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Phase transitions of semiflexible hard-sphere chain liquids

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We present a density-functional theory for describing liquid-crystalline phase transitions in a fluid of semiflexible hard-sphere chain molecules based on the Onsager second-virial approximation for the free energy. Key ingredients of this theory are the generation of semiflexible chain conformations and calculation of the pair excluded volume and excluded area using a single-chain Monte Carlo enumeration method. First, we investigate the isotropic-nematic phase transition. Next, the theory is extended to account for a smectic-A phase by a bifurcation analysis around the nematic solution. The perturbation is calculated using a lowest-order Fourier series representation.

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The system of hard-sphere chain molecules has been studied extensively, as it is reasonable to expect that this model provides a suitable reference system in a perturbation theory for polyatomic molecular fluids interacting by more complex and realistic intermolecular forces [1,2]. Computer simulations have shown that fused hard-sphere chains with a sufficient degree of rigidity exhibit both nematic and smectic-A liquid-crystalline phases, in addition to the usual isotropic liquid and solid phases [1,3–7]. Studies of liquid-crystalline ordering in this model using density-functional theories have also been done [1,2,5,8,9], but so far have been restricted to the uniform isotropic and nematic phases. In this paper, we describe some preliminary steps to extend the density-functional treatment of fused hard-sphere chain fluids to consideration of smectic-A phases, which are characterized by a periodic one-dimensional spatial variation of the chain probability density. The Helmholtz free-energy functional F of the system is based on the Onsager second-virial approximation [10]. Minimizing F yields a self-consistent equation for the molecular probability density. For uniform (i.e., isotropic and nematic) phases, this equation involves the excluded volumes between pairs of chains, while the smectic-A phase depends on "excluded areas" between pairs of chains, both of which are evaluated by a Monte Carlo (MC) partial enumeration technique.

In this work, each molecule is modeled as a "pearl necklace" of N_c fused hard spheres, where the distance between two adjacent beads, i.e., the bond length, is denoted b, while the diameter of each sphere is denoted D. The conformation of a chain molecule is described by the positions $\mathbf{r}_1,\mathbf{r}_2,\ldots,\mathbf{r}_{N_c}$ of its N_c spheres, which is denoted $\mathbf{R}$ for simplicity. We denote the orientation of bonds in the chain by $\omega_1,\omega_2,\ldots\omega_{N_c-1}$. In a system containing N chain molecules, $\rho(\mathbf{R})$ is defined as the probability density of finding a molecule with configuration $\mathbf{R}$, which we take to be normalized as follows:

$$\int d\mathbf{R}\rho(\mathbf{R}) \equiv \int d\mathbf{r}_c d\omega_1 d\omega_2 \ldots d\omega_{N_c-1}\rho(\mathbf{R}) = N, \qquad (1)$$

where $\mathbf{r}_c$ denotes the position of any one sphere in the chain. Besides repulsive hard-sphere intramolecular and intermolecular forces between the chains, we assume a simple bond-bending energy for each chain, which is modeled by

$$\beta u_{n,n+1} = -\kappa \cos\theta_{n,n+1}\ (\kappa > 0), \qquad (2)$$

where $\theta_{n,n+1}$ is the angle between bonds n and $n+1$.

In the Onsager second-virial approximation, the Helmholtz free-energy functional of the system is given by [11]

$$\beta F = \int d\mathbf{R}\rho(\mathbf{R})[\ln\rho(\mathbf{R})\nu^{N_c} - 1 + \beta u_1(\mathbf{R})] - \frac{1}{2}\int d\mathbf{R}_1 d\mathbf{R}_2 \rho(\mathbf{R}_1)\rho(\mathbf{R}_2) f_M(\mathbf{R}_1,\mathbf{R}_2). \qquad (3)$$

The thermal volume, ν, is an unimportant parameter. Here $u_1(\mathbf{R})$ is the total one-body potential of a molecule, which includes the intrachain hard-sphere repulsions, the bending energies Eq. (2), as well as any possible external fields (which are not considered in this work). The second integral of Eq. (3) is related to interactions between chains: $f_M(\mathbf{R}_i,\mathbf{R}_j)$ is the standard Mayer function. For the hard-sphere model, the latter has values of 0 if there is no overlap between any spheres on two separate chains and -1 if there is any such overlap. Minimizing βF under the condition of the constraint Eq. (1) gives the following "self-consistent" equation for $\rho(\mathbf{R}_1)$:

$$\rho(\mathbf{R}_1) = c\exp[-\beta u_1(\mathbf{R}_1) + I(\mathbf{R}_1)], \qquad (4)$$

where c is a normalization constant, determined by Eq. (1), and $I(\mathbf{R}_1)$ is defined as

$$I(\mathbf{R}_1) \equiv \int d\mathbf{R}_2 f_M(\mathbf{R}_1,\mathbf{R}_2)\rho(\mathbf{R}_2). \qquad (5)$$

