Fluid Mixtures of Parallel Hard Cubes

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The direct correlation function of a fluid mixture of parallel hard cubes is obtained by using Rosenfeld's fundamental measure approximation. This approximation is thermodynamically consistent (compressibility and virial equations of state are equal) and predicts a spinodal instability of the binary mixture for large-to-small side ratio larger than roughly 10, in qualitative agreement with simulations on the lattice version of the model. In two dimensions the system never demixes, also in agreement with the simulations. [S0031-9007(96)00203-7]

The theory of liquids is still looking for its "Ising model," i.e., an exactly solvable model which provides detailed information on the mechanisms involved in liquid behavior, and against which approximate theories could be tested. Instead the situation is the opposite, and the only analytical knowledge we have about liquid models has been obtained within the Percus-Yevick (PY) closure approximation of the Ornstein-Zernike integral equation, and consists of the direct correlation function (DCF) of a fluid mixture of hard spheres with an arbitrary number of component species [1], and that of a one-component fluid of adhesive spheres [2]. No other approximation has provided any new analytical results yet. Recently a very promising approximate scheme has been proposed: the *fundamental measure theory* (FMT) [3], which, as in the scaled particle theory, is based upon an interpolation between the low and high density limits of the fluid. By an appropriate choice of geometric measures, the FMT provides the following expression for the DCF of a fluid mixture of hard convex particles:

$$c_{\mu\nu}(\mathbf{r}) = [\chi_0 + \chi_1 R_{\mu\nu}(\mathbf{r}) + \chi_2 S_{\mu\nu}(\mathbf{r}) + \chi_3 V_{\mu\nu}(\mathbf{r})]$$
$$\times f_{\mu\nu}(\mathbf{r}), \qquad (1)$$

where $V_{\mu\nu}(\mathbf{r})$, $S_{\mu\nu}(\mathbf{r})$, and $R_{\mu\nu}(\mathbf{r})$ are, respectively, the volume, surface, and mean radius of the overlap region of particles of species μ and ν whose center-to-center vector is $\mathbf{r}$; $f_{\mu\nu}(\mathbf{r})$ is the Mayer function, and the χ_j's are density-dependent coefficients which can be obtained by means of the scaled particle prescription. When applied to a mixture of hard spheres, Eq. (1) reproduces the PY solution; besides, the same scheme can be generalized to any odd dimension and thus obtain the DCF of mixtures of hyperspheres (in one dimension it reproduces the exact DCF). In spite of these remarkable results, the FMT has never been applied to any molecular shape other than spheres, and it has recently been shown that, in general, Eq. (1) cannot be obtained for arbitrary molecular shapes without further approximations [4].

While the one-component hard-sphere model has provided an excellent starting point for the study of simple liquids, either as a reference system for perturbation theories [5] or as an ingredient for density functionals of inhomogeneous liquids [6], the situation is far poorer for additive fluid mixtures, due to the fact that the PY DCF predicts stability of a binary mixture of asymmetric hard spheres for any diameter ratio and any densities of the components [1]. This places the demixing transition out of the scope of an analytical treatment. Furthermore, this fact settled the belief that, contrary to what happens in other phase transitions (such as freezing), demixing cannot be driven by a pure entropic mechanism. This conclusion was questioned by Biben and Hansen [7], who found, by means of a numeric solution of the Ornstein-Zernike equation with a more accurate closure relation, that a mixture of additive hard spheres of diameter ratio larger than 5 and similar concentrations demixes. Further evidence of this fact has subsequently been provided by means of alternative approximations [8]. The question of whether a purely entropic mechanism can account for phase separation was affirmatively answered by Frenkel and Louis [9] by providing the exact solution of a two-dimensional lattice model of two types of particles. For continuous three-dimensional models the controversy is still open. Simulations cannot yet help because for too asymmetric mixtures relaxation times are prohibitively large [7]. Nevertheless, a recent simulation of a three-dimensional lattice model of hard cubes [10] provides strong evidence of phase separation for mixtures of cubes of side ratio 3, while no such evidence exists when the side ratio is 2 (in both cases the side of the small cubes is 2 lattice spacings). Besides its computational simplicity, this model is interesting on its own because even in the mixed phase it can completely fill the whole space at close packing, and therefore there is no trivial volume-driven phase separation. For the continuous version of the model, the fourth order virial expansion of the pair correlation function diverges at contact when the side ratio goes to infinity [10], thus suggesting the existence of a demixing transition.

