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Structure of molecular liquids

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We present a method for calculating, by computer simulation, the direct correlation function $c(1,2)$ for a molecular liquid in the form of a spherical harmonic expansion. This allows us to test, at the most fundamental level, predictions of the structure of molecular liquids using density functional and integral equation approaches. As an example, we test some simple *Ansätze* for $c(1,2)$ for prolate hard ellipsoids of revolution.

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Structure in atomic and molecular fluids is described by the pair distribution function $g(\mathbf{r}_1,\mathbf{r}_2,\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2)\equiv g(1,2)$, where $\mathbf{r}_1,\mathbf{r}_2$ are the center of mass coordinates of particles 1 and 2, and $\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2$ are unit vectors defining the orientations (we focus throughout on the case of axially symmetric molecules having a center of inversion). For some purposes the corresponding correlation function $h(1,2)=g(1,2)-1$ is more convenient than $g(1,2)$ and this is naturally expanded in a complete set of angular functions which depend on the separation $r=|\mathbf{r}_{12}|$ where $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$ [1–5]. There are two common choices, one based on a laboratory frame of reference, giving expansion coefficients $h^{mnl}(r)$, and one using a frame based on the intermolecular vector $\mathbf{r}_{12}$, giving coefficients $h_{mn\chi}(r)$:

$$h(1,2)=\sum_{mnl} h^{mnl}(r)\Phi^{mnl}(\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2,\hat{\mathbf{r}})$$

$$=4\pi\sum_{mn\chi} h_{mn\chi}(r)Y^m_\chi(\hat{\mathbf{u}}_1)Y^n_{-\chi}(\hat{\mathbf{u}}_2)\ . \qquad (1)$$

Here the $\Phi^{mnl}(\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2,\hat{\mathbf{r}})$ are rotational invariants (as defined in Ref. [6]) and the $Y^m_\chi(\hat{\mathbf{u}}_1)$ are spherical harmonics; $\hat{\mathbf{r}}$ is the unit vector in the direction of $\mathbf{r}_{12}$. For the chosen molecular symmetry, m,n,l are all even and there is $m\leftrightarrow n$ symmetry. The $h_{mn\chi}$ coefficients are termed the "χ transforms" of the h^{mnl}; both sets arise naturally in theoretical predictions of the structure of molecular liquids [6–8]. They are easily calculated in computer simulations [9,10] and some of them may be determined experimentally.

The direct correlation function $c(1,2)$ is traditionally defined through the Ornstein-Zernike equation [2]

$$h(1,2)=c(1,2)+\frac{\rho}{4\pi}\int \mathrm{d}\mathbf{r}_3\mathrm{d}\hat{\mathbf{u}}_3 h(1,3)c(3,2), \qquad (2)$$

where ρ is the number density. (We restrict ourselves throughout to the isotropic, homogeneous fluid phase.) $c(1,2)$ is intrinsically a shorter-ranged function than $h(1,2)$, acting as a kernel in the above relation. Although experiments and simulations do not provide a direct route to this function, it is of equal importance to $h(1,2)$ in the statistical mechanics of liquids, and there has been a dramatic growth in interest in $c(1,2)$ in recent years. This is because of the rapid development of density functional theories of fluids [11,12]: $c(1,2)$ is simply related to the excess free energy F^{ex} of the fluid by functional differentiation with respect to the local density $\rho(1)\equiv\rho(\mathbf{r}_1,\hat{\mathbf{u}}_1)$:

$$c(1,2)=\delta^2(-F^{\mathrm{ex}}/k_BT)/\delta\rho(1)\,\delta\rho(2), \qquad (3)$$

where k_B is Boltzmann's constant and T the temperature. This expression leads to a variety of theories of both homogeneous and inhomogeneous fluids, mostly based on assumptions regarding $c(1,2)$ in the system of interest, or in some reference system used as the basis of a perturbation treatment. Onsager's theory [13] of the isotropic-nematic phase transition in liquid crystals, for instance, is a density functional theory in all but name. Also, it is possible to express the condition of mechanical stability of the isotropic phase relative to the nematic liquid crystal in terms of expansion coefficients of $c(1,2)$ [14,15]; this gives an approximate estimate of the location of the thermodynamic phase transition between the two phases.

