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Theory of Inelastic Neutron Scattering from Molecular Fluids

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The time-dependent angular pair correlation function is discussed and its use in the analysis of inelastic neutron scattering experiments from polyatomic fluids is described, including both the coherent and incoherent spectra. The set of formal results given here permits a systematic interpretation of neutron inelastic scattering spectra on simple molecular liquids. Neutron spectra second moments are reviewed, and a new result for the fourth moment is given for the incoherent spectrum. Numerical results for the moments are obtained. The fourth moment depends on the mean squared torque and the mean squared force acting on a molecule in the fluid, and may provide a means for studying intermolecular forces in dense fluids. In addition, a method of calculating the correlation function for weak anisotropic forces is outlined.

KEY WORDS: Neutron scattering; polyatomic fluids.

1. INTRODUCTION

In his now classic paper, Van Hove[(22)] showed that (in first Born approximation) the neutron inelastic scattering cross section for monatomic systems

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gives direct experimental access to the space–time correlation function $G(\mathbf{R}_1\mathbf{R}_2t)$. This function gives the probability density that a molecule will be at position $\mathbf{R}_2$ at time t, given that a molecule was at $\mathbf{R}_1$ initially. The fundamental relations obtained by Van Hove laid the foundation for the interpretation of experimental studies of monatomic gases, liquids, and solids; studying the cross section for a wide range of momentum and energy transfers provides a probe of the structure and dynamics of the system (cf. Egelstaff(3) for a review).

Inelastic neutron scattering from polyatomic systems has been studied for various models of free and hindered rotators (Sachs and Teller,(14) Pope,(13) Zemach and Glauber,(25) Krieger and Nelkin,(8) Sears(16–18)). The problem has been formulated in a general way by Steele and Pecora(20) in terms of an angular space–time correlation function $G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2t)$. This function gives the probability of finding at time t a molecule at $\mathbf{R}_2$ with orientation Ω_2, given that a molecule was present at $\mathbf{R}_1$ with orientation Ω_1 initially.

In this paper we first review the extension of the Van Hove formalism to classical (rigid) polyatomic liquids. To make this section accessible to experimentalists, we reformulate the theory in customary neutron scattering notation. The results are easily compared with the diffraction theory given previously (Gubbins *et al.*(6)). We also discuss the coherent and incoherent scattering, and give some new results for the moments of the inelastic scattering. Numerical results are given for the second and fourth moments. For weak angle-dependent forces we outline a perturbation method of calculating the pair correlation functions.

Section 2 defines the function $G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2t)$ and briefly considers its properties. In Section 3 the relation between the scattering cross section and the angular Van Hove correlation function is derived. This section is an extension to the time-dependent case of the theory previously given by Gubbins *et al.*(6) for the structure factor $S(q)$ for molecular fluids. Some limiting cases are considered in Section 4. This is followed by the evaluation of some low-order moments in Section 5. In the appendix we sketch the perturbation theory for calculating G.

2. ANGULAR VAN HOVE CORRELATION FUNCTION

We first briefly define the notation to be used. Angle brackets will denote a grand canonical ensemble average over initial values of the phase of the system of N (rigid) molecules; thus for any function A of the phase

$$\langle A\rangle = \sum_{N\geqslant 0} \int dx_1 \cdots dx_N f_N A_N \tag{1}$$

where

$$f_N = \frac{z^N}{N!h^{6N}} e^{-\beta H_N} \Bigg/ \sum_{N \geqslant 0} \frac{z^N}{N!h^{6N}} \int dx_1 \cdots dx_N \, e^{-\beta H_N} \tag{2}$$

and $\beta = 1/kT$, $z = \exp(\mu/kT)$ is the activity, h is Planck's constant, and x_i is an abbreviation for the phase coordinates $\mathbf{R}_i$, $\mathbf{p}_i$. Ω_i, and $\mathbf{p}_{\Omega i}$; here $\mathbf{R}_i$ is the position of the center of mass of molecule i, $\mathbf{p}_i$ is its linear momentum, and $\mathbf{p}_{\Omega i}$ is the momentum conjugate to Ω_i, where $\Omega_i \equiv \phi_i, \theta_i, \chi_i$ are the Euler angles. In (2) the N-molecule Hamiltonian is given by

$$H_N = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \mathscr{U}_N(\mathbf{R}^N\Omega^N) + \sum_{i=1}^{N} \sum_{\alpha} \frac{J_{i\alpha}^2}{2I_\alpha} \tag{3}$$

where $\mathscr{U}_N$ is the potential energy of the N-molecule system, m is the molecular mass, and $J_{i\alpha}$ is the angular momentum along the principal axis α, and I_α is the moment of inertia along axis α. In what follows it will frequently be convenient to express the time dependence of a phase variable A in terms of the N-particle streaming operator S_t, defined by

$$S_t \equiv e^{i\mathscr{L}_N t} \tag{4}$$

where $\mathscr{L}_N$ is the Liouville operator,

$$\mathscr{L}_N = -i \sum_{j=1}^{N} \left[\frac{\partial H_N}{\partial \mathbf{p}_j} \cdot \frac{\partial}{\partial \mathbf{R}_j} - \frac{\partial H_N}{\partial \mathbf{R}_j} \cdot \frac{\partial}{\partial \mathbf{p}_j} \right] - i \sum_{j=1}^{N} \left[\frac{\partial H_N}{\partial \mathbf{p}_{\Omega j}} \cdot \frac{\partial}{\partial \Omega_j} - \frac{\partial H_N}{\partial \Omega_j} \cdot \frac{\partial}{\partial p_{\Omega j}} \right] \tag{5}$$

Physically, S_t is the operator that changes the phase variables of a function from their initial values to the values at time t later, i.e.,

$$S_t A_N(0) = A_N(t) \tag{6}$$

We note that the term $\mathscr{U}_N(\mathbf{R}^N\Omega^N)$ in (3) leads to coupling of the rotational and translational motions, as seen from (5); only when $\mathscr{U}$ is independent of molecular orientations (free rotation) will these two motions be dynamically independent.