In this work, integrals such as in Eq. (5) over chain conformations represented by $\mathbf{R}_2$ are evaluated by partial enumeration of self-avoiding single-chain conformations generated by Monte Carlo methods.

The main step in solving Eq. (4) is to evaluate the integral $I(\mathbf{R}_1)$. First we consider the simplified case of a spatially uniform system, which applies to isotropic and nematic

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phases. In this case, it can be assumed that $\rho(\mathbf{R}_i)$ is translationally invariant and only depends on the set of bond orientations $\boldsymbol{\omega}_i \equiv (\omega_{i,1} \ldots \omega_{i,N_{c-1}})$, not on the positions of the spheres. Then Eq. (5) becomes

$$I(\mathbf{R}_1) \equiv I(\boldsymbol{\omega}_1) = -\int d\boldsymbol{\omega}_2 V_{ex}(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2)\rho(\boldsymbol{\omega}_2), \tag{6}$$

where $V_{ex}(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$ is the "excluded volume" between two chains with configurations $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$. In this work, for our discrete MC-generated single-chain configurations, the excluded volume was evaluated by Barrett's algorithm [12].

We define the conformation probability distribution function $f(\boldsymbol{\omega}) = \rho(\boldsymbol{\omega})/\rho$, where the average number density $\rho = N/V$. From Eq. (1), this satisfies

$$\int d\boldsymbol{\omega} f(\boldsymbol{\omega}) = 1. \tag{7}$$

It follows from the last four equations that the distribution function $f(\boldsymbol{\omega}_1)$ can be expressed as

$$f(\boldsymbol{\omega}_1) = c' f_0(\boldsymbol{\omega}_1) e^{I(\boldsymbol{\omega}_1)}, \tag{8}$$

where $f_0(\boldsymbol{\omega})$ is the "ideal gas" or unperturbed distribution function, $f_0(\boldsymbol{\omega}) \propto \exp[-\beta u_1(\boldsymbol{\omega})]$, and c' is an appropriate normalization constant. The average value of any function $g(\boldsymbol{\omega})$ with respect to the unperturbed distribution function is defined as

$$\langle g \rangle_{(0)} \equiv \int d\boldsymbol{\omega} f_0(\boldsymbol{\omega}) g(\boldsymbol{\omega}). \tag{9}$$

In the Monte Carlo enumeration method used in this work, a large number N_{MC} of single-chain conformations with probability proportional to $f_0(\boldsymbol{\omega})$ are generated, so the above equation becomes

$$\langle g \rangle_{(0)} \approx \frac{1}{N_{MC}} \sum_{i=1}^{N_{MC}} g(\boldsymbol{\omega}_i). \tag{10}$$

From Eqs. (6) and (8)–(10), for chains generated with probability proportional to $f_0(\boldsymbol{\omega}_2)$, we can express the final self-consistent equation in terms of $I(\boldsymbol{\omega}_1)$ as

$$I(\boldsymbol{\omega}_1) = -\rho \frac{\sum_{i=1}^{N_{MC}} V_{ex}(\boldsymbol{\omega}_1, \boldsymbol{\omega}_i) e^{I(\boldsymbol{\omega}_i)}}{\sum_{i=1}^{N_{MC}} e^{I(\boldsymbol{\omega}_i)}}. \tag{11}$$

We have solved Eq. (11) by an iteration method, which is started using an appropriate initial guess for $I(\boldsymbol{\omega})$ on the right-hand side of that equation, and is continued until successive iterates for $I(\boldsymbol{\omega})$ converge to unchanging values within some tolerance for each of the chain configurations $\boldsymbol{\omega}_1$ generated by the Monte Carlo method. In practice, we have found it worthwhile to use a "mixing" method [13] to achieve convergence, i.e., using the relation $I_{in}^{(n+1)} = \alpha I_{in}^{(n)} + (1-\alpha) I_{out}^{(n)}$, where $I_{in}^{(n)}$ is the input for the nth iteration of I [on the right-hand side of Eq. (11)] and $I_{out}^{(n)}$ is the output of that iteration [on the left-hand side of Eq. (11)]. Using values of $\alpha \approx 0.15$, together with filtering techniques [14] which minimize the variance of the unperturbed distribution $f_0(\boldsymbol{\omega})$ of end-to-end vectors, we have obtained accurate results using values of N_{MC} as low as 2000. In the Barrett algorithm [12] used for calculating the excluded volume, the number of random "Barrett" points for overlapping pairs of spheres on two molecules was chosen to be 5, a compromise between accuracy and computing time.

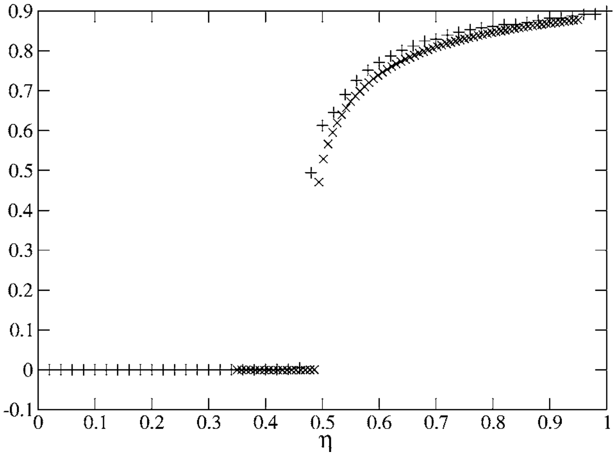

FIG. 1. Results for S_2 vs η, comparing the present theory for 14 000 chains (+) with the previous results (×) of Jaffer *et al.* [8].

We test the theory above by determining the nematic-isotropic phase transition for a chain of eight spheres with a high bending energy $\kappa = 50$, and compare with the results obtained by Jaffer *et al.* [8]. The latter work was based on an approximate analytical evaluation of the excluded volume for semiflexible hard sphere chains, which agreed well with computer simulations, and which should give nearly the same results as ours in the high bending energy regime. (We note that the theory described in Ref. [8] included scaled-particle theory corrections for high densities, which have been turned off in the present comparisons.) The main results are shown in Figs. 1 and 2, which plot the nematic order parameter S_2 and reduced pressure $P^* \equiv \beta P v_{mol}$ against the volume fraction $\eta \equiv \rho v_{mol}$, respectively. Here v_{mol} is the volume of a chain molecule [8], while the pressure P is obtained

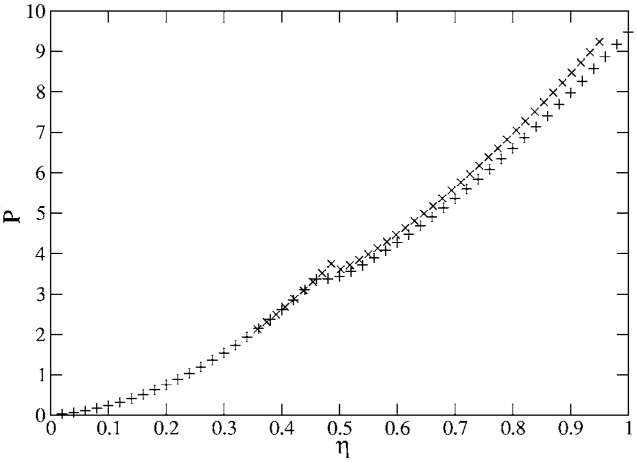

FIG. 2. Comparison between results for P^* vs η of the present theory for 11 000 chains (+) and previous results (×) (see Ref. [8]).

from a density derivative of the Helmholtz free energy F. Here the order parameter is given by the largest eigenvalue of the ordering tensor [4] with Cartesian components $Q_{\alpha,\beta} = \frac{1}{2}\langle 3r_{e,\alpha}r_{e,\beta} - \delta_{\alpha,\beta}\rangle$, where $\mathbf{r}_e$ is the end-to-end vector and the brackets denote averaging with the distribution function $f(\boldsymbol{\omega})$. The corresponding eigenvector is the mean direction of alignment (or *director*), which is found to fluctuate slightly during the numerical calculations [14]. The results for S_2 and P^* are in close agreement with those of Jaffer *et al.* [8]. In Fig. 1, the onset of nematic ordering is indicated by the abrupt jump to nonzero values of S_2 near a density $\eta \approx 0.49$. This is reflected in Fig. 2 by the appearance of a local maximum (minimum) in the isotropic (nematic) branches of P^* vs η. The precise values of the first-order isotropic-nematic transition densities should be determined by a Maxwell construction, but we have not performed this. It is uncertain at this stage if the small differences between the present results and those of Ref. [8] are due to numerical limitations in the present treatment or to differences between the theories. In principle, the present work is an exact implementation of the Onsager theory for semiflexible chains while that of Ref. [8] contains further approximations, although we expect these differences to have slight effects for the high bending energies κ considered here.