In this Letter I will show how the FMT provides an expression for the DCF of a mixture of parallel hard

cubes. By means of this function the free energy of the mixture can be computed, and its concavity requirement leads to a spinodal instability for a large enough side ratio.

The starting point of the FMT is the choice of the geometric measures. This can be easily done if the Fourier transform of the Mayer function can be expressed as a sum of products of single particle functions. In our case, the Mayer function of two parallel hard cubes of sides σ_μ and σ_ν is simply

$$f_{\mu\nu}(\mathbf{r}) = -\Theta(\sigma_{\mu\nu} - |x|)\Theta(\sigma_{\mu\nu} - |y|)\Theta(\sigma_{\mu\nu} - |z|), \tag{2}$$

$\Theta(u)$ being the Heaviside step function ($=1$ for $u \geq 0$ and $=0$ otherwise), and $\sigma_{\mu\nu} = (\sigma_\mu + \sigma_\nu)/2$. Therefore, since the Fourier transform of any of the step functions appearing in (2) is

$$\int_{-\infty}^{\infty} dx\, e^{ikx}\Theta(\sigma_{\mu\nu} - |x|) = \frac{1}{2}[\hat{\tau}_\mu(k)\hat{\zeta}_\nu(k) \\ + \hat{\tau}_\nu(k)\hat{\zeta}_\mu(k)],$$

$\hat{\tau}_\mu(k) \equiv 2k^{-1}\sin(\sigma_\mu k/2)$ and $\hat{\zeta}_\mu(k) \equiv 2\cos(\sigma_\mu k/2)$, then the Fourier transform of the Mayer function can be expressed as

$$\hat{f}_{\mu\nu}(\mathbf{k}) = \frac{1}{8}[\hat{w}_\mu^{(3)}(\mathbf{k})\hat{w}_\nu^{(0)}(\mathbf{k}) + \hat{w}_\mu^{(0)}(\mathbf{k})\hat{w}_\nu^{(3)}(\mathbf{k}) \\ + \hat{\mathbf{w}}_\mu^{(2)}(\mathbf{k}) \cdot \hat{\mathbf{w}}_\nu^{(1)}(\mathbf{k}) + \hat{\mathbf{w}}_\mu^{(1)}(\mathbf{k}) \cdot \hat{\mathbf{w}}_\nu^{(2)}(\mathbf{k})], \tag{3}$$

where

$$\hat{w}_\mu^{(3)}(\mathbf{k}) \equiv \hat{\tau}_\mu(k_x)\hat{\tau}_\mu(k_y)\hat{\tau}_\mu(k_z), \tag{4a}$$

$$\hat{\mathbf{w}}_\mu^{(2)}(\mathbf{k}) \equiv (\hat{\zeta}_\mu(k_x)\hat{\tau}_\mu(k_y)\hat{\tau}_\mu(k_z), \hat{\tau}_\mu(k_x)\hat{\zeta}_\mu(k_y)\hat{\tau}_\mu(k_z), \\ \hat{\tau}_\mu(k_x)\hat{\tau}_\mu(k_y)\hat{\zeta}_\mu(k_z)), \tag{4b}$$

$$\hat{\mathbf{w}}_\mu^{(1)}(\mathbf{k}) \equiv (\hat{\tau}_\mu(k_x)\hat{\zeta}_\mu(k_y)\hat{\zeta}_\mu(k_z), \hat{\zeta}_\mu(k_x)\hat{\tau}_\mu(k_y)\hat{\zeta}_\mu(k_z), \\ \hat{\zeta}_\mu(k_x)\hat{\zeta}_\mu(k_y)\hat{\tau}_\mu(k_z)), \tag{4c}$$

$$\hat{w}_\mu^{(0)}(\mathbf{k}) \equiv \hat{\zeta}_\mu(k_x)\hat{\zeta}_\mu(k_y)\hat{\zeta}_\mu(k_z). \tag{4d}$$

Now that we have identified the so-called fundamental measures, the FMT postulates the following excess (over the ideal one) free energy functional of the set of density profiles for each component [3]:

$$\beta F^{\text{ex}}[\{\rho_\mu(\mathbf{r})\}] = \int d\mathbf{r}\, \Phi(\{n_i(\mathbf{r}), \mathbf{n}_j(\mathbf{r})\}) \tag{5}$$

