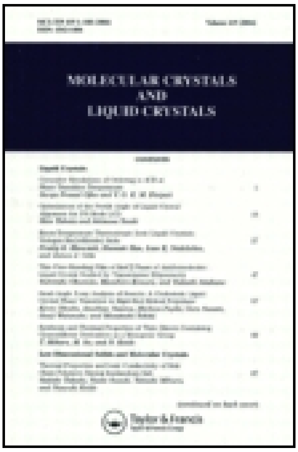

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Computer Simulation of Liquid Crystal-Mixtures with the Gay-Berne Potential

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COMPUTER SIMULATION OF LIQUID CRYSTAL - MIXTURES WITH THE GAY - BERNE POTENTIAL

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ABSTRACT We combined the Gay-Berne potential (with parameters optimized for typical liquid crystals) and the technique for simulation of mixtures. Using the Monte Carlo method, we studied spatial and orientational correlations for equimolar concentration. Preliminary two dimensional (2D) molecular dynamics results on time correlation functions are also presented.

INTRODUCTION

We used a Gaussian overlap potential as introduced by Berne and Pechukas[1] and modified by Gay and Berne[2] (GB)

$$U(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}) = 4\varepsilon(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}')\left(\left(\frac{\sigma_o}{r-\sigma(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}')+\sigma_o}\right)^{12} - \left(\frac{\sigma_o}{r-\sigma(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}')+\sigma_o}\right)^{6}\right),$$

where $\varepsilon(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}')$ and $\sigma(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}')$ are orientation-dependent Lennard-Jones parameters which serve to mimic an interaction between two ellipsoidal molecules. The orientation of the two particles is given by unit vectors $\mathbf{u}'_1$ and $\mathbf{u}'_2$, their separation by r; **r** is the intermolecular vector and **r'** the associated unit vector. For a detailed discussion of this model, see Luckhurst et al.[3]; suffice it to say that the full expressions for $\varepsilon(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}')$ and $\sigma(\mathbf{u}'_1,\mathbf{u}'_2,\mathbf{r}')$ contain 4 model parameters: ratio σ_e/σ_s, ratio $\varepsilon_e/\varepsilon_s$, ν and μ, which together describe the anisotropic interaction in detail.

To simulate a mixture of liquid crystal molecules, we used two types of GB molecules. They are introduced with quotients[4,5]

$\mu_2=\sigma_{22}/\sigma_{11}$, $\mu_{12}=\sigma_{12}/\sigma_{12}^{av}$,

$\nu_2=\varepsilon_{22}/\varepsilon_{11}$ and $\nu_{12}=\varepsilon_{12}/\varepsilon_{12}^{av}$,

where σ_{12}^{av} and ε_{12}^{av} are the arithmetic and geometric means, respectively:

$$\sigma_{12}^{av} = \frac{\sigma_{11}+\sigma_{22}}{2} \quad \text{and} \quad \varepsilon_{12}^{av} = \sqrt{\varepsilon_{11}\cdot\varepsilon_{22}}\,.$$

This is in accordance with the usual Lorentz-Berthelot rule. If we have interaction between two molecules of type 1, then the potential has parameters ε_{11} and σ_{11}...

MONTE CARLO SIMULATION

We have done Monte Carlo (MC) simulations[6,7] with **N=216** molecules in a cubic box, using periodic boundary conditions and the nearest image convention. The GB parameters ν and μ were set equal to **2** and **1**, respectively, furthermore σ_e/σ_s**=3** and $\varepsilon_e/\varepsilon_s$**=0.2**[3]. The reduced variables are: $T^*=k_BT/\varepsilon_o$, $\rho^*=N\sigma_o^3/V$ and $r^*=r/\sigma_o$. As usual, $\sigma_{11}=\sigma_o=1$ and $\varepsilon_{11}=\varepsilon_o=1$.

For thermalization we did at least 10.000 iterations per molecule. Initially all molecules were assumed to be of one type. They were given random orientations and situated at scc positions, initial density was $\rho^*=0.25$. After thermalizing at temperature $T^*=2$ and compressing to $\rho^*=0.3$ the temperature was lowered to $T^*=1$ Now the particles were randomly assigned to the two molecular types, and another thermalization followed. Finally, the temperature was lowered to $T^*=0.5$.

