10
20
30
40

FIG. 4:

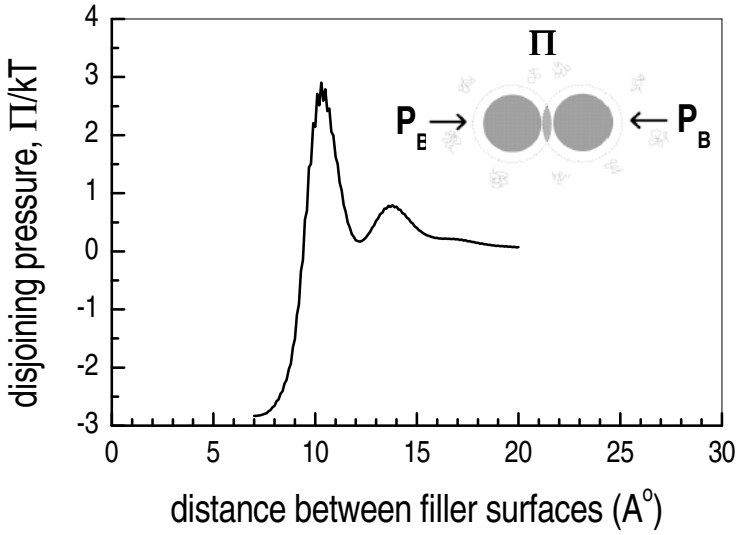
Π
P_B
P_B
disjoining pressure, Π/kT
distance between filler surfaces (A°)
4
3
2
1
0
-1
-2
-3
0
5
10
15
20
25
30

FIG. 5:

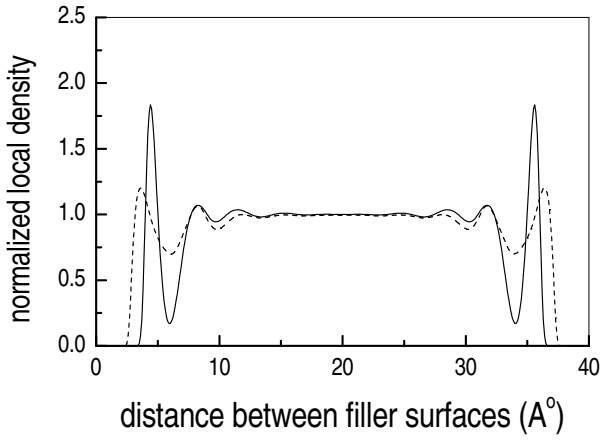
normalized local density
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
distance between filler surfaces (A°)

FIG. 6: