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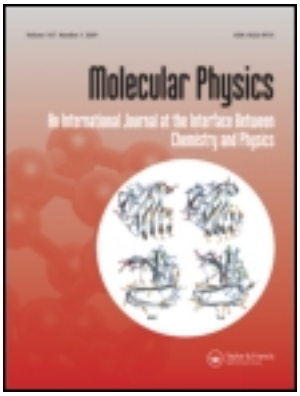

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Integral equations for fluids of linear molecules

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Integral equations for fluids of linear molecules
III. Orientational ordering

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The connection between the orientation correlation function, Kirkwood parameters, and spherical harmonic coefficients of the pair distribution function is obtained for classical fluids of linear molecules. The general results are illustrated with computed values from a recent integral equation solution for a fluid of hard dumbells.

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1. INTRODUCTION

In recent publications [1, 2], a procedure was described whereby any integral equation may be solved for the structure and thermodynamics of any classical fluid of linear molecules, and its use illustrated with a study of the hard dumbell model. In this paper, we examine how the results of the integral equation solution may be used to describe orientational ordering in a molecular fluid.

This is an application of particular interest in the study of nematic liquid crystals [3], where the state of orientational order is often described in terms of a singlet distribution function

$$f(\theta)=\tfrac{1}{2}\sum_l (2l+1)\bar{P}_l P_l(\cos\theta). \tag{1}$$

In this expression, θ is the angle between the molecular axis and an externally-imposed ' director ', $P_l(x)$ the lth-order Legendre polynomial, and $\bar{P}_l$ the orientational order parameters, commonly calculated in mean field approximation. We note in the next section that in the absence of an external field imposing a special direction, the singlet description is inadequate and ordering must be sought in pair correlations. The final result, however, has the *same* form as equation (1), with θ reinterpreted as the relative angle between two molecules and the $\bar{P}_l$ determined in terms of the spherical harmonic coefficients of the pair distribution function.

2. ORIENTATION CORRELATION FUNCTION

In the absence of any *external* potential, the configuration energy of a molecular system can depend only on the relative separations and relative orientations of the N molecules. With the use of periodic boundary conditions for convenience, this property may be expressed by saying that there is an

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essential arbitrariness in the origin and orientation of the coordinate frame. As a consequence, the singlet number density

$$\rho^{(1)}(\mathbf{r}) = \left\langle \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) \right\rangle = N/V \tag{2}$$

is uniform, whether the system is in the crystalline or fluid phase [4]. Similarly, the singlet distribution function for molecular orientations

$$f(\omega) = \left\langle \sum_{j=1}^{N} \delta(\omega - \omega_j) \right\rangle = \frac{N}{4\pi} \tag{3}$$

is also uniform, regardless of the extent of orientational ordering in the system. Evidence of ordered structures in either case is to be sought in correlations between pairs of molecules.

We define the orientation correlation function as

$$G(\omega, \omega') = \frac{1}{N} \left\langle \left[\sum_i \delta(\omega - \omega_i) - \frac{N}{4\pi} \right] \left[\sum_j \delta(\omega' - \omega_j) - \frac{N}{4\pi} \right] \right\rangle, \tag{4}$$

where, as also above, the brackets denote a canonical ensemble average and $\omega = (\theta, \phi)$, referred to an arbitrary axis. (Keeping N and V fixed will ensure that $G(\omega, \omega')$ vanishes for orientationally disordered states, eliminating an extraneous contribution to (4) from density fluctuations.) Expanding the product in (4), we have

$$G(\omega, \omega') = \frac{1}{N} \left[\left\langle \sum_{i,j}' \delta(\omega - \omega_i) \delta(\omega' - \omega_j) \right\rangle - \left(\frac{N}{4\pi} \right)^2 + \frac{N}{4\pi} \delta(\omega - \omega') \right], \tag{5}$$

where the prime on the summation means $i \neq j$. In terms of the generalized pair density [5]

$$\rho^{(2)}(12) = \frac{N(N-1)}{Q} \int d\mathbf{r}^{N-2}\, d\omega^{N-2} \exp\left[-\beta U(\mathbf{r}^N, \omega^N) \right] \tag{6}$$

$$Q = \int d\mathbf{r}^N\, d\omega^N \exp\left[-\beta U(\mathbf{r}^N, \omega^N) \right], \tag{7}$$