The time-dependent angular pair correlation function $G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)$ is defined by

$$G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) = (\hat{\Omega}^2/\rho^2) \Big\langle \sum_{ij} \delta(\mathbf{R}_1 - \mathbf{R}_i(0))\, \delta(\mathbf{R}_2 - \mathbf{R}_j(t)) \times \delta(\Omega_1 - \Omega_i(0))\, \delta(\Omega_2 - \Omega_j(t)) \Big\rangle \tag{7}$$

where ρ is the number density, $\hat{\Omega} = \int d\Omega$ and is 4π for linear and $8\pi^2$ for nonlinear molecules, respectively, and summations run from 1 to N. For a homogeneous, isotropic fluid, G depends only on the relative position $\mathbf{R} =$

$\mathbf{R}_1 - \mathbf{R}_2$ and relative orientation $\Omega = \Omega_1 - \Omega_2$, i.e., G can be written $G(\mathbf{R}\Omega t)$. An alternative form of (7) is

$$G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) = (\hat{\Omega}^2/\rho^2)\langle\rho(\mathbf{R}_1\Omega_1 0)\rho(\mathbf{R}_2\Omega_2 t)\rangle \tag{8}$$

where

$$\rho(\mathbf{R}\Omega t) = \sum_i \delta(\mathbf{R} - \mathbf{R}_i(t))\,\delta(\Omega - \Omega_i(t)) \tag{9}$$

is a local number density per unit solid angle for molecules with orientation Ω at $\mathbf{R}$, t. Also, for an isotropic, homogeneous system

$$\langle\rho(\mathbf{R}\Omega t)\rangle = \rho/\hat{\Omega} \tag{10}$$

The angular Van Hove correlation function can be split into self and distinct parts in the usual way, $G = G_s + G_d$, where

$$\begin{aligned} G_s(\mathbf{R}_1\mathbf{R}_1\Omega_1\Omega_2 t) = (\hat{\Omega}^2/\rho^2)\Big\langle\sum_i \delta(\mathbf{R}_1 - \mathbf{R}_i(0))\,\delta(\mathbf{R}_2 - \mathbf{R}_i(t))& \\ \times\, \delta(\Omega_1 - \Omega_i(0))\,\delta(\Omega_2 - \Omega_i(t))\Big\rangle& \end{aligned} \tag{11}$$

$$\begin{aligned} G_d(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) = (\hat{\Omega}^2/\rho^2)\Big\langle\sum_{i\neq j} \delta(\mathbf{R}_1 - \mathbf{R}_i(0))\,\delta(\mathbf{R}_2 - \mathbf{R}_j(t))& \\ \delta(\Omega_1 - \Omega_i(0))\,\delta(\Omega_2 - \Omega_j(t))\Big\rangle& \end{aligned} \tag{12}$$

The self function G_s is proportional to the probability density that a particular molecule will be at $\mathbf{R}_2\Omega_2$ at t, given that the *same* molecule was at $\mathbf{R}_1\Omega_1$ initially, whereas the distinct function G_d is proportional to the probability density that a molecule is at $\mathbf{R}_2\Omega_2$ at t given that a *different* molecule was at $\mathbf{R}_1\Omega_1$ initially.

The static limits of the self and distinct parts of $G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)$ are obtained by putting $t = 0$ in (11) and (12). For an isotropic, homogeneous fluid

$$G_s(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t = 0) = (\hat{\Omega}/\rho)\,\delta(\mathbf{R}_1 - \mathbf{R}_2)\,\delta(\Omega_1 - \Omega_2) \tag{13}$$

$$G_d(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t = 0) = g(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2) \tag{14}$$

In (14), $g(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2)$ is the static angular pair correlation function, defined as

$$g(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2) = (\hat{\Omega}^2/\rho^2)\Big\langle\sum_{i\neq j} \delta(\mathbf{R}_1 - \mathbf{R}_i)\,\delta(\mathbf{R}_2 - \mathbf{R}_j)\,\delta(\Omega_1 - \Omega_i)\,\delta(\Omega_2 - \Omega_j)\Big\rangle \tag{15}$$

which for rigid molecules becomes

$$g(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2) = \frac{\hat{\Omega}^2}{\rho^2\Xi}\sum_N \frac{q_{\text{rot}}^N z^N}{\Lambda^{3N}(N-2)!}\int \exp(-\beta\mathscr{U})\,d\mathbf{R}^{N-2}\,d\Omega^{N-2} \tag{16}$$

where Ξ is the grand partition function , q_{rot} is the rotational kinetic energy partition function for a single molecule, and $\Lambda = (h^2/2\pi mkT)^{1/2}$

In the limit of large time or large $|\mathbf{R}_1 - \mathbf{R}_2|$, the molecules at $(\mathbf{R}_1\Omega_1 0)$ and at $(\mathbf{R}_2\Omega_2 t)$ are uncorrelated. Thus (8) gives

$$G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t = \infty) = (\hat{\Omega}^2/\rho^2)\langle\rho(\mathbf{R}_1\Omega_1 0)\rangle\langle\rho(\mathbf{R}_2\Omega_2\infty)\rangle \tag{17}$$

For an isotropic, homogeneous fluid, (10) and (16) give

$$G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t = \infty) = 1 \tag{18}$$

Also,

$$G_s(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t = \infty) = 0 \tag{19}$$

with similar expressions (for all t) when $|\mathbf{R}_1 - \mathbf{R}_2| \rightarrow \infty$.

In addition to the angular Van Hove correlation function defined in (7), it is also useful to define the Van Hove function for molecular centers, $G(\mathbf{R}_1\mathbf{R}_2 t)$. This is proportional to the probability density that there will be a molecule at $\mathbf{R}_2$ at t given a molecule at $\mathbf{R}_1$ initially, irrespective of the molecular orientations. It is given by

$$G(\mathbf{R}_1\mathbf{R}_2 t) = \langle G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)\rangle_{\Omega_1\Omega_2} \tag{20}$$

$$= (1/\rho^2)\left\langle \sum_{ij} \delta(\mathbf{R}_1 - \mathbf{R}_i(0))\, \delta(\mathbf{R}_2 - \mathbf{R}_j(t)) \right\rangle \tag{20$'$}$$

where

$$\langle\cdots\rangle_{\Omega_1\Omega_2} = (1/\hat{\Omega}^2) \int \cdots d\Omega_1\, d\Omega_2 \tag{21}$$

In the final form of (20) it should be noted that the intermolecular potential energy $\mathscr{U}(\mathbf{R}^N\Omega^N)$ depends on molecular orientations; consequently, $G(\mathbf{R}_1\mathbf{R}_2 t)$ will be influenced by angular correlations between molecules, through both the ensemble averaging and the time evolution of $\mathbf{R}_i(t)$.