In the following we present the results for $\mathbf{T^*=1}$ and $\boldsymbol{\rho^*=0.3}$. Only one mixing parameter was changed for every experiment.

The order parameter P_2 was calculated from the Q tensor[6]

$$Q_{\alpha,\beta}=\frac{1}{N}\sum_{i=1}^{N}\frac{3u^i_\alpha u^i_\beta-\delta_{\alpha\beta}}{2}$$

as the largest eigenvalue. P_2 is for whole system, P_{21} for type 1 and P_{22} for type 2. The pair correlation function $g(r^*)$ is defined as[6,8] :

$$g(r^*)=\frac{V}{N^2}\left\langle\sum_i\sum_{j\neq i}\delta\,(r^*-r_{ij}^*)\right\rangle \quad .$$

$g_{11}(r^*)$ is $g(r^*)$ for molecules of type 1, $g_{22}(r^*)$ of type 2 and $g_{12}(r^*)$ for different species. We used the reduced pair correlation functions $g_r(r^*)$ for analyzing the mixing/demixing processes[9]:

$$g_r(r^*)=\frac{g_{11}(r^*)+g_{22}(r^*)}{2\cdot g_{12}(r^*)} \quad .$$

For an ideal mixture $g_r(r^*)$ is unity, while for demixed structures it is significantly greater than 1.

Results

At $T^*=1$ and $\rho^*=0.3$ all structures are in the smectic phase (Fig. 1). Immediately after separation in two types there was no significant difference between $g_{11}(r^*)$, $g_{22}(r^*)$ and $g_{12}(r^*)$, so that $g_r(r^*)$ fluctuated just around value one. This shows that the separation was done randomly.

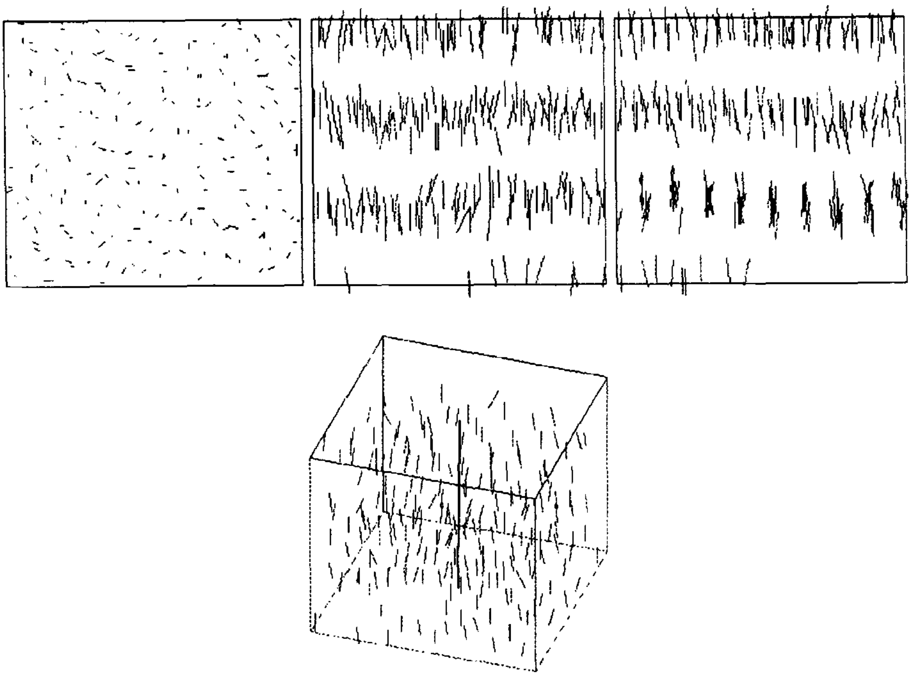

FIGURE 1 Configuration for the ideal GB mixture from different points of view.

The influence of the mixing parameter v_{12} on the liquid structure is demonstrated in terms of $g(r^*)$. v_{12} describes the depth of the potential well for two different molecules.