We now go on to describe the application of the theory to smectic-A phases, again based on the fundamental self-consistent Eqs. (4) and (5). In the smectic-A phase the molecules are positionally ordered in the direction parallel to the director and disordered in the other two directions. Defining the z axis to be along the director, this means that now $\rho(\mathbf{R}) = \rho(z,\boldsymbol{\omega})$, where z is taken to be the z coordinate of the midpoint of a chain. As before, we represent the probability density in terms of the conformation distribution function $f(z,\boldsymbol{\omega}) = \rho(z,\boldsymbol{\omega})/\rho$, which now satisfies the normalization condition

$$\frac{1}{d}\int_0^d dz d\boldsymbol{\omega} f(z,\boldsymbol{\omega}) = 1, \tag{12}$$

where d is the smectic period. The function $I(\mathbf{R}_1)$ in Eqs. (4) and (5) becomes

$$I(z_1,\boldsymbol{\omega}_1) = -\rho\int dz_2 d\boldsymbol{\omega}_2 A(z_1,\boldsymbol{\omega}_1;z_2,\boldsymbol{\omega}_2) f(z_2,\boldsymbol{\omega}_2), \tag{13}$$

where $A(z_1,\boldsymbol{\omega}_1;z_2,\boldsymbol{\omega}_2)$ is the excluded area between chains 1 and 2, defined as

$$A(z_1,\boldsymbol{\omega}_1;z_2,\boldsymbol{\omega}_2) = -\int dx_2 dy_2 f_M(\mathbf{R}_1,\mathbf{R}_2). \tag{14}$$

Due to translational invariance, the function $A(z_1\boldsymbol{\omega}_1, z_2\boldsymbol{\omega}_2)$ only depends on the relative distance $z_{21} \equiv (z_2 - z_1)$ and not on z_1 and z_2 separately. Again, we used Barrett's algorithm [12] for the calculation of the excluded area.

Following the analyses of Mulder [15], Poniewierski [16], and van Roij *et al.* [17] for perfectly rigid molecules, we assume that the solution for $f(z,\boldsymbol{\omega})$ is a small perturbation around the nematic solution $f(\boldsymbol{\omega})$ discussed previously, i.e.,

$$f(z,\boldsymbol{\omega}) = f(\boldsymbol{\omega}) + \epsilon\Delta f(z,\boldsymbol{\omega}), \tag{15}$$

where ϵ is a control parameter, assumed to be $|\epsilon| \ll 1$. From Eqs. (13) and (15), $I(z_1,\boldsymbol{\omega}_1)$ can be written as

$$I(z_1,\boldsymbol{\omega}_1) = I(\boldsymbol{\omega}_1) + \epsilon\Delta I(z_1,\boldsymbol{\omega}_1), \tag{16}$$

where

$$\Delta I(z_1,\boldsymbol{\omega}_1) = -\rho\int dz_2 d\boldsymbol{\omega}_2 A(z_1,\boldsymbol{\omega}_1;z_2,\boldsymbol{\omega}_2)\Delta f(z_2,\boldsymbol{\omega}_2). \tag{17}$$

$\Delta f(z,\boldsymbol{\omega})$ should be a periodic function in the z direction for all chain configurations $\boldsymbol{\omega}$ with period of d. Due to the asymmetry of chain conformations, generally $\Delta f(z,\boldsymbol{\omega})$ is not an even or odd function of z, and therefore both cosine and sine terms should appear in its Fourier series representation. In the lowest order Fourier representation, this function is approximated by

$$\Delta f(z,\boldsymbol{\omega}) = \phi_e(\boldsymbol{\omega})\cos(qz) + \phi_o(\boldsymbol{\omega})\sin(qz), \tag{18}$$

where $q = 2\pi/d$ is the smectic wave number.

To leading order in ϵ, it can be shown from Eqs. (4), (5), and (15)–(18) that

$$\Delta f(z,\boldsymbol{\omega}) \approx f(\boldsymbol{\omega})\Delta I(z,\boldsymbol{\omega}). \tag{19}$$

Using the translational invariance discussed above, $A(z_1,\boldsymbol{\omega}_1;z_2,\boldsymbol{\omega}_2) = A(0,\boldsymbol{\omega}_1;z_{21},\boldsymbol{\omega}_2)$. Expressing $z_2 = z_{21} + z_1$ in the integrand of Eq. (17) and using the sine and cosine rules together with Eqs. (18) and (19), we obtain the following two coupled equations for the functions $\phi_e(\boldsymbol{\omega}_1)$ and $\phi_o(\boldsymbol{\omega}_1)$, namely:

$$\phi_e(\boldsymbol{\omega}_1) = -\rho f(\boldsymbol{\omega}_1)\left[\int d\boldsymbol{\omega}_2 A_c(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2;q)\phi_e(\boldsymbol{\omega}_2) + \int d\boldsymbol{\omega}_2 A_s(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2;q)\phi_o(\boldsymbol{\omega}_2)\right], \tag{20}$$

$$\phi_o(\boldsymbol{\omega}_1) = -\rho f(\boldsymbol{\omega}_1)\left[\int d\boldsymbol{\omega}_2 A_c(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2;q)\phi_o(\boldsymbol{\omega}_2) - \int d\boldsymbol{\omega}_2 A_s(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2;q)\phi_e(\boldsymbol{\omega}_2)\right], \tag{21}$$

where

$$A_c(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2;q) \equiv \int dz_{21} A(0,\boldsymbol{\omega}_1;z_{21},\boldsymbol{\omega}_2)\cos(qz_{21}), \tag{22}$$

and

$$A_s(\boldsymbol{\omega}_1,\boldsymbol{\omega}_2;q) \equiv \int dz_{21} A(0,\boldsymbol{\omega}_1;z_{21},\boldsymbol{\omega}_2)\sin(qz_{21}). \tag{23}$$

The above homogeneous equations always have trivial solutions of $\phi_e(\boldsymbol{\omega}) = \phi_o(\boldsymbol{\omega}) = 0$. Our objective is to find the smallest value of ρ which gives nontrivial solutions of those equations. As earlier, we have found that mixing methods are required to obtain convergent solutions: by trial and error, we have found that a suitable value of α for the present analysis

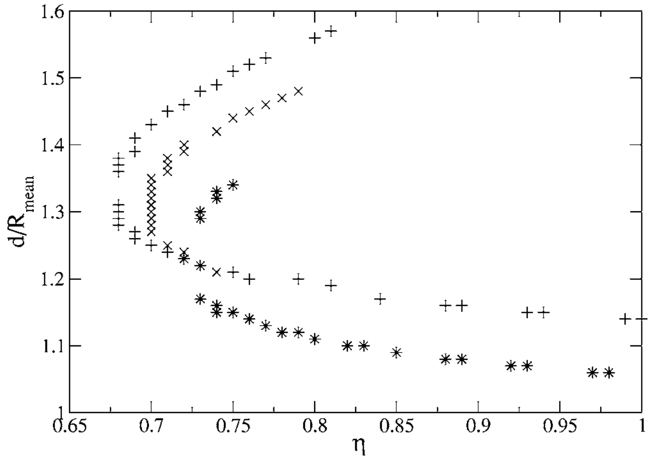

FIG. 3. Range of period d vs volume fraction η giving a nontrivial solution for the smectic-A phase, employing 2000 (+), 2500 (×), and 3000 (*) chains.

is near $\alpha=0.85$, much larger than needed earlier. Suitable values of $q\equiv 2\pi/d$ also had to be explored, generally starting with values for the period d near $R_{mean}\equiv\langle|\mathbf{r}_e|\rangle$. For the present case of high bending energy, chain conformations are nearly symmetrical under inversion and thus we find that $|\phi_o|$ is usually much smaller than $|\phi_e|$.