It is similarly possible to define a correction function for molecular orientations, $G(\Omega_1\Omega_2 t)$; this gives the probability density that a molecule has orientation Ω_2 at time t, given that a molecule had orientation Ω_1 initially, irrespective of the positions $\mathbf{R}_1$ and $\mathbf{R}_2$ of the centers. It is defined by

$$G(\Omega_1\Omega_2 t) \equiv \langle G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)\rangle_{\mathbf{R}_1\mathbf{R}_2}$$

$$= (\hat{\Omega}^2/N_m{}^2)\left\langle \sum_{ij} \delta(\Omega_1 - \Omega_i(0))\, \delta(\Omega_2 - \Omega_j(t)) \right\rangle \tag{22}$$

where

$$\langle\cdots\rangle_{\mathbf{R}_1\mathbf{R}_2} = (1/V^2) \int \cdots d\mathbf{R}_1\, d\mathbf{R}_2 \tag{23}$$

and $N_m \equiv \langle N \rangle = \rho V$. The self-part of $G(\Omega_1\Omega_2 t)$ arises in the theory of rotational diffusion.

For monatomic fluids the averaging over orientations in (7) can be performed immediately to give

$$G(\mathbf{R}_1\mathbf{R}_2 t) = (1/\rho^2)\left\langle \sum_{ij} \delta(\mathbf{R}_1 - \mathbf{R}_i(0))\, \delta(\mathbf{R}_2 - \mathbf{R}_j(t)) \right\rangle \tag{24}$$

which is the usual Van Hove function. In (24) both the ensemble average $\langle \cdots \rangle$ and the time evolution operator are for the system with potential energy $\mathscr{U}_0(\mathbf{R}^N)$. It should be noted that the definitions of $G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)$ and $G(\mathbf{R}_1\mathbf{R}_2 t)$ given in (7) and (23) differ from the original definitions of Van Hove by a factor ρ^{-1}; the normalization used here preserves the customary definition for the static pair correlation function [e.g., Eq. (16)].

In the case of free rotation it is possible to factorize the self- and distinct parts of $G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)$ into parts depending on molecular centers and molecular orientations. The function $\mathscr{U}$ in (3) is then independent of molecular orientations, and the Hamiltonian separates into parts H_N^{trans} and H_N^{rot} which depend on center-of-mass and rotational coordinates, respectively. Furthermore, from (5) the Liouville operator undergoes a similar decoupling, $\mathscr{L}_N = \mathscr{L}_N^{\text{trans}} + \mathscr{L}_N^{\text{rot}}$. Moreover, these last two operators commute, so that (4) becomes

$$S_t = S_t^{\text{trans}} S_t^{\text{rot}} \tag{25}$$

where S_t^{trans} describes the center-of-mass motion and S_t^{rot} describes the rotational motions. When these results are substituted in (7) and $i = j$ and $i \neq j$ terms are considered separately, we obtain

$$G_d(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) = G_d(\mathbf{R}_1\mathbf{R}_2 t) \tag{26}$$

$$G_s(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) = N_m G_s(\mathbf{R}_1\mathbf{R}_2 t) G_s(\Omega_1\Omega_2 t) \tag{27}$$

where $G(\mathbf{R}_1\mathbf{R}_2 t)$ and $G(\Omega_1\Omega_2 t)$ are given by (20) and (22), respectively. Spherical harmonic expansions for the rotational time correlation function $G_s(\Omega_1\Omega_2 t)$ have been studied by several workers for the case of free rotation. Thus Sears(16–18) has calculated the first few terms in such a series for homonuclear diatomic and tetrahedral molecules, while Steele and Pecora(20) and St. Pierre and Steele(19) have considered more general shapes. Such expansions converge rapidly, so that the first two terms are usually sufficient to give a satisfactory approximation. [We note that the function $G(\Omega_1\Omega_2 t)$ used by Sears is $(N_m/\hat{\Omega}^2)$ times the function $G_s(\Omega_1\Omega_2 t)$ used here.]

For the case that the translational and rotational motions are strongly correlated, only the diffusion limit (cf., e.g., Maeda and Saito,(9) Schaefer *et al.*(15)) seems to have been discussed.

For weakly coupled translational and rotational motions, a perturbation treatment should prove satisfactory. In the appendix we outline the formal development of such a theory, using as a reference a system of freely rotating molecules. We write the potential as

$$\mathscr{U} = \mathscr{U}_0 + \lambda \mathscr{U}_a \tag{28}$$

where $\mathscr{U}_0(\mathbf{R}^N) \equiv \langle \mathscr{U} \rangle_{\Omega^N}$ is the isotropic part and $\mathscr{U}_a$ is the anisotropic part. One useful result of the perturbation treatment is that the centers correlation function is equal to the reference centers function to first order:

$$G(\mathbf{R}_1 \mathbf{R}_2 t) = G_0(\mathbf{R}_1 \mathbf{R}_2 t) + O(\lambda^2) \tag{29}$$

where G_0 corresponds to $\mathscr{U}_0$. An analogous result for the static case was proved by Ananth *et al.*(1) In the static case, one knows from Monte Carlo studies (Wang *et al.*(24); Verlet and Weis(23)) that the higher order terms in (29) are negligible even for strong multipolar forces in liquids; for strongly anisotropic overlap forces there are significant differences, however.

3. THE DYNAMIC STRUCTURE FACTOR

We assume that all molecules are in their ground electronic states, and that classical statistical mechanics applies. In the first Born approximation the neutron differential scattering cross section for all nuclei in the sample is given by

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{k}{k_0} \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt\, (\exp - i\omega t) \times \sum_{\alpha\beta} \left\langle \sum_{ij} b_{i\alpha} b_{j\beta} \exp[-i\mathbf{q} \cdot \mathbf{r}_{i\alpha}(0)] \exp[-i\mathbf{q} \cdot \mathbf{r}_{j\beta}(t)] \right\rangle \tag{30}$$

where $\mathbf{k}_0$ and $\mathbf{k}$ are the initial and final wave vectors, $\mathbf{q} = \mathbf{k}_0 - \mathbf{k}$, $\hbar\omega$ is the energy transferred to the neutron in the scattering process, $b_{i\alpha}$ is the bound scattering length of nucleus α in molecule i, and $\mathbf{r}_{j\beta}(t)$ is the vector location of nucleus β in molecule j at time t.

Summations over i and j are over all molecules in the system, and summations over α and β are over all the nuclei in a single molecule. Angular brackets here indicate both a grand canonical ensemble average, and also an averaging over isotopic species and nuclear spin states. Assuming that there is no correlation between nuclear spin states and particle positions or velocities, or between the nuclear spins themselves, it is possible to perform the averaging over nuclear spins and isotopes separately:

$$\overline{b_{i\alpha} b_{j\beta}} \equiv \bar{b}_\alpha \bar{b}_\beta + [\overline{b_{i\alpha} b_{j\beta}} - \bar{b}_\alpha \bar{b}_\beta] = \bar{b}_\alpha \bar{b}_\beta + [\overline{b_\alpha^2} - \bar{b}_\alpha^2]\, \delta_{\alpha\beta} \delta_{ij} \tag{31}$$

In (31) bars over b_α and $b_\alpha{}^2$ indicate averaging over both nuclear spin states and isotopic composition; $\bar{b}_\alpha$ is the mean coherent scattering length and $b_{\mathrm{inc},\alpha} \equiv [\overline{b_\alpha{}^2} - \bar{b}_\alpha{}^2]^{1/2}$ is the incoherent scattering length, each for nucleus α. From (31) and (30), the cross section may be separated into coherent and incoherent contributions

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{k}{k_0} N_m \left\{ \left(\sum_\alpha \bar{b}_\alpha \right)^2 S(\mathbf{q}\omega) + \left(\sum_\alpha b^2_{\mathrm{inc},\alpha} \right) S_s(\mathbf{q}\omega) \right\} \tag{32}$$

where N_m is the average number of molecules in the system, and $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$ are the coherent and incoherent dynamic structure factors, given by

$$S(\mathbf{q}\omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} I(\mathbf{q}t) \tag{33}$$

$$S_s(\mathbf{q}\omega) = (1/2\pi) \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} I_s(\mathbf{q}t) \tag{34}$$

In (33) and (34) the coherent and incoherent intermediate scattering functions $I(\mathbf{q}t)$ and $I_s(\mathbf{q}t)$, have been introduced, and are given by

$$I(\mathbf{q}t) = \left[1 \Big/ N_m \left(\sum_\alpha \bar{b}_\alpha \right)^2 \right] \sum_{\alpha\beta} \bar{b}_\alpha \bar{b}_\beta \left\langle \sum_{ij} \exp[-i\mathbf{q}\cdot\mathbf{r}_{i\alpha}(0)] \exp[i\mathbf{q}\cdot\mathbf{r}_{j\beta}(t)] \right\rangle \tag{35}$$

$$I_s(\mathbf{q}t) = \left(1 \Big/ N_m \sum_\alpha b^2_{\mathrm{inc},\alpha} \right) \sum_\alpha b^2_{\mathrm{inc},\alpha} \left\langle \sum_i \exp[-i\mathbf{q}\cdot\mathbf{r}_{i\alpha}(0)] \exp[i\mathbf{q}\cdot\mathbf{r}_{i\alpha}(t)] \right\rangle \tag{36}$$

It is convenient to separate those structural effects that arise from intermolecular correlations from those arising from intramolecular correlations. We therefore write

$$\mathbf{r}_{i\alpha} = \mathbf{R}_i + \mathbf{r}_{ci\alpha} \tag{37}$$

where $\mathbf{R}_i$ is the vector locating the center (arbitrarily defined) of molecule i and $\mathbf{r}_{ci\alpha}$ is the vector from the center of molecule i to the α nucleus of i. We also define $F_\alpha(\mathbf{q}\Omega_i)$ and $F(\mathbf{q}\Omega_i)$ by (Gubbins *et al.*$^{(6)}$)

$$F_\alpha(\mathbf{q}\Omega_i) = \exp(i\mathbf{q}\cdot\mathbf{r}_{ci\alpha}) \tag{38}$$

$$F(\mathbf{q}\Omega_i) = \left[\sum_\alpha \bar{b}_\alpha F_\alpha(\mathbf{q}\Omega_i) \right] \Big/ \sum_\alpha \bar{b}_\alpha \tag{39}$$

$F(\mathbf{q}\Omega_i)$ is proportional to the scattering amplitude for molecule i in the orientation Ω_i. Substituting (37) into (35), and separating the $i = j$ and $i \neq j$ terms in the ij summation, we obtain, with the use of (38) and (39),

$$I(\mathbf{q}t) = I_{\mathrm{intra}}(\mathbf{q}t) + I_{\mathrm{inter}}(\mathbf{q}t) \tag{40}$$

where

$$I_{\text{intra}}(\mathbf{q}t) = (1/N_m)\left\langle \sum_i \{\exp[i\mathbf{q}\cdot(\mathbf{R}_i(t) - \mathbf{R}_i(0))]\} F(\mathbf{q}\Omega_i(t)) F(\mathbf{q}\Omega_i(0))^* \right\rangle \tag{41}$$

$$I_{\text{inter}}(\mathbf{q}t) = (1/N_m)\left\langle \sum_{i\neq j} \{\exp[i\mathbf{q}\cdot(\mathbf{R}_j(t) - \mathbf{R}_i(0))]\} F(\mathbf{q}\Omega_j(t)) F(\mathbf{q}\Omega_i(0))^* \right\rangle \tag{42}$$

Here $I_{\text{intra}}(\mathbf{q}t)$ corresponds to the single-molecule part of the coherent scattering, and is independent of the choice of molecular center; $I_{\text{inter}}(\mathbf{q}t)$ corresponds to the intermolecular part of the coherent scattering. The corresponding expression for the incoherent intermediate scattering function is obtained from (36)–(38) as

$$\begin{aligned} I_s(\mathbf{q}t) = {} & \left(1\Big/N_m \sum_\alpha b^2_{\text{inc},\alpha}\right) \sum_\alpha b^2_{\text{inc},\alpha} \\ & \times \left\langle \sum_i \{\exp[i\mathbf{q}\cdot(\mathbf{R}_i(t) - \mathbf{R}_i(0))]\} F_\alpha(\mathbf{q}\Omega_i(t)) F_\alpha(\mathbf{q}\Omega_i(0))^* \right\rangle \end{aligned} \tag{43}$$