For $v_{12}=0.5$ the "unequal" potential is only half as deep as the one-component potential. In this case $g_{11}(r^*)$ and $g_{22}(r^*)$ are practically equal, while $g_{12}(r^*)$ is significantly lower up to $r^*=3$ (Fig.2.a). $g_r(r^*)$ has a strong peak at $r^*=1.15$ and is equal to one above $r^*=3$ (Fig.2.b), indicating demixing tendencies.

For $v_{12}=1.5$ the potential between two different molecules is 50% stronger than the potential of one kind. This leads to mixing, so $g_{12}(r^*)$ is higher than $g_{11}(r^*)$ and $g_{22}(r^*)$ (Fig.3.a), particularly near the first peak, and $g_r(r^*)$ fluctuates around one (Fig.3 b)

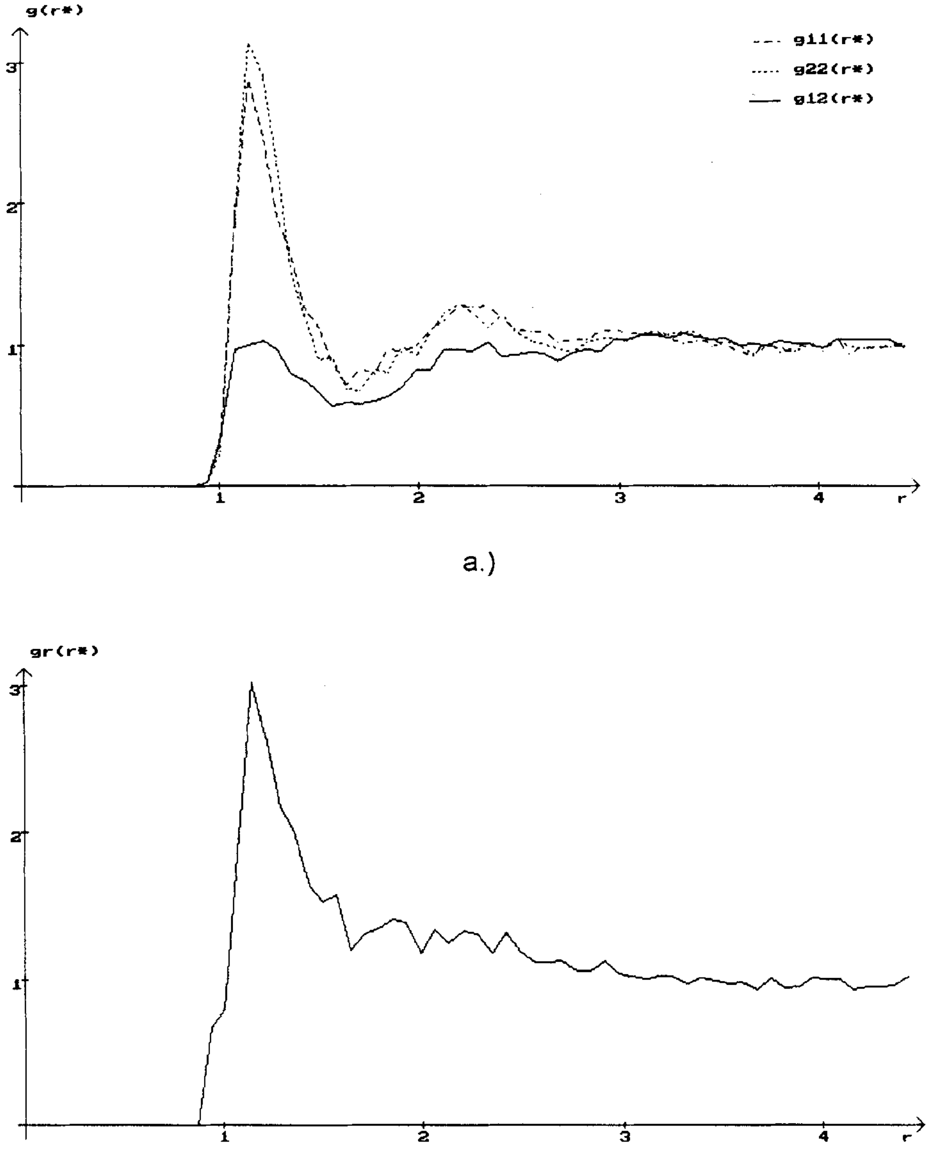

FIGURE 2 Pair correlation functions g(r*) for ν_{12}=0.5:
a.)$g_{11}(r^*)$, $g_{22}(r^*)$ and $g_{12}(r^*)$,
b.)$g_r(r^*)$

