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Sum rules and atomic correlations in classical liquids*

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The sixth frequency moment of the spectral functions of both the longitudinal and transverse current correlations along with their self-parts has been derived for a system of particles interacting through a two-body potential. The first two frequency moments of the spectral function of the energy-density fluctuation, and the first four frequency moments of the spectral function of the kinetic-energy-density fluctuation-correlation functions have also been derived. Numerical estimates for the fourth and sixth frequency moments of the spectral function of the longitudinal current correlations have been made for liquid argon. From this some information about the behavior of the contributions of triplet and quadruplet correlation functions to the frequency moments of liquid argon have been obtained. Numerical estimates have also been made for the first four frequency moments of the kinetic-energy-density fluctuation-correlation function in the long-wavelength limit for liquid argon.

I. INTRODUCTION

In the study of atomic and molecular processes in liquids, the calculation of the space- and time-dependent correlation functions of the dynamical variables which describe the decay of fluctuations in an equilibrium system, is the fundamental problem. Many phenomena in liquids including transport coefficients and scattering processes can be described in terms of these correlation functions. For example, in the hydrodynamic region, the longitudinal viscosity and diffusion coefficient of a fluid are related to the appropriate limits of the coherent- and incoherent-scattering law, respectively.[1] The difficulty, of course, is that there is no first-principles theory except the machine solution of Newton's equations for calculating these correlation functions for a classical fluid. There are, however, a number of useful calculable properties, which can be obtained from the knowledge of only the static correlation functions and the interparticle potential. Among these are the moment sum rules—the coefficients in the short-time expansion of the correlation functions. These relations are exact and can serve to check the internal consistency of any experiment or theory which calculates the space-time-dependent correlation functions.

In the past, the frequency-moment sum rules have played a significant role in analyzing the results for the correlation functions obtained from both the molecular-dynamics calculations and from the neutron inelastic-scattering experiments.[2-7] In view of this important application of the frequency-moment sum rules, in this paper we have extended the existing sum-rule calculations. The first four frequency moments of the spectral functions of both the longitudinal and transverse current correlations are known.[8,9] We have derived the results for the sixth frequency moment of both the longitudinal and transverse current correlations. The self-part of the sixth frequency moment of the current correlations (both longitudinal and transverse) have also been obtained. The fourth and sixth frequency moments of the longitudinal current-correlation function have been estimated for liquid argon at 76°K in the range of momentum transfer 0.5–3.3 Å^{-1} using the molecular-dynamics results of Rahman.[10] The contributions to the fourth and sixth frequency moments arising due to the static pair correlation function have been calculated numerically using the molecular-dynamics data of Verlet.[11] From the above calculations we have estimated the contributions of the triplet and quadruplet correlation functions to the frequency moments.

Recently Rahman[12] has calculated from the molecular-dynamics experiments the kinetic-energy-density (KED) correlation function for a liquid-sodium-like system. KED is a part of the energy density which occurs in the study of hydrodynamic phenomena where one is concerned with the space- and time-dependent fluctuations of the number and the energy density in the system. Rahman[12] has used the memory-function approach[13] and the first two frequency moments of the KED correlation function to analyze his molecular-dynamics data for liquid sodium. The KED is not a conserved variable whereas the energy density is, and thus the correlation function of energy density is physically a more important quantity than KED. We have, therefore, calculated its first two frequency moments. These involve static correlations up to three and four particles. It seems that the fourth frequency moment of the energy-density correlation function will involve still higher correlations (up to five or even more particles). However, the first four frequency moments of the correlation function of the KED fluctuations involve correlations up to three particles. Explicit expressions for these have also been obtained.

In Sec. II, we describe our method of calculation and the results for the various frequency moments of the current correlations and energy-density correlations. The fourth and sixth frequency moments of the spectral function of the longitudinal current correlation function have been estimated for liquid argon in Sec. III. The first four frequency moments of the kinetic-energy-density fluctuation-correlation function have also been estimated in the long-wavelength limit for liquid argon in Sec. III. Concluding remarks are given in Sec. IV.