We now specialize to the case in which the molecules may be treated as rigid structures, i.e., internal rotation and vibration effects may be ignored. Equations (41)–(43) can be expressed in terms of the time-dependent angular pair correlation function. Thus (41) is equivalent to

$$\begin{aligned} I_{\text{intra}}(\mathbf{q}t) = {} & (1/N_m) \int d\mathbf{R}_1\, d\mathbf{R}_2\, d\Omega_1\, d\Omega_2 \{\exp[i\mathbf{q}\cdot(\mathbf{R}_2 - \mathbf{R}_1)]\} F(\mathbf{q}\Omega_1)^* F(\mathbf{q}\Omega_2) \\ & \times \Big\langle \sum_i \delta(\mathbf{R}_1 - \mathbf{R}_i(0))\, \delta(\mathbf{R}_2 - \mathbf{R}_i(t))\, \delta(\Omega_1 - \Omega_i(0)) \\ & \times \delta(\Omega_2 - \Omega_i(t)) \Big\rangle \end{aligned}$$

which, together with (5), becomes

$$I_{\text{intra}}(\mathbf{q}t) = \rho \int d\mathbf{R}_{12}\, [\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})] \langle G_s(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) F(\mathbf{q}\Omega_1)^* F(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \tag{44}$$

Here $\mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$ and $\langle\cdots\rangle_{\Omega_1\Omega_2}$ has the meaning given in (14). In (44) the fluid is assumed to be homogeneous, but it is not necessarily isotropic. The corresponding expressions for $I_{\text{inter}}(\mathbf{q}t)$ and $I_s(\mathbf{q}t)$ in terms of distribution functions are obtained from (42), (43), (5), and (6) as

$$I_{\text{inter}}(\mathbf{q}t) = \rho \int d\mathbf{R}_{12}\, [\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})] \langle G_d(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) F(\mathbf{q}\Omega_1)^* F(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \tag{45}$$

$$\begin{aligned} I_s(\mathbf{q}t) = {} & \left(\rho\Big/\sum_\alpha b^2_{\text{inc},\alpha}\right) \sum_\alpha b^2_{\text{inc},\alpha} \int d\mathbf{R}_{12} \\ & \times [\exp(-i\mathbf{q}\cdot R_{12})] \langle G_s(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t) F_\alpha(\mathbf{q}\Omega_1)^* F_\alpha(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \end{aligned} \tag{46}$$

Finally, from (33), (34), (40), and (44)–(46), the coherent and incoherent dynamic structure factors are given by

$$S(\mathbf{q}\omega) = (\rho/2\pi)\int_{-\infty}^{+\infty} dt\,[\exp(-i\omega t)]\int d\mathbf{R}_{12}$$

$$\times\,[\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})]\langle G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)F(\mathbf{q}\Omega_1)^*F(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \tag{47}$$

$$S_s(\mathbf{q}\omega) = \left(\rho\Big/2\pi\sum_\alpha b^2_{\text{inc},\alpha}\right)\sum_\alpha b^2_{\text{inc},\alpha}\int_{-\infty}^{+\infty} dt\,[\exp(-i\omega t)]\int d\mathbf{R}_{12}$$

$$\times\,[\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})]\langle G_s(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2 t)F_\alpha(\mathbf{q}\Omega_1)^*F_\alpha(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \tag{48}$$

In contrast to the case of monatomic fluids, it is not possible to invert Eq. (47) or Eq. (48) to obtain the time-dependent angular pair correlation functions.

4. LIMITING CASES

We now briefly consider various limiting conditions for $S(\mathbf{q}\omega)$. For monatomic fluids both $F_\alpha(\mathbf{q}\Omega_i)$ and $F(\mathbf{q}\Omega_i)$ reduce to unity, and (32), (47), and (48) become the usual equations,

$$\frac{d^2\sigma}{d\Omega\,d\omega} = \frac{k}{k_0}N_m\{\bar{b}^2S(\mathbf{q}\omega) + b^2_{\text{inc}}S_s(\mathbf{q}\omega)\} \tag{49}$$

with

$$S(\mathbf{q}\omega) = \frac{\rho}{2\pi}\int_{-\infty}^{+\infty} dt\,[\exp(-i\omega t)]\int d\mathbf{R}_{12}\,[\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})]G(\mathbf{R}_1\mathbf{R}_2 t) \tag{50}$$

$$S_s(\mathbf{q}\omega) = \frac{\rho}{2\pi}\int_{-\infty}^{+\infty} dt\,[\exp(-i\omega t)]\int d\mathbf{R}_{12}[\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})]G_s(\mathbf{R}_1\mathbf{R}_2 t) \tag{51}$$

In these equations $G(\mathbf{R}_1\mathbf{R}_2 t)$ is the usual Van Hove function, given by (24).

The static limit is obtained in the usual way, by integrating the differential scattering cross section over all values of the energy transfer ω. Thus, from (32), (47), (13), and (14), together with the static approximation (replacement of k/k_0 by unity),

$$(d\sigma/d\Omega)_{\text{coh}} = N_m\left(\sum_\alpha \bar{b}_\alpha\right)^2\int S(q\omega)\,d\omega = N_m\left(\sum_\alpha \bar{b}_\alpha\right)^2[S_{\text{intra}}(q) + S_{\text{inter}}(q)] \tag{52}$$

where

$$S_{\text{intra}}(\mathbf{q}) = \langle|F(\mathbf{q}\Omega_i)|^2\rangle_{\Omega_i} \tag{53}$$

$$S_{\text{inter}}(\mathbf{q}) = \rho\int d\mathbf{R}_{12}\,[\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})]\langle g(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2)F(\mathbf{q}\Omega_1)^*F(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \tag{54}$$

Similarly, the static limit for the incoherent cross section gives

$$(d\sigma/d\Omega)_{\rm inc} = N_m \sum_\alpha b^2_{{\rm inc},\alpha} \tag{55}$$

from (32), (48), and (13). Equations (52)–(55) have been previously derived elsewhere (Gubbins *et al.*⁽⁶⁾)