($\beta^{-1} = k_B T$), where Φ is assumed to be a function of the following weighted densities:

$$n_0(\mathbf{r}) \equiv \sum_\mu \int \rho_\mu(\mathbf{r}')\frac{1}{8}w_\mu^{(0)}(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}', \tag{6a}$$

$$\mathbf{n}_1(\mathbf{r}) \equiv \sum_\mu \int \rho_\mu(\mathbf{r}')\frac{1}{24}\mathbf{w}_\mu^{(1)}(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}', \tag{6b}$$

$$\mathbf{n}_2(\mathbf{r}) \equiv \sum_\mu \int \rho_\mu(\mathbf{r}')\mathbf{w}_\mu^{(2)}(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}', \tag{6c}$$

$$n_3(\mathbf{r}) \equiv \sum_\mu \int \rho_\mu(\mathbf{r}')w_\mu^{(3)}(\mathbf{r} - \mathbf{r}')\, d\mathbf{r}' \tag{6d}$$

(the numerical coefficients have been chosen for convenience). The uniform limit of $n_i(\mathbf{r})$ is ξ_i ($i = 0, 3$), and that of $\mathbf{n}_j(\mathbf{r})$ is $\xi_j\mathbf{u}/3$ ($j = 1, 2$), where $\mathbf{u} \equiv (1, 1, 1)$ and the ξ's are the average density, mean radius, surface, and volume of the cubes:

$$(\xi_0, \xi_1, \xi_2, \xi_3) = \sum_\mu \left(1, \frac{\sigma_\mu}{2}, 6\sigma_\mu^2, \sigma_\mu^3\right)\rho_\mu. \tag{7}$$

The ith averaged density ($i = 0, 1, 2, 3$) is a function with dimensions (volume)$^{(i-3)/3}$; therefore Φ, whose dimensions are (volume)$^{-1}$, can be expanded as

$$\Phi = an_0 + A\mathbf{n}_1\mathbf{n}_2 + B\mathbf{n}_2\mathbf{n}_2\mathbf{n}_2, \tag{8}$$

where a, A, and B are, respectively, a scalar, a 2-index tensor, and a 3-index tensor, all dependent on n_3. The scaled-particle prescription imposes on Φ the following differential equation [3]:

$$-\Phi + \sum_\mu \rho_\mu\frac{\partial\Phi}{\partial\rho_\mu} + n_0 = \frac{\partial\Phi}{\partial n_3}, \tag{9}$$

which yields $a = a_0 - \ln(1 - n_3)$, A $= (1 - n_3)^{-1}$A$_0$, and B $= (1 - n_3)^{-2}$B$_0$, with a_0, A$_0$, and B$_0$ denoting a constant scalar, a constant 2-index tensor, and a constant 3-index tensor. The vanishing of the excess free energy per particle in the zero density limit leads to $a_0 = 0$. On the other hand, the uniform limit of this free energy imposes a simplified form for the tensors:

$$(A_0)_{ij} = \alpha_1\mathbf{u}_i\mathbf{u}_j + \gamma_1\delta_{ij}, \tag{10a}$$

$$(B_0)_{ijk} = \alpha_2\mathbf{u}_i\mathbf{u}_j\mathbf{u}_k + \gamma_2\mathbf{u}_i\delta_{ij}, \tag{10b}$$

$\alpha_{1,2}$ and $\gamma_{1,2}$ being numerical coefficients. Then

$$\Phi = -n_0\ln(1 - n_3) + \frac{\alpha_1 n_1 n_2 + \gamma_1\mathbf{n}_1 \cdot \mathbf{n}_2}{1 - n_3} \\ + \frac{\alpha_2 n_2^3 + \gamma_2 n_2\mathbf{n}_2 \cdot \mathbf{n}_2}{(1 - n_3)^2}, \tag{11}$$

where $n_i \equiv \mathbf{n}_i \cdot \mathbf{u}$ ($i = 1, 2$).