equation (5) becomes

$$\begin{aligned} G(\omega_1, \omega_2) &= \frac{1}{N} \left[\int d\mathbf{r}_1\, d\mathbf{r}_2\, \rho^{(2)}(12) - \left(\frac{N}{4\pi} \right)^2 + \frac{N}{4\pi} \delta(\omega_1 - \omega_2) \right] \\ &= \frac{\rho}{(4\pi)^2} \int d\mathbf{r}_{12}\, h(12) + \frac{1}{4\pi} \delta(\omega_1 - \omega_2), \end{aligned} \tag{8}$$

where we have put

$$\rho^{(2)}(12) = \frac{\rho^2}{(4\pi)^2} g(12) \tag{9}$$

and $h = g - 1$. The total correlation function $h(12)$ is most conveniently obtained from an integral equation solution in the form

$$h(12) = 4\pi \sum_{l_1 l_2 m} h_{l_1 l_2 m}(r_{12})\, Y_{l_1 m}(\omega_1)\, Y_{l_2 \bar{m}}(\omega_2), \tag{10}$$

where $\bar{m} = -m$ and the orientations ω_1, ω_2 are referred to the intermolecular vector $\mathbf{r}_{12}$ as polar axis. Rotation of the coordinate frame to an arbitrary

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orientation converts (10) to [6]

$$h(12)=4\pi\sum_{l_1l_2l}h(r_{12}\,;\,l_1l_2l)\sum_{m_1m_2}\langle l_1m_1l_2m_2|l_1l_2lm_1+m_2\rangle \times Y_{l_1m_1}(\omega'_1)\,Y_{l_2m_2}(\omega'_2)\,Y^*_{l,m_1+m_2}(\omega'), \tag{11}$$

where the bracket is a Clebsch–Gordan coefficient, ω' is the orientation of $\mathbf{r}_{12}$, and

$$h(r\,;\,l_1l_2l)=\left(\frac{4\pi}{2l+1}\right)^{1/2}\sum_m\langle l_1ml_2\bar{m}|l_1l_2l0\rangle h_{l_1l_2m}(r), \tag{12}$$

which has the inverse

$$h_{l_1l_2m}(r)=\sum_l\langle l_1ml_2\bar{m}|l_1l_2l0\rangle\left(\frac{2l+1}{4\pi}\right)^{1/2}h(r\,;\,l_1l_2l). \tag{13}$$

The integral over $\mathbf{r}_{12}$ now gives

$$\begin{aligned}\int d\mathbf{r}_{12}\,h(12)&=4\pi\sum_{l_1l_2}\int_0^\infty dr_{12}\,r_{12}^2\,h(r_{12}\,;\,l_1l_20)\\&\quad\times\sum_m\langle l_1ml_2\bar{m}|l_1l_200\rangle Y_{l_1m}(\omega'_1)\,Y_{l_2\bar{m}}(\omega'_2)(4\pi)^{1/2}\\&=\sum_l\tilde{h}(0\,;\,ll0)(-1)^l\left(\frac{2l+1}{4\pi}\right)^{1/2}P_l(\cos\theta_{12}),\\&=\sum_l(2l+1)\tilde{h}_{ll0}(0)P_l(\cos\theta_{12}),\end{aligned} \tag{14}$$

where

$$\tilde{h}(0\,;\,ll0)=4\pi\int_0^\infty dr\,r^2\,h(r\,;\,ll0) \tag{15}$$

is a Fourier transform evaluated at $k=0$,

$$\tilde{h}_{ll0}(0)=(-1)^l[4\pi(2l+1)]^{-1/2}\,\tilde{h}(0\,;\,ll0) \tag{16}$$

from the transform version of (13) (noting that $\tilde{h}(0\,;\,l_1l_2l)\equiv 0$ for $l\neq 0$), and we have used the spherical harmonics addition theorem [7]

$$P_l(\cos\theta_{12})=\frac{4\pi}{2l+1}\sum_m Y_{lm}{}^*(\omega'_2)\,Y_{lm}(\omega'_1) \tag{17}$$

and the particular Clebsch–Gordan coefficient [7]

$$\langle l_1ml_2\bar{m}|l_1l_200\rangle=(-1)^{l_1-m}(2l_1+1)^{-1/2}\,\delta_{l_1l_2}. \tag{18}$$