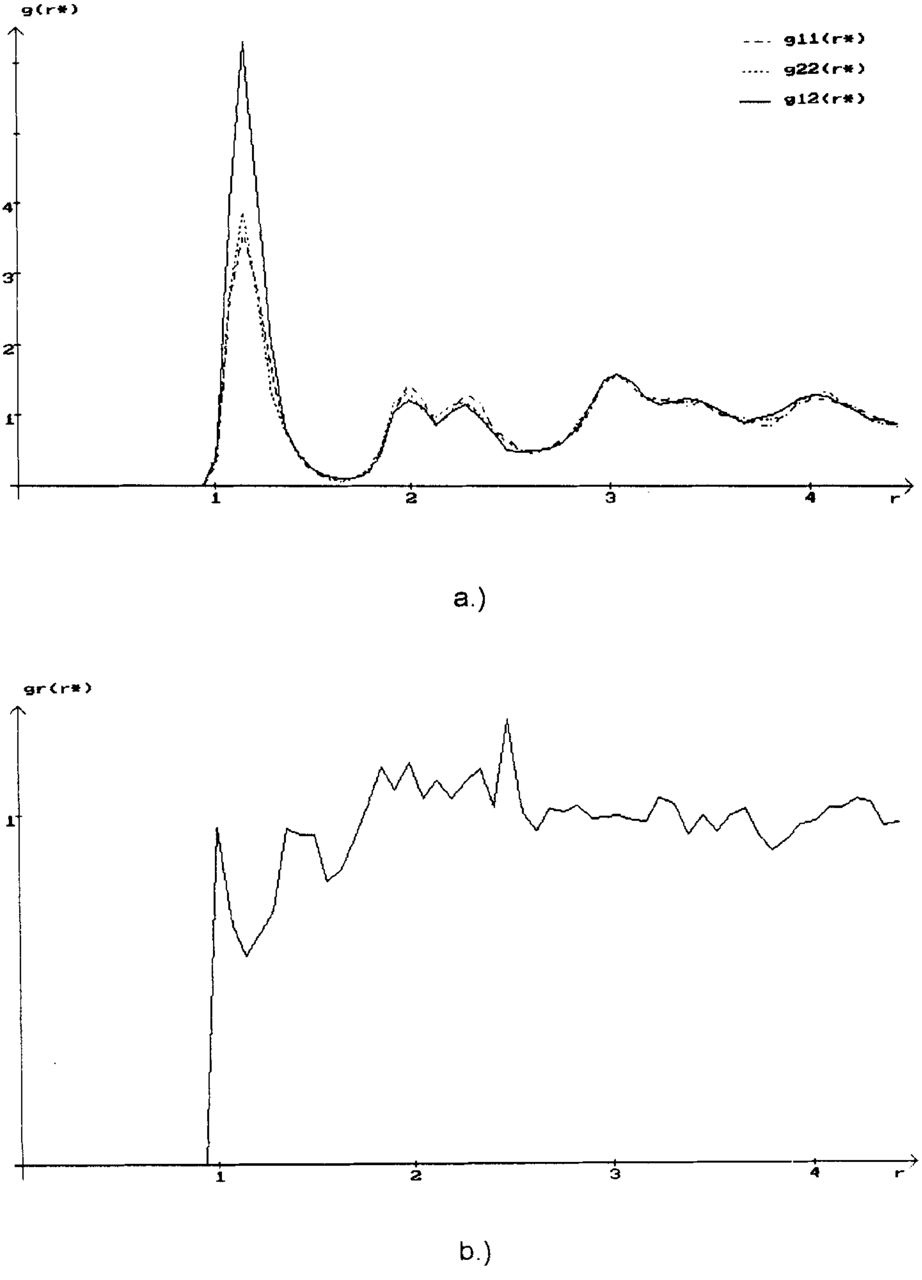

FIGURE 3 Pair correlation functions g(r*) for $\nu_{12}=1.5$:
a.) $g_{11}(r^*)$, $g_{22}(r^*)$ and $g_{12}(r^*)$,
b.) $g_r(r^*)$

To demonstrate how intensive the mixing was, we determined the maximum value of $g_r(r^*)$ (g_{max}) and the value r^* at which it happens (r_{max}). For g_{max} up to 1.5 the structure shows mixing tendencies, while above 2 the demixing process is evident. The results for different configurations are summarized in Table I together with the order parameters.