Now we have two routes to obtain the DCF of the fluid mixture: (i) from Eqs. (5), (6), and (11), as [6]

$$c_{\mu\nu}(\mathbf{r} - \mathbf{r}') = -\beta\frac{\delta F^{\text{ex}}[\{\rho_\mu(\mathbf{r})\}]}{\delta\rho_\mu(\mathbf{r})\delta\rho_\nu(\mathbf{r}')}\bigg|_{\{\rho_\mu(\mathbf{r})\}=\{\rho_\mu\}}, \tag{12}$$

and (ii) from Eq. (1), by explicitly obtaining the involved functions. This latter expression can easily be computed

because the overlap region of two parallel cubes of sides σ_μ and σ_ν is a parallelepiped of sides $L_{\mu\nu}(x)$, $L_{\mu\nu}(y)$, and $L_{\mu\nu}(z)$ [provided they do overlap, i.e., $f_{\mu\nu}(\mathbf{r}) = -1$], where

$$L_{\mu\nu}(s) = \begin{cases} \sigma_{\mu\nu} - \lambda_{\mu\nu} & \text{if } |s| \le \lambda_{\mu\nu}, \\ l\sigma_{\mu\nu} - |s| & \text{if } |s| > \lambda_{\mu\nu} \end{cases} \quad (13)$$

($\lambda_{\mu\nu} \equiv |\sigma_\mu - \sigma_\nu|/2$). Therefore

$$V_{\mu\nu}(\mathbf{r}) = L_{\mu\nu}(x)L_{\mu\nu}(y)L_{\mu\nu}(z), \quad (14a)$$

$$S_{\mu\nu}(\mathbf{r}) = 2\{L_{\mu\nu}(x)L_{\mu\nu}(y) + L_{\mu\nu}(x)L_{\mu\nu}(z) + L_{\mu\nu}(y)L_{\mu\nu}(z)\}, \quad (14b)$$

$$R_{\mu\nu}(\mathbf{r}) = \frac{1}{6}\{L_{\mu\nu}(x) + L_{\mu\nu}(y) + L_{\mu\nu}(z)\}. \quad (14c)$$

By matching both expressions of the DCF it follows that $\alpha_1 = 0$, $\gamma_1 = 3$, $\alpha_2 = 5/432$, and $\gamma_2 = -1/48$. Then

$$\chi_0 = \frac{1}{1 - \xi_3}, \quad (15a)$$

$$\chi_1 = \frac{\xi_2}{(1 - \xi_3)^2}, \quad (15b)$$

$$\chi_2 = \frac{\xi_1}{(1 - \xi_3)^2} + \frac{1}{36}\frac{\xi_2^2}{(1 - \xi_3)^3}, \quad (15c)$$

$$\chi_3 = \frac{\xi_0}{(1 - \xi_3)^2} + \frac{2\xi_1\xi_2}{(1 - \xi_3)^3} + \frac{1}{36}\frac{\xi_2^3}{(1 - \xi_3)^4}, \quad (15d)$$

and the excess free energy per unit volume turns out to be, in the uniform limit,

$$\Phi = -\xi_0 \ln(1 - \xi_3) + \frac{\xi_1\xi_2}{1 - \xi_3} + \frac{1}{216}\frac{\xi_2^3}{(1 - \xi_3)^2}. \quad (16)$$

The compressibility equation of state

$$\beta \frac{\partial P^c}{\partial \rho_\mu} = 1 - \sum_\mu \rho_\mu \hat{c}_{\mu\nu}(\mathbf{0}) \quad (17)$$

leads to

$$\beta P^c = \frac{\xi_0}{1 - \xi_3} + \frac{\xi_1\xi_2}{(1 - \xi_3)^2} + \frac{1}{108}\frac{\xi_2^3}{(1 - \xi_3)^3}. \quad (18)$$

On the other hand, the virial theorem provides a different expression for the pressure:

$$\beta P^v = \xi_0 + \frac{1}{6} \sum_{\mu,\nu} \rho_\mu \rho_\nu \int d\mathbf{r}\, \mathbf{r} \cdot \nabla f_{\mu\nu}(\mathbf{r}) g_{\mu\nu}(\mathbf{r}), \quad (19)$$

with $g_{\mu\nu}(\mathbf{r})$ the pair correlation function. Straightforward manipulations lead to

$$\beta P^v = \xi_0 - 4 \sum_{\mu,\nu} \rho_\mu \rho_\nu \sigma_{\mu\nu} \\ \times \int_0^{\sigma_{\mu\nu}} dy \int_0^{\sigma_{\mu\nu}} dz\, c_{\mu\nu}(\sigma_{\mu\nu}^-, y, z), \quad (20)$$