Density functional theories supplement the traditional integral equation approaches (hypernetted chain, Percus-Yevick, and developments thereof). Tests of these theories are generally performed by comparing predicted $h(1,2)$ functions with the results of computer simulations [10]; only in isolated cases, and only for atomic liquids to date, have comparisons been made between theory and simulation results for $c(1,2)$. Our understanding of atomic liquid structure has been greatly advanced by the success of these approaches for the hard-sphere reference fluid, and by our possession of a quite accurate analytical form for the hard-sphere direct correlation function $c_{\mathrm{HS}}(r/\sigma,\eta)$ over the full range of packing fractions η in which the fluid is stable (σ is the hard-sphere diameter and $\eta=\pi\rho\sigma^3/6$) [2]. Theories of

structure in *molecular* fluids frequently make an *Ansatz* relating $c(1,2)$ to this hard-sphere form (see later).

All of the above observations provide strong motivation to determine the direct correlation function from simulation results for molecular liquids, and compare directly with theoretical predictions. In this paper we present such a comparison for fluids composed of hard ellipsoids of revolution, the simplest generalization of hard spheres, but the techniques apply equally well to other molecules having the same symmetry, and are easily generalized.

Blum [3–5] (see also [1]) has expressed the Ornstein-Zernike equation in the reciprocal-space (k-space) form

$$\tilde{h}_{mn\chi}(k)=\tilde{c}_{mn\chi}(k)+(-1)^{\chi}\rho\sum_{j}\tilde{h}_{mj\chi}(k)\tilde{c}_{jn\chi}(k)$$

or

$$\tilde{\mathscr{H}}_{\chi}(k)=\tilde{\mathscr{C}}_{\chi}(k)+(-1)^{\chi}\rho\tilde{\mathscr{H}}_{\chi}(k)\tilde{\mathscr{C}}_{\chi}(k), \tag{4}$$

i.e., formally a separate matrix equation for each χ,k. In practical applications, the (infinite) matrices $\tilde{\mathscr{H}}$ and $\tilde{\mathscr{C}}$ are truncated by imposing an upper limit $n,m\leq n_{\max}$. In these equations, $\tilde{\mathscr{H}}_{\chi}(k)$ is the χ transform of $\tilde{\mathscr{H}}^{l}(k)$. This is in turn the Fourier-Bessel transform of $\hat{\mathscr{H}}^{l}(r)$: $\tilde{\mathscr{H}}^{l}(k)=4\pi\int_0^{\infty}dr\ r^2 j_0(kr)\hat{\mathscr{H}}^{l}(r)$ where $j_0(x)=\sin x/x$. Finally, $\hat{\mathscr{H}}^{l}(r)$ is the so-called "hat" transform of $\mathscr{H}^{l}(r)$: $\hat{\mathscr{H}}^{l}(r)=\mathscr{H}^{l}(r)-\int_r^{\infty}ds\ s^{-1}\mathscr{H}^{l}(s)P_l^e(r/s)$ where $P_l^e(x)=x^{-1}dP_l/dx$ and $P_l(x)$ is the usual Legendre function. The $\tilde{\mathscr{C}}_{\chi}(k)$ matrix is similarly defined. These equations apply to the particular molecular symmetry mentioned above; for full details consult [1–8].

Direct inversion of simulation data in k space through Eq. (4) is possible; for our purposes it is more convenient to adopt a real-space version which relies on a Wiener-Hopf factorization proposed by Baxter for the case of atomic fluids [16], and now also part of the standard literature in the theory of molecular fluids [1,17,18]. It is possible to write

$$r\hat{\mathscr{C}}_{\chi}(r)=-\mathscr{Q}'_{\chi}(r)+2\pi(-1)^{\chi}\rho\int_r^R ds\,\mathscr{Q}'_{\chi}(s)\mathscr{Q}_{\chi}^{\mathrm{T}}(s-r), \tag{5a}$$

$$r\hat{\mathscr{H}}_{\chi}(r)=-\mathscr{Q}'_{\chi}(r)+2\pi(-1)^{\chi}\rho\times\int_0^R ds(r-s)\hat{\mathscr{H}}_{\chi}(r-s)\mathscr{Q}_{\chi}(s), \tag{5b}$$

where a new matrix $\mathscr{Q}_{\chi}(r)$ has been introduced and $\mathscr{Q}'_{\chi}(r)=d\mathscr{Q}_{\chi}/dr$; $\mathscr{Q}_{\chi}^{\mathrm{T}}$ is the transpose of $\mathscr{Q}_{\chi}$. Here $\hat{\mathscr{H}}_{\chi}(r)$ is the χ transform of $\hat{\mathscr{H}}^{l}(r)$, and similarly for $\hat{\mathscr{C}}_{\chi}(r)$. It is assumed that a separation R exists such that $\mathscr{Q}_{\chi}(r)=0$, $\mathscr{Q}'_{\chi}(r)=0$, and $\hat{\mathscr{C}}_{\chi}(r)=0$ for $r>R$. We use Eq. (5b) to determine $\mathscr{Q}'_{\chi}(r)$ and $\mathscr{Q}_{\chi}(r)$ from the simulation data $\hat{\mathscr{H}}_{\chi}(r)$ through an iteration scheme loosely based on the approach of Jolly *et al.* [19] and Dixon and Hutchinson [20] for the atomic case. Full details will be given in a separate publication [21]. We find that convergence is easily achieved within a few tens of iterations for $n_{\max}=4,6,8$; taking $n_{\max}=8$ is easily sufficient (as it is when solving integral equations [7,10]) to determine accurately the functions of most interest here (with $m,n=0,2,4$).

Once the scheme has converged, Eq. (5a) is used to determine $\hat{\mathscr{C}}_{\chi}(r)$ directly by quadrature. At *very* small r this procedure is inaccurate, because of the factor of r on the left; there is a small difference between two large quantities on the right. To avoid this, we differentiate both equations (5a) and (5b) with respect to r, subtract, and allow $r\to 0$. Some rearrangement and an integration by parts yields

$$\hat{\mathscr{C}}_{\chi}(0)-\hat{\mathscr{H}}_{\chi}(0)=2\pi(-1)^{\chi}\rho\left\{\left(\int_0^R dr\ r\hat{\mathscr{H}}_{\chi}(r)\mathscr{Q}'_{\chi}(r)-\mathscr{Q}'_{\chi}(r)\mathscr{Q}_{\chi}^{\mathrm{T}}(r)\right)-\mathscr{Q}'_{\chi}(0)\mathscr{Q}_{\chi}^{\mathrm{T}}(0)\right\}. \tag{6}$$

This allows us to calculate $\hat{\mathscr{C}}_{\chi}(0)$ accurately, and the lowest few values of $\hat{\mathscr{C}}_{\chi}(r)$ are obtained by interpolation. Finally, the desired functions $\mathscr{C}_{\chi}(r)$ are obtained from $\hat{\mathscr{C}}_{\chi}(r)$ by inverting the hat transform.

We have carried out this procedure for hard ellipsoids of revolution at various elongations and densities; these results will be presented in full elsewhere [21]. Here we report selected results for ellipsoids of elongation $e=a/b=3$ where a is the major and b the minor axis, at a density ρ equal to half the close-packed density (packing fraction $\eta=0.37$). We carried out standard collision-by-collision molecular dynamics for a system of $N=512$ molecules in truncated octahedral periodic boundaries; the run length was approximately 10^7 collisions. Full details of the method are available elsewhere [22]. The $h_{mn\chi}(r)$ coefficients were calculated directly in the simulations as averages over 20 000 equally spaced configurations, and tabulated at intervals $\delta r=0.01b$.