TABLE 1 Order parameters, maximum of $g_r(r^*)$, the r^* at which it is and a kind of tendencies for different mixing parameters.

mix.param.	——	μ_{12}=1.5	μ_{12}=0.5	μ_2=1.5	μ_2=0.5	ν_{12}=1.5	ν_{12}=0.5	ν_2=1.5	ν_2=0.5
P_2	0,961	0,946	0,957	0,945	0,953	0,966	0,929	0,968	0,914
P_{21}	0,963	0,950	0,961	0,943	0,955	0,968	0,924	0,968	0,932
P_{22}	0,960	0,943	0,954	0,949	0,951	0,964	0,935	0,969	0,899
r_{max}	1,435	1,085	1,505	1,365	1,015	2,485	1,155	1,715	1,715
g_{max}	1,220	1,987	2,208	1,255	1,337	1,268	3,021	1,411	2,823
mixing/dem.	mix	dem.	dem.	mix	mix	mix	dem.	mix	dem.

For the structure in the first column all mixing parameters are set to 1. This is an example of an ideal mixture. In the case of changed μ_{12} we find demixing with g_{max} approximately 2 and in the case of μ_2 mixing with g_{max} approx. 1.3. The influence of parameters ν_2 and ν_{12} is different. For $\nu_2=\nu_{12}=1.5$ there is good mixing with g_{max} approx. 1.3 and very high order parameter: $P_2 \cong 0.967$. If we set one of them to 0.5, then we have very strong demixing with g_{max} approx. 2.9 and a somewhat lower order parameter $P_2 \cong 0.92$. P_2 is greater for longer molecules; for $\mu_2=1.5$ we have $P_{22}>P_{21}$ and for $\mu_2=0.5$ we find $P_{22}<P_{21}$, which means that the smaller particles have more orientational freedom between the longer ones.

MOLECULAR DYNAMICS OF A 2-D GAY-BERNE FLUID

The microscopic dynamics in mesophases is at least as rich of detail as are the structural and thermodynamic properties. While there have been many MC-type computer simulation studies of model nematics[10,11], only a small number of dynamical simulations have been published so far[12,13]. We have started on a project to investigate dynamical correlations in one-component (and later two-component) model liquids of the GB type, looking out for the footprints of the isotropic-nematic phase transition.

As a first step the dynamics of a two-dimensional system of GB molecules was studied. The motions of N=90 particles were followed for 20-40.000 time steps of length 0.004 (reduced to $\sqrt{m\sigma_s^2/\varepsilon}$). The standard model parameters were used (see previous section); for mass and moment of inertia we chose m=10.0 and I=2.0. A packing density may be defined by $\eta=\rho^*\pi\sqrt{(1+\chi)/(1-\chi)}/(2\sqrt{3})$, where $\rho^*=N\sqrt{3}\sigma_o^2/(2A)$ (with A the area of the basic cell) is the reduced density. (χ is a potential anisotropy parameter that has the value 0.8 in our case.) So far the following thermodynamic states were investigated:

TABLE 2

Packing fraction	0.800	0.700	0.550
(Density	0.294	0.257	0.202)
Temperature	1.121	1.102	1.161
Order parameter	0.950	0.802	0.519

Figures 4 and 5 show the velocity and angular velocity autocorrelations, respectively. At a high density (η=0.8) the velocity autocorrelation is first decaying fast, then flattening off, finally exhibiting a belated trace of velocity reversal. A point of future development will be to split up this correlation function into parts parallel and perpendicular to the director. The origin of the shoulder on the early slope is then expected to be cleared up. For decreasing densities the velocity correlation shows the expected change towards a softer decay without backscattering.