The limit $q \rightarrow 0$ gives $F_\alpha(\mathbf{q}\Omega_i) = F(\mathbf{q}\Omega_i) = 1$, so that (47) and (48) then become

$$S(0\omega) = [\rho kT\chi + N_m]\,\delta(\omega) \tag{56}$$

$$S_s(0\omega) = \delta(\omega) \tag{57}$$

as for monatomic fluids; here χ is the isothermal compressibility. In (56) the term $N_m\,\delta(\omega)$ represents forward scattering, and is omitted by some authors. The $q \rightarrow \infty$ limit corresponds to neutrons scattering from individual nuclei. Thus $I_{\rm inter}(\mathbf{q}t)$ vanishes for all t in this limit, while the other parts of the intermediate scattering function vanish except at $t = 0$, where they are given by

$$I_{\rm intra}(\infty 0) = \sum_\alpha \bar{b}_\alpha^{\,2} \Big/ \Big(\sum_\alpha \bar{b}_\alpha\Big)^2 \tag{58}$$

$$I_s(\infty 0) = 1 \tag{59}$$

It is readily verified that these results agree with those already derived for $q \rightarrow \infty$ in the static limit (Gubbins *et al.*⁽⁶⁾); thus

$$S(\infty) = I_{\rm intra}(\infty 0) \tag{60}$$

In the free rotation limit the intermediate scattering function factorizes into a translational and a rotational part. Thus, from (44)–(46) together with (26) and (27) the free rotation expressions are

$$I_s(\mathbf{q}t) = I_s^{\rm trans}(\mathbf{q}t)\,I_s^{\rm rot}(\mathbf{q}t) \tag{61}$$

$$I_{\rm intra}(\mathbf{q}t) = I_s^{\rm trans}(\mathbf{q}t)\,I_{\rm intra}^{\rm rot}(\mathbf{q}t) \tag{62}$$

$$I_{\rm inter}(\mathbf{q}t) = I_{\rm inter}^{\rm trans}(\mathbf{q}t)\,I_{\rm inter}^{\rm rot}(\mathbf{q}) \tag{63}$$

where

$$I_s^{\rm trans}(\mathbf{q}t) = \rho \int d\mathbf{R}_{12}\,[\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})]\,G_s(\mathbf{R}_1\mathbf{R}_2 t) \tag{64}$$

$$I_{\rm inter}^{\rm trans}(\mathbf{q}t) = \rho \int d\mathbf{R}_{12}\,[\exp(-i\mathbf{q}\cdot\mathbf{R}_{12})]\,G_d(\mathbf{R}_1\mathbf{R}_2 t) \tag{65}$$

$$I_s^{\rm rot}(\mathbf{q}t) = \Big(N_m \Big/ \sum_\alpha b^2_{{\rm inc},\alpha}\Big) \sum_\alpha b^2_{{\rm inc},\alpha} \langle G_s(\Omega_1\Omega_2 t) F_\alpha(\mathbf{q}\Omega_1)^* F_\alpha(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \tag{66}$$

$$I_{\rm intra}^{\rm rot}(\mathbf{q}t) = N_m \langle G_s(\Omega_1\Omega_2 t) F(\mathbf{q}\Omega_1)^* F(\mathbf{q}\Omega_2)\rangle_{\Omega_1\Omega_2} \tag{67}$$

$$I_{\rm inter}^{\rm rot}(\mathbf{q}) = \langle F(\mathbf{q}\Omega_i)\rangle^2_{\Omega_i} \tag{68}$$

5. SPECTRAL MOMENTS

The lower order spectral moments were worked out for atomic fluids by Placzek(12) and de Gennes.(2) Here we give a few simple lower order moments for homonuclear diatomic molecules, and comment on possible uses of these moments. The moments up to fourth order will be derived for general polyatomic molecules elsewhere (Mo *et al.*(10)).

The nth moment of the coherent spectrum is defined as

$$M(n) = \int_{-\infty}^{+\infty} d\omega \, S(\mathbf{q}\omega)\omega^n \tag{69}$$

with a similar expression for moments $M_s(n)$ of the incoherent spectrum $S_s(\mathbf{q}\omega)$. The normalizations of $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$ are such that $M(0) = S(q)$ and $M_s(0) = 1$. For classical systems the odd moments vanish since $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$ are even functions of ω.

From (33) and (69) we find that

$$M(n) = (-i)^n[\partial^n I(\mathbf{q}t)/\partial t^n]_{t=0} \tag{70}$$

From (70), (35), and (36) we find the following expressions for a homonuclear diatomic molecular fluid:

$$M(2) = \tfrac{1}{6}(kT/m)q^2[5 + j_0(ql) - 2j_2(ql)] \tag{71}$$

$$M_s(2) = (5/3)(kT/m)q^2 \tag{72}$$

$$M_s(4) = \frac{43}{5}\left(\frac{kT}{m}\right)^2 q^4 + \frac{q^2}{3m^2}\left[\langle F^2\rangle + \frac{4}{l^2}\langle \tau^2\rangle + 32\left(\frac{kT}{l}\right)^2\right] \tag{73}$$

In these expressions m is the molecular mass, l is the bond length, and $j_l(x)$ is a spherical Bessel function. $\langle F^2\rangle$ is the mean squared force on a molecule, and $\langle \tau^2\rangle$ is the mean squared torque.

The expressions (71) and (72) have been derived previously by de Gennes.(2) In Fig. 1 we plot the function

$$f(x) = \tfrac{1}{6}[5 + j_0(x) - 2j_2(x)] \tag{74}$$

where $x = ql$, and which appears in $M(2)$. It is seen that f passes through a minimum at $x_m \simeq (5/4)\pi$. Hence, from a plot of $M(2)/q^2$ vs. q, one can obtain the bond length in the liquid from the relation $q_m l \simeq (5/4)\pi$.