For illustration, we compare our results for $c(1,2)$ with some common *Ansätze* used in theoretical predictions of $h(1,2)$. Perhaps the simplest is due to Parsons [23] and Lee [24], and amounts to taking the low-density limiting form $c(1,2)\to f(1,2)$, and inserting a density-dependent scaling factor: $c_{\mathrm{Parsons}}(1,2)=\varphi(\eta)f(1,2)$. The Mayer f function is $f(1,2)=-1$ for $r\leq\sigma(1,2)$, $f(1,2)=0$ for $r>\sigma(1,2)$, where $\sigma(1,2)=\sigma(\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2,\hat{\mathbf{r}})$ is the closest approach distance for given orientations of molecules and center-center vector. As before, η is the packing fraction, and the choice $\varphi(\eta)=(1-\eta/4)/(1-\eta)^4$ generates an accurate equation of state in the case of hard spheres.

A second well-known *Ansatz* is due to Pynn [25] and Wulf [26]: $c_{\mathrm{Pynn}}(1,2)=c_{\mathrm{HS}}(r/\sigma(1,2),\eta)$, where c_{HS} is the hard-sphere function evaluated at the same packing fraction η as the molecular fluid, and $\sigma(1,2)$ is defined above. This approach has recently been adapted by Marko [27]: $c_{\mathrm{Marko}}(1,2)=[1+\alpha P_2(\hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_2)]c_{\mathrm{HS}}(r/\sigma(1,2),\eta)$, where P_2 is the second Legendre polynomial and α depends upon elongation and packing fraction in a way determined by an optimization procedure based on the Percus-Yevick integral equation.

Finally, Baus *et al.* [28] propose a factorization: $c_{\mathrm{Baus}}(1,2)=\varepsilon(\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2)c_{\mathrm{HS}}(r/\sigma_0,\eta)$, where $\varepsilon(\hat{\mathbf{u}}_1,\hat{\mathbf{u}}_2)$ is a function representing excluded volume effects, the effective diameter σ_0 is chosen to make $\pi\sigma_0^3/6$ equal to the ellipsoid molecular volume, and once again η is the packing fraction of the molecular fluid.