The orientation correlation function

$$G(\omega_1,\omega_2)=\frac{\rho}{(4\pi)^2}\sum_l(2l+1)\tilde{h}_{ll0}(0)P_l(\cos\theta_{12})+\frac{1}{4\pi}\,\delta(\omega_1-\omega_2) \tag{19}$$

is now manifestly dependent on just the relative orientation of the two molecules. We may reduce the description by integrating over ω_1 to get

$$\begin{aligned}G(\omega_{12})&\equiv\int d\omega_1\,G(\omega_1,\omega_2)\\&=\frac{1}{4\pi}\left\{1+\rho\sum_{l=0}^\infty(2l+1)\tilde{h}_{ll0}(0)P_l(\cos\theta_{12})\right\}\\&=\frac{\rho}{4\pi}\sum_{l=1}^\infty(2l+1)\tilde{h}_{ll0}(0)P_l(\cos\theta_{12}),\end{aligned} \tag{20}$$

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since in the canonical ensemble

$$1+\rho\tilde{h}_{000}(0)=0, \tag{21}$$

density fluctuations having been suppressed. Another reduction can be made by integrating out the irrelevant ϕ_{12} variable to give finally

$$\begin{aligned} G(\theta_{12}) &\equiv \int d\phi_{12}\, G(\omega_{12}) \\ &= \tfrac{1}{2}\sum_{l=1}^{\infty}(2l+1)\rho\tilde{h}_{ll0}(0)P_l(\cos\theta_{12}). \end{aligned} \tag{22}$$

It is easy to show that the coefficients of this expansion are just the Kirkwood parameters [5]

$$\begin{aligned} G_l &\equiv \frac{2}{N}\left\langle \sum_{i<j} P_l(\cos\theta_{ij})\right\rangle \\ &= \rho\tilde{h}_{ll0}(0), \end{aligned} \tag{23}$$

which play the role of order parameters in liquid crystals [3].

Computed order parameters for a fluid of hard dumbells.

		l/σ			
ρd^3		0·2	0·4	0·6	0·8
0·2	G_2	0·0015	0·0044	0·0090	0·0141
	G_4	0·0005	0·0010	0·0017	0·0027
0·4	G_2	0·0033	0·0092	0·0185	0·0287
	G_4	0·0013	0·0029	0·0055	0·0089
0·6	G_2	0·0043	0·0105	0·0197	0·0309
	G_4	0·0029	0·0069	0·0128	0·0205
0·8	G_2	0·0011	−0·0047	−0·0216	−0·0585
	G_4	0·0060	0·0145	0·0234	0·0253

These coefficients are readily determined from an integral equation solution. We show in the table the first two non-vanishing parameters, G_2 and G_4, for fused hard spheres (hard dumbells) of diameter σ and centre-to-centre elongation l [2]. All the values are quite small, confirming that orientational ordering in this system is very short ranged. The tendency of G_2 to turn negative with increasing density and elongation, indicating a preference for perpendicular alignment under these conditions, is clear. This is further illustrated in the graph of the (truncated) correlation function in the figure for $\rho d^3=0{\cdot}896$, and $l/\sigma=0{\cdot}6$, for which G_2 and G_4 are $-0{\cdot}0685$ and $0{\cdot}0232$, respectively. (Here d is the diameter of a sphere with volume equal to that of the dumbell.)

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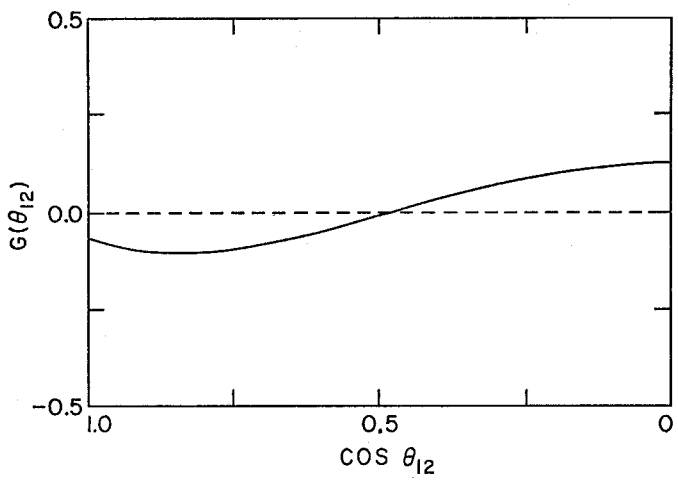

Orientation correlation function for hard dumbells of elongation $l=0{\cdot}6\sigma$ at the density $\rho d^3=0{\cdot}896$.

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