from which it follows that $P^v = P^c$. The expression found for the DCF of this system has thus the remark-

able property of being *thermodynamically consistent* without having imposed such a feature anywhere in the approximate scheme. Furthermore, this (unique) equation of state matches the second and third virial coefficients, which can be readily computed to be $B_2\rho^2 = \xi_0\xi_3 + \frac{2}{3}\xi_1\xi_2$ and $B_3\rho^3 = \xi_0\xi_3^2 + 2\xi_1\xi_2\xi_3 + \xi_2^3/108$ (where $\rho = \sum_\mu \rho_\mu = \xi_0$), but this is implicitly assumed in the theory [3].

A direct comparison with the simulations of Ref. [10] is meaningless, because the latter are performed on a lattice system with a lattice spacing comparable to the small particle size; moreover, there are no other results of this kind available for this model, so the accuracy of the result just presented still has to be tested. For the one-component system, however, both the exact virial coefficients and the virial expansion of approximate theories (such as PY) are known up to seventh order [11]. From them we can see that the values obtained from Eq. (18) match neither the exact ones nor those obtained from the PY approximation, from the fourth coefficient on. Thus we can conclude that the present results are—as expected—approximate, but they differ from the PY approximation, contrary to what happens for hard spheres (the equivalence for hard spheres might indeed be an exception rather than a rule).

But the most striking consequence which follows from the results presented thus far is the prediction of a spinodal instability of a binary mixture of hard cubes for large enough side ratio. Furthermore, this spinodal can be analytically computed within this approximation. Let us see how it can be done. The instability is caused by a violation of the concavity of the free energy. The concavity of this function can be expressed as the positive definiteness of the hessian matrix of the free energy per unit volume $f \equiv F/V$ as a function of the partial densities ρ_ν. Since f is given by $f = \sum_\nu \rho_\nu \mu_\nu - P$, with μ_ν the chemical potential of the ν component, by using the Gibbs-Duhem relation we can obtain [1]

$$M_{\nu\lambda} \equiv \beta \frac{\partial^2 f}{\partial \rho_\nu \partial \rho_\lambda} = \beta \frac{\partial \mu_\nu}{\partial \rho_\lambda} = \frac{1}{\rho_\nu}\delta_{\nu\lambda} - \hat{c}_{\nu\lambda}(\mathbf{0}). \quad (21)$$

From the expression for the DCF the 2×2 matrix M of the binary mixture can be readily computed, and the stability condition follows from the positiveness of its determinant—since all its elements are positive. By defining $\eta_\nu \equiv \sigma_\nu^3 \rho_\nu$, the packing fraction of species ν; $\eta \equiv \eta_1 + \eta_2 = \xi_3$, the total packing fraction of the fluid; $r \equiv \sigma_1/\sigma_2$, the large-to-small side ratio ($r \ge 1$); and $x \equiv \eta_1/\eta$, the relative packing fraction of the large component, a tedious but straightforward calculation yields

$$\rho_1\rho_2|M| = \frac{\eta^2}{(1 - \eta)^4}\left[1 + \frac{4}{\eta} + \frac{1}{\eta^2} - \frac{3(r - 1)^2}{r}x(1 - x)\right], \quad (22)$$
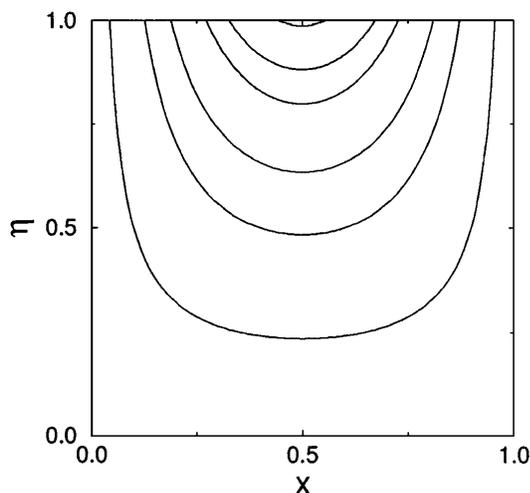
FIG. 1. Demixing phase diagram for a binary mixture of parallel hard cubes: η is the total packing fraction and x the relative packing fraction of the large cubes. Curves represent the spinodal lines for side ratios 10, 11, 12, 15, 20, and 50 (from top to bottom).

and thus the mixture is stable provided the expression within square brackets is positive.