From (73) it is seen that the fourth moment of the incoherent spectrum involves the mean squared torque, as well as the mean squared force term which occurs for atomic liquids. The kT terms also differ from the atomic fluid case because of the rotational kinetic energy of the molecules. We have studied the influence of anisotropic intermolecular potentials on $M_s(4)$ using a pair potential of the form

$$u(\mathbf{R}_{12}\Omega_1\Omega_1) = u_0(R_{12}) + u_a(\mathbf{R}_{12}\Omega_1\Omega_2) \tag{75}$$

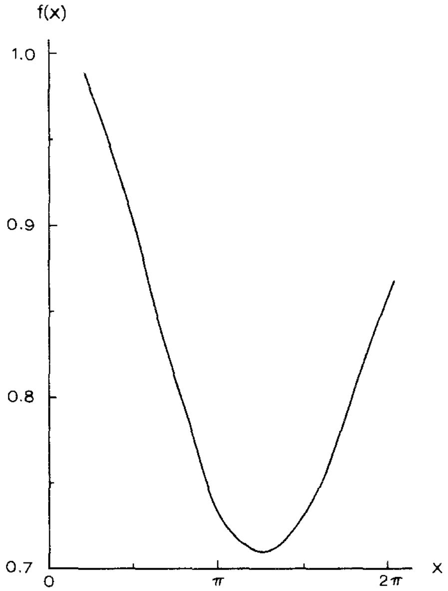

Fig. 1. The function $f(x)$, defined by Eq. (74), which appears in the equation for $M(2)$ for homonuclear diatomics.

where $u_0(R_{12})$ is the Lennard-Jones (12, 6) model, and $u_a(\mathbf{R}_{12}\Omega_1\Omega_2)$ is either a dipole–dipole or a quadrupole–quadrupole interaction. Monte Carlo calculations using this potential model are available for both the mean squared force (Gray *et al.*(4)) and the mean squared torque (Twu *et al.*(21)). Figure 2 shows a sample calculation of the reduced fourth moment, given by

$$\frac{M_s(4)}{(\epsilon/m\sigma^2)^2} = \frac{43}{5}T^{*2}q^{*4} + \frac{q^{*2}}{3}\left[\frac{\langle F^2\rangle}{(\epsilon/\sigma)^2} + \frac{4}{l^{*2}}\frac{\langle \tau^2\rangle}{\epsilon^2} + \frac{32T^{*2}}{l^{*2}}\right] \tag{76}$$

at $q^* = 5$ for two values of the reduced bond length. Here ϵ and σ are the Lennard-Jones parameters, $T^* = kT/\epsilon$, $q^* = q\sigma$, and $l^* = l/\sigma$. The effect of the anisotropic forces is less at larger q^* or T^* values. In principle the fourth incoherent moment provides an experimental method for estimating the mean squared torque, if the mean squared force is known, and vice versa. Other experiments depending on the mean squared torque and the mean squared force are reviewed by Twu *et al.*(21) and Gray *et al.*(4), respectively.

It is difficult to compare the theoretical moments (71)–(73) with moments derived from neutron data, because of the accuracy needed in the wings of the spectrum. One potential use of these moments is in conjunction with molecular dynamics data for $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$ for molecular liquids, as has

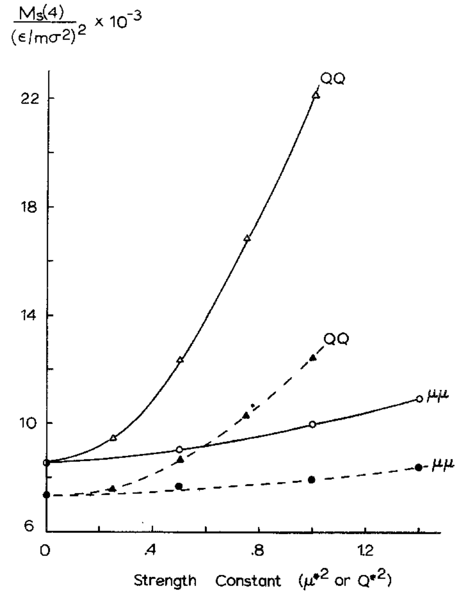

Fig. 2. Fourth moment of the incoherent spectrum for homonuclear diatomic molecules having the intermolecular potential given by Eq. (75), based on Monte Carlo data. Results are for dipolar (curves labeled $\mu\mu$) and quadrupolar (QQ curves) potentials at reduced bond lengths $l^* = 0.3$ (solid lines) and $l^* = 0.6$ (dashed lines). The state condition is $\rho^* = 0.800$, $T^* = 0.719$, and all curves are for $q^* = 5$.

been done for atomic liquids (Nijboer and Rahman$^{(11)}$). The moments also provide a check for theoretical models of $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$.

6. SUMMARY

The time-dependent angular pair correlation functions $G(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2t)$ and $G_s(\mathbf{R}_1\mathbf{R}_2\Omega_1\Omega_2t)$ have been introduced and their properties discussed. These functions provide the most natural theoretical framework for the interpretation of the inelastic neutron scattering functions $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$ for molecular liquids. Most models to date for the time-dependent angular correlation functions have assumed uncorrelated translational and rotational motions. This approximation should be tested more extensively. The lower order frequency moments of $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$ have been evaluated exactly for diatomic molecules. The fourth moment of $S_s(\mathbf{q}\omega)$ depends on the mean squared torque acting on a molecule, as well as on the mean squared force, and in principle provides a means of obtaining information about the nature and strength of the forces in the fluid. Alternatively, these moment results can be used as sum rules to check molecular dynamics results or theoretical models for $S(\mathbf{q}\omega)$ and $S_s(\mathbf{q}\omega)$.

APPENDIX. PERTURBATION THEORY FOR THE ANGULAR VAN HOVE FUNCTION

We consider "real" and "reference" systems with potentials $\mathcal{U}(\mathbf{R}^N\Omega^N)$ and $\mathcal{U}_0(\mathbf{R}^N)$, respectively, where

$$\mathcal{U}_0(\mathbf{R}^N) \equiv \langle \mathcal{U}(\mathbf{R}^N\Omega^N)\rangle_{\Omega^N} = (1/\hat{\Omega}^N) \int d\Omega^N\, \mathcal{U}(\mathbf{R}^N\Omega^N) \qquad \text{(A.1)}$$