The range of d/R_{mean} vs η in which the final self-consistent equations Eqs. (20) and (21) have nontrivial solutions is shown in Fig. 3. All the points which exhibit a nontrivial solution are in the range $\eta>0.67$, although the exact location of the bifurcation point is not certain. All the d/R_{mean} values are greater than one, which is consistent with earlier studies [15]. The results shown in Fig. 3 exhibit features similar to that of the analysis of perfectly aligned hard rods in [15], namely that for a given value of η there is a range of values of q which allow a smectic-A solution. The true nematic-smectic-A bifurcation point should be at the lowest volume fraction η for which a smectic-A solution exists. For the eight-bead chains studied, this is roughly estimated to be at $\eta\approx 0.70$. To compare this value with available computer simulation studies, we should take account of higher-virial corrections, such as by the Parsons-Lee method [18,19] as applied in Ref. [20]. Applying also the "effective molecular volume" ideas of Ref. [2] for mapping hard-sphere chains to spherocylinders, we find that the nematic-smectic bifurcation at $\eta\approx 0.70$ is shifted to a much lower value $\eta\approx 0.36$. This is comparable with results obtained for the system of linear ($\kappa=\infty$) tangent hard-sphere chains with $N_c=7$ [1,6], which indicate that the lowest density for the smectic-A phase is between $\eta=0.356$ and 0.396. It is likely that the effects of the smaller N_c value (7 vs 8) and the infinite rigidity used in those studies approximately cancel.

The present studies have been limited to considering only eight-bead chains and a weak flexibility (i.e., high bending energy $\kappa=50$). It is of interest to extend the studies both to longer chains and to more flexible molecules. For more flexible molecules, it is likely that the approximations made in the theory by Jaffer *et al.* [8] with which we have compared our results (as well as those in related work by Fynewever and Yethiraj [5]) become less valid, and the results of the present theory should show greater differences from those works. The present studies of the smectic-A phase also were limited to a bifurcation treatment about the nematic phase and use of a lowest-order Fourier series representation of the probability density, which should only be accurate close to a second order or the spinodal point of a first-order nematic-smectic transition. For a more in-depth study of the smectic-A phase, the full nonlinear theory for this phase as well as higher-order terms in the Fourier series representation of the probability density should be retained.

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[1] D. C. Williamson and G. Jackson, J. Chem. Phys. **108**, 10294 (1998).
[2] S. Varga and I. Szalai, Mol. Phys. **98**, 693 (2000).
[3] M. Whittle and A. J. Masters, Mol. Phys. **72**, 247 (1991).
[4] M. R. Wilson and M. P. Allen, Mol. Phys. **80**, 277 (1993); M. R. Wilson, *ibid.* **81**, 675 (1994).
[5] H. Fynewever and A. Yethiraj, J. Chem. Phys. **108**, 1636 (1998); A. Yethiraj and H. Fynewever, Mol. Phys. **93**, 693 (1998).
[6] C. Vega, C. McBride, and L. G. MacDowell, J. Chem. Phys. **115**, 4203 (2001).
[7] C. McBride, C. Vega, and L. G. MacDowell, Phys. Rev. E **64**, 011703 (2001); C. McBride and C. Vega, J. Chem. Phys. **117**, 10370 (2002).
[8] K. M. Jaffer, S. B. Opps, D. E. Sullivan, B. G. Nickel, and L. Mederos, J. Chem. Phys. **114**, 3314 (2001).
[9] R. Diplock, D. E. Sullivan, K. M. Jaffer, and S. B. Opps, Phys. Rev. E **69**, 062701 (2004).
[10] L. Onsager, Ann. N.Y. Acad. Sci. **51**, 627 (1949).
[11] M. P. Allen, G. T. Evans, D. Frenkel, and B. M. Mulder, Adv. Chem. Phys. **86**, 1 (1993).
[12] A. J. Barrett, Macromolecules **18**, 196 (1985).
[13] A. A. Broyles, J. Chem. Phys. **33**, 456 (1960).
[14] H. B. Movahed, M.Sc. thesis, University of Guelph, 2005.
[15] B. Mulder, Phys. Rev. A **35**, 3095 (1987).
[16] A. Poniewierski, Phys. Rev. A **45**, 5605 (1992).
[17] R. van Roij, P. Bolhuis, B. Mulder, and D. Frenkel, Phys. Rev. E **52**, R1277 (1995).
[18] J. D. Parsons, Phys. Rev. A **19**, 1225 (1979).
[19] S.-D. Lee, J. Chem. Phys. **87**, 4972 (1987).
[20] M. Esposito and G. T. Evans, Mol. Phys. **83**, 835 (1994).