The angular velocity acf is very sensitive to the extent of alignment of the molecules. At the highest density, with an order parameter P_2=0.95, we find a harsh, early backscattering followed by a fast (then slightly leveled-off) decay to zero. At the lowest density studied so far (η=0.55) the order parameter is still 0.519, and the backscattering is still there, although delayed and softened. Further states will be studies in the near future.

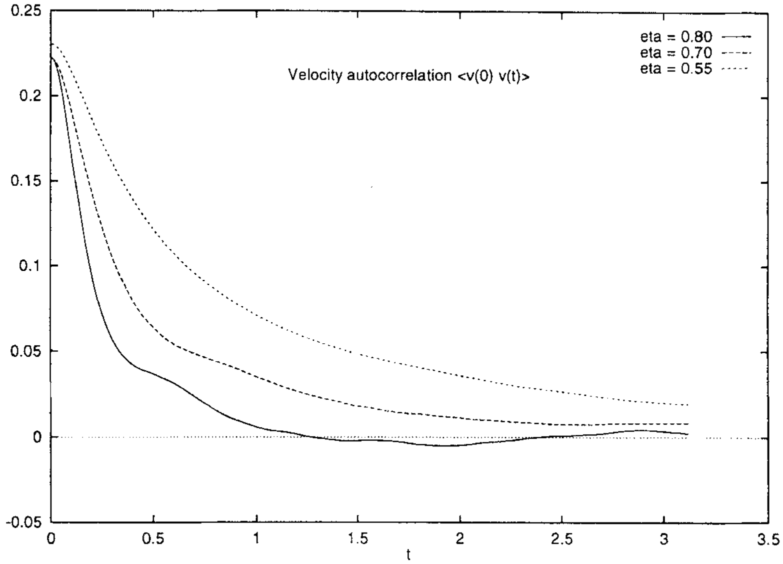

FIGURE 4 Velocity autocorrelation at various densities.

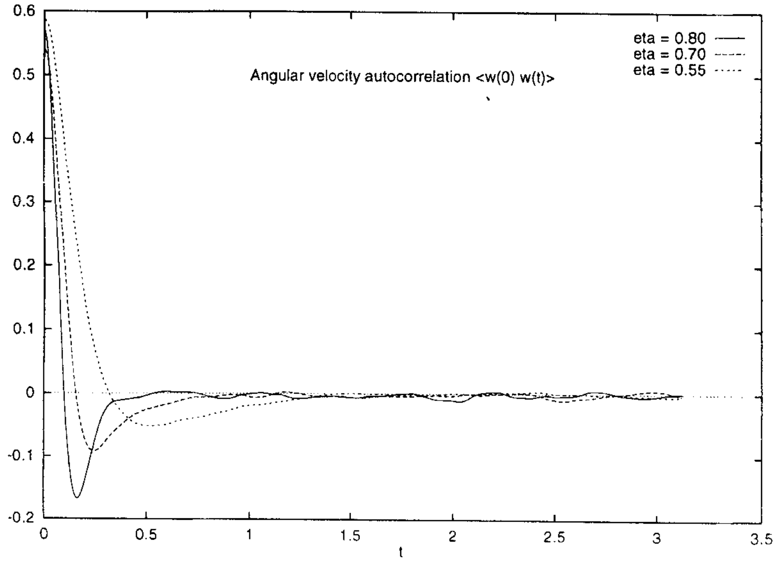

FIGURE 5 Angular velocity autocorrelation at several densities.

CONCLUSION

So far we have investigated only equimolar mixtures. Extension to other mole fractions is under way. It seems that it is not a particularly good choice to introduce mixtures at temperature $T^*=1$, because both translational and orientational order are rather high and it is hard for molecules to change their place or orientation. The better way to produce realistic mixtures is to mix them in the isotropic phase, i.e. at high temperature and low density and then compress or cool them. Still, the tendencies for mixing or demixing are evident. To investigate the phase separation larger structures will be studied. Also, more combinations of the parameter ratios describing the two particle classes should be tested. It is planned to compare the simulated scattering law S(k) (=Fourier transform of $g(r^*)$) with neutron scattering data[14]. Extension of molecular dynamic to three dimensions and mixtures will also be made.

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