The perturbing potential is $\mathcal{U}_a(\mathbf{R}^N\Omega^N) = \mathcal{U} - \mathcal{U}_0$. The Liouville operator (5) splits into

$$\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_a \qquad \text{(A.2)}$$

where

$$\mathcal{L}_0 = -i \sum_{j=1}^{N} \left[\frac{\partial H_N}{\partial \mathbf{p}_j}\cdot\frac{\partial}{\partial \mathbf{R}_j} - \frac{\partial \mathcal{U}_0}{\partial \mathbf{R}_j}\cdot\frac{\partial}{\partial \mathbf{p}_j} + \frac{\partial H_N}{\partial \mathbf{p}_{\Omega_j}}\cdot\frac{\partial}{\partial \Omega_j}\right] \qquad \text{(A.3)}$$

$$\mathcal{L}_a = i \sum_{j=1}^{N} \left[\frac{\partial H_N}{\partial \Omega_j}\cdot\frac{\partial}{\partial \mathbf{p}_{\Omega_j}} + \frac{\partial \mathcal{U}_a}{\partial \mathbf{R}_j}\cdot\frac{\partial}{\partial \mathbf{p}_j}\right] \qquad \text{(A.4)}$$

The perturbation theory for general time correlation functions $\langle A(0)B(t)\rangle$ in the canonical ensemble has been derived by Harris$^{(7)}$ (cf. Gubbins$^{(5)}$ for a review). Applying the general result to (8), we get to first order

$$\begin{aligned}\langle \rho(\mathbf{R}_1\Omega_1 0)\rho(\mathbf{R}_2\Omega_2 t)\rangle &= \langle \rho_0(\mathbf{R}_1\Omega_1 0)\rho_0(\mathbf{R}_2\Omega_2 t)\rangle_0 \\ &\quad - \beta\langle \mathcal{U}_a\rho_0(\mathbf{R}_1\Omega_1 0)\rho_0(\mathbf{R}_2\Omega_2 t)\rangle_0 \\ &\quad + i\int_0^t d\tau\, \langle \rho_0(\mathbf{R}_1\Omega_1 0)S_\tau^0\mathcal{L}_a\rho_0(\mathbf{R}_2\Omega_2 t-\tau)\rangle_0 \qquad \text{(A.5)}\end{aligned}$$

where $\rho_0(\mathbf{R}\Omega t) \equiv S_t^0\rho(\mathbf{R}\Omega 0)$ is the time-dependent density in the reference system, and $\langle\cdots\rangle_0$ indicates a reference system ensemble averaging.

In principle (A.5) allows one to calculate the angular Van Hove function from spherical reference system time correlation functions.

To calculate the correlation function of the centers $G(\mathbf{R}_1\mathbf{R}_2 t)$ from (A.5) we use (20) to get

$$\begin{aligned}G(\mathbf{R}_1\mathbf{R}_2 t) &= G_0(\mathbf{R}_1\mathbf{R}_2 t) - (\hat{\Omega}^2/\rho^2)\beta\langle \mathcal{U}_a\rho_0(\mathbf{R}_1 0)\rho_0(\mathbf{R}_2 t)\rangle_0 \\ &\quad + (i\hat{\Omega}^2/\rho^2)\int_0^t d\tau\, \langle \rho_0(\mathbf{R}_1 0)S_\tau^0\mathcal{L}_a\rho_0(\mathbf{R}_2 t-\tau)\rangle_0\end{aligned}$$

The reference averaging $\langle\cdots\rangle_0$ contains the unweighted angular average $\langle\cdots\rangle_{\Omega^N}$, which annuls the $\mathcal{U}_a$ term by virtue of $\langle\mathcal{U}_a\rangle_{\Omega^N} = 0$. The time integral term vanishes as $\mathcal{L}_a\rho_0(\mathbf{R}_2 t-\tau) = 0$; this follows because ρ_0 is independent of the p_Ω's and $\langle\mathcal{U}_a\rangle_\Omega{}^N = 0$. Thus to first order

$$G(\mathbf{R}_1\mathbf{R}_2 t) = G_0(\mathbf{R}_1\mathbf{R}_2 t) \qquad \text{(A.6)}$$

as stated in (29).

REFERENCES

1. M. S. Ananth, K. E. Gubbins, and C. G. Gray, *Mol. Phys.* **28**:1005 (1974).
2. P. G. de Gennes, *Physica* **25**:825 (1959).
3. P. A. Egelstaff, Ed., *Thermal Neutron Scattering*, Academic Press, New York (1965), Chapters 7 and 8.
4. C. G. Gray, S. S. Wang, and K. E. Gubbins, *Chem. Phys. Lett.* **26**:610 (1974).
5. K. E. Gubbins, *Statistical Mechanics*, Vol. I, *Specialist Periodical Reports*, ed. by K. Singer, The Chemical Society, London (1973), Chapter 4.
6. K. E. Gubbins, C. G. Gray, P. A. Egelstaff, and M. S. Ananth, *Mol. Phys.* **25**:1353 (1973).
7. S. Harris, *Mol. Phys.* **21**:933 (1971).
8. T. J. Krieger and M. S. Nelkin, *Phys. Rev.* **106**:290 (1957).
9. H. Maeda and N. Saito, *J. Phys. Soc. Japan* **27**:984 (1969).
10. K. C. Mo, K. E. Gubbins, and C. G. Gray, to be published (1975).
11. B. R. A. Nijboer and A. Rahman, *Physica* **32**:415 (1966).
12. G. Placzek, *Phys. Rev.* **86**:377 (1952).
13. N. K. Pope, *Can. J. Phys.* **30**:597 (1952).
14. R. G. Sachs and E. Teller, *Phys. Rev.* **60**:18 (1941).
15. D. W. Schaefer, G. B. Benedek, P. Schofield, and E. Bradford, *J. Chem. Phys.* **55**:3884 (1971).
16. V. F. Sears, *Can. J. Phys.* **44**:1279 (1966a).
17. V. F. Sears, *Can. J. Phys.* **44**:1299 (1966b).
18. V. F. Sears, *Can. J. Phys.* **45**:237 (1967).
19. A. G. St. Pierre and W. A. Steele, *Phys. Rev.* **184**:172 (1969).
20. W. A. Steele and R. Pecora, *J. Chem. Phys.* **42**:1863 (1965).
21. C. H. Twu, C. G. Gray, and K. E. Gubbins, *Mol. Phys.* **27**:1601 (1974).
22. L. Van Hove, *Phys. Rev.* **95** 249 (1954).
23. L. Verlet and J. Weis, *Mol. Phys.* **28**:665 (1974).
24. S. S. Wang, C. G. Gray, P. A. Egelstaff, and K. E. Gubbins, *Chem. Phys. Lett.* **21**:123 (1973).
25. A. C. Zemach and R. J. Glauber, *Phys. Rev.* **101**:118, 129 (1956).