An immediate consequence of this result is that the mixture is stable if and only if $1 \leq r < 5(1 + \sqrt{1 - 1/25}) \approx 9.98$. Above this threshold there is a region where the mixture phase separates (see Fig. 1), limited below by the curve

$$\eta^{-1} = 3^{1/2}\left[1 + \frac{(r-1)^2}{r} x(1-x) \right]^{1/2} - 2 . \quad (23)$$

Thus we have achieved a qualitative agreement with the simulations of Ref. [10]; however, a direct comparison of the results is, perhaps, too naive. In the simulations the authors find demixing for $r \geq 3$, while these calculations shift this value up to ≈ 10. But the simulations are performed on a lattice, and then the size of the small particle (2 lattice spacings in this case) is also important, for a larger size with the same size ratio implies a larger number of accessible sites on the lattice for the small particles, with the corresponding gain in entropy. Therefore, if the small particles are larger, it is plausible that the stability of the mixture increases to larger size ratios. The results for the continuous model we are dealing with in this Letter would correspond to the limit $\sigma_1 \longrightarrow \infty$ and $\sigma_2 \longrightarrow \infty$, while keeping σ_1/σ_2 constant, which explains its larger stability. Some simulations could ascertain this conclusion.

The two-dimensional case, i.e., a mixture of hard squares, is a simple reproduction of the calculations presented here. This is unusual in view of what happens for hard spheres [3], for which the FMT can be applied only in odd dimensions. For cubes the calculations can be done in a similar way no matter what the dimension.

In two dimensions, for instance, the form of the DCF is that of Eq. (1) except for the volume term, which is logically missing. Again the equation of state reproduces the three first terms of the virial expansion, as expected from the FMT. The novelty is that it can be shown that the binary mixture of hard squares is *always* stable, whichever the size ratio. It is interesting to note that the authors of Ref. [10] arrived at the same conclusion in their simulations. Full details on the hard-square mixture will be given elsewhere [12].

In summary, I have provided in this Letter the DCF of a new model, namely, a mixture of hard cubes, obtained by means of the FMT, an approximation introduced by Rosenfeld and thus far applied only to reproduce the results of a mixture of hard spheres. Apart from the importance of having analytical results for new models of liquids, the relevance of these calculations relies on the fact that a spinodal instability is predicted for the binary mixture, in qualitative agreement with the simulations performed on an equivalent lattice model. The calculations may serve as a reference for further studies on a related system, for instance, the orientational freezing of liquid crystals, if the model is extended to a mixture of parallelepipeds, or the polymer collapse, of which Ref. [10] reports some simulations. Of course it would also be interesting to apply these results to the lattice system in order to see whether they can reproduce the simulations quantitatively.

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[1] J. L. Lebowitz, Phys. Rev. A **133**, 895 (1964); J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).

[2] R. J. Baxter, J. Chem. Phys. **49**, 2770 (1991).

[3] Y. Rosenfeld, J. Chem. Phys. **89**, 4272 (1988); Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989).

[4] Y. Rosenfeld, Phys. Rev. E **50**, R3318 (1994).

[5] J.-P. Hansen and I. R. McDonal, *Theory of Simple Liquids* (Academic Press, London, 1986), 2nd ed.

[6] R. Evans, in *Inhomogeneous Fluids,* edited by D. Henderson (Dekker, New York, 1992).

[7] T. Biben and J.-P. Hansen, Phys. Rev. Lett. **66**, 2215 (1991).

[8] H. N. W. Lekkerkerker and A. Stroobants, Physica (Amsterdam) **195A**, 387 (1993); Y. Rosenfeld, Phys. Rev. Lett. **72**, 3831 (1994).

[9] D. Frenkel and A. A. Louis, Phys. Rev. Lett. **68**, 3363 (1992).

[10] M. Dijkstra and D. Frenkel, Phys. Rev. Lett. **72**, 298 (1994); M. Dijkstra, D. Frenkel, and J.-P. Hansen, J. Chem. Phys. **101**, 3179 (1994).

[11] W. G. Hoover and A. G. de Rocco, J. Chem. Phys. **36**, 3141 (1962); W. G. Hoover and J. C. Poirier, J. Chem. Phys. **38**, 327 (1963).

[12] J. A. Cuesta (to be published).