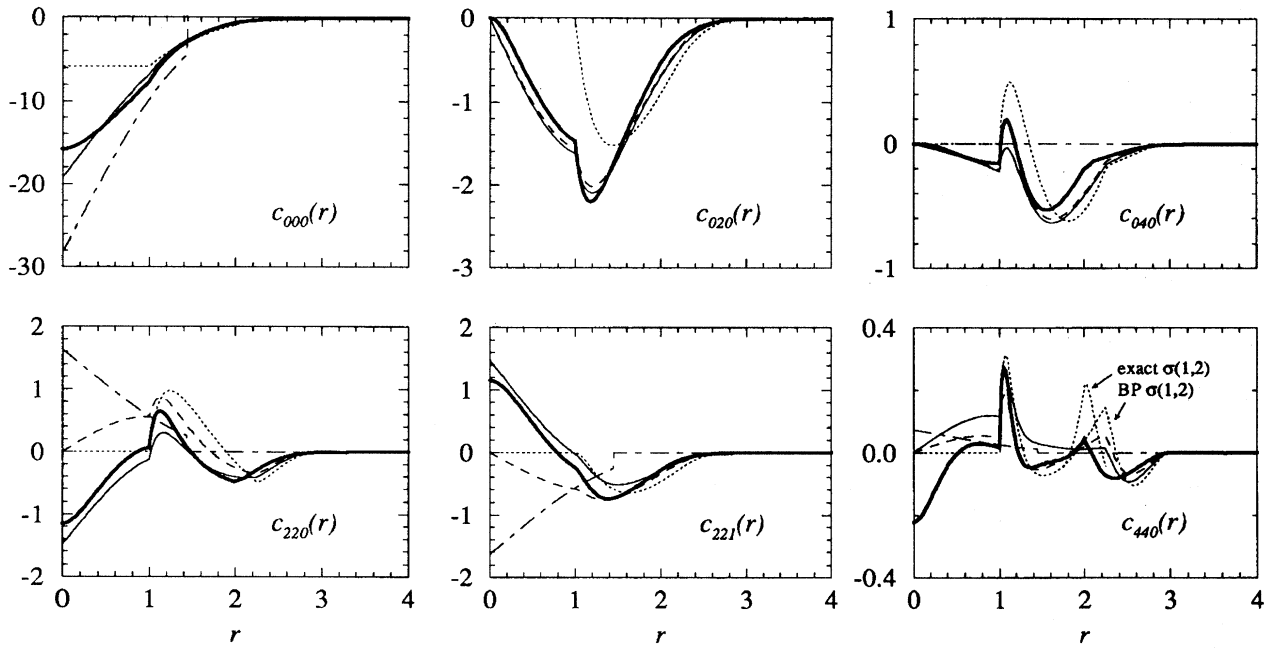

FIG. 1. Selected direct correlation function components with $mn\chi =$ 000, 020, 040, 220, 221, 440, from simulation (thick solid line), compared with theoretical *Ansätze* due to Parsons [23] and Lee [24] (dots), Pynn [25] and Wulf [26] (dashed line), Marko [27] (thin solid line), and Baus [28] (dash-dot line).

In calculating the α parameter, Marko [27] used a simple, analytical, *approximation* to $\sigma(1,2)$ defined by the Gaussian overlap prescription of Berne and Pechukas [29]; the prefactor ε of the Baus theory [28] is also most easily expressed within this approximation. For consistency and simplicity, we make this approximation in all the theories with which we compare our results here, although it should be borne in mind that small but systematic improvements will result from using the *exact* ellipsoid contact separation $\sigma(1,2)$, corresponding to the simulation (see below).

Figure 1 shows comparisons between simulation and theory for a selection of $c_{mn\chi}(r)$ coefficients. Separations are measured in units based on ellipsoid diameter, $b=1$. We note that all the functions are short-ranged, decaying very quickly outside the overlap region $r \geqslant 3$. The Parsons scaling of the Mayer $f(1,2)$ function is moderately successful in the partial overlap region $1 \leqslant r \leqslant 3$, giving the right qualitative shape and approximate magnitude, but because $f(1,2) = -1$ inside the core region $r \leqslant 1$ it fails dramatically here. The Pynn approximation is also quite good, notably where m and/or n is zero. Where both these indices are nonzero, notably for those components that do not vanish as $r \to 0$, the Pynn approximation breaks down within the inner core where, as is well known, it predicts an isotropic function in this limit. Marko's form constitutes an improvement over the basic Pynn approximation in the core for $m=n=2$, where it yields a reasonable $r \to 0$ limit, but it does not improve higher-order functions such as $mn\chi = 440$. Also for this component the deficiencies of the approximation for $\sigma(1,2)$ are apparent: a weak cusp in the simulation results at $r=2$ appears at larger r in all of these theories, whereas the peak position is correctly given (e.g., for the Parsons theory, labeled "exact" in the figure) if the exact $\sigma(1,2)$ is used. Finally, the factorized form proposed by Baus *et al.* fares quite badly: only the $m=n$ components do not vanish, each curve has identical shape, including a step discontinuity at the effective diameter σ_0, and the function cannot reproduce the sign changes seen for $r \leqslant 1$ in some components.

In summary, the determination of the expansion coefficients of $c(1,2)$ by simulation provides a different perspective on this function, which is at the heart of many theories of liquid structure. In the partial overlap region, for the hard ellipsoid example studied here, some of the simpler *Ansätze* for $c(1,2)$ are surprisingly successful at fitting low-order spherical harmonic components, but require some systematic improvement to match at higher order and shorter distance. The replacement of the contact distance $\sigma(1,2)$ by the approximate Berne-Pechukas form, in theoretical treatments, adversely affects some higher-order components. It is anticipated that further study of simulation-determined direct correlation functions will help refine our understanding of molecular liquid structure. Especially promising is the possible use of $c(1,2)$ to calculate liquid crystal elastic constants [30]. A more extensive study of the hard ellipsoid, and related, systems at various state points, comparisons with integral equation theories, and analysis of the thermodynamic properties related to $c(1,2)$, will be the subject of future papers [21].

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