II. METHOD OF CALCULATION OF FREQUENCY MOMENT SUM RULES

The time-correlation function of any dynamical variable $D(\vec{q}, t)$, which is defined as

$$f(\vec{q}, t) = \langle D(\vec{q}, t) D^*(\vec{q}, 0)\rangle , \tag{1}$$

is a real and even function of time with the short-time expansion (i.e., Taylor's expansion) given by

$$f(\vec{q}, t) = f_0 - f_2 \frac{t^2}{2!} + f_4 \frac{t^4}{4!} - \cdots , \tag{2}$$

where the angular brackets denote an equilibrium ensemble average. f_0, $-f_2$, f_4 denote the time derivatives of $f(\vec{q}, t)$ at $t=0$ of the zeroth, second and fourth order. Since we are concerned with the isotropic systems, we will write $f(\vec{q}, t)$ and various other quantities as a function of $q = |\vec{q}|$. We define the Fourier transform of $f(q, t)$ as

$$f(q, t) = \int_{-\infty}^{\infty} d\omega\, e^{i\omega t} f(q, \omega). \tag{3}$$

Then the nth frequency moment of $f(q, \omega)$ is given by the relation

$$\langle \omega^n \rangle = \int_{-\infty}^{\infty} d\omega\, \omega^n f(q, \omega) \Big/ f(q, t=0), \tag{4a}$$

which using (2) becomes

$$\langle \omega^n \rangle = (-1)^n \left. \frac{d^n f(q, t)}{dt^n} \right|_{t=0} \Big/ f(q, t=0), \tag{4b}$$

where $n = 0, 2, 4, 6, \ldots$, etc. For a classical system odd moments vanish. We shall now calculate the frequency moments of the correlation functions of various dynamical variables of interest.

A. Current correlations

For a classical system of N particles, we define the longitudinal- and transverse-current-density-fluctuation operators as

$$J_l(q, t) = N^{-1/2} \sum_i v_{ix}(t) e^{iqx_i(t)} \tag{5a}$$

and

$$J_t(q, t) = N^{-1/2} \sum_i v_{iy}(t) e^{iqx_i(t)}, \tag{5b}$$

respectively. We have taken the wave vector $\vec{q}$ along the x axis; $v_{ix}(t)$ and $x_i(t)$ are the x components of the velocity and position of the ith particle at any time t. If $C_l(q, t)$ and $C_t(q, t)$ represent the correlations of the longitudinal and transverse current density, respectively, then the Fourier transform of the density correlation function $S(q, \omega)$, which is observed in coherent inelastic neutron-scattering experiments, is related to the spectral function of the longitudinal current correlation function as

$$C_l(q, \omega) = \omega^2 S(q, \omega)/q^2. \tag{6}$$

It can be easily seen that

$$C_l(q, t=0) = C_t(q, t=0) = k_B T/M. \tag{7}$$

In the derivation of the frequency moments of the spectral functions of the time-correlation functions, we use the following well-known results:
(i) For a system in equilibrium the time-correlation functions depend only on the time difference, so that they satisfy

$$\langle \dot{x}(0) x^{2m+1}(t)\rangle = (-1)^m \langle x^{m+1}(0) x^{m+1}(t)\rangle , \tag{8}$$

where $x^m(t)$ denotes the mth time derivative of $x(t)$. (ii) The Yvon theorem, i.e.,

$$\left\langle F(r) \frac{\partial H(r,p)}{\partial r_i} \right\rangle = k_B T \left\langle \frac{\partial F(r)}{\partial r_i} \right\rangle , \tag{9}$$

where r and p represent the position and momentum, respectively; $F(r)$ is any regular function of the positions of the particles; and H is the Hamiltonian of the system given by

$$H = \sum_i \frac{p_i^2}{2M} + \Phi(r). \tag{10}$$

$\Phi(r)$ is the total interaction potential and we assume it to be the sum of pairwise interactions, so that

$$\Phi(r) = \frac{1}{2} \sum_{j \neq i} \varphi(|\vec{r}_i - \vec{r}_j|) = \frac{1}{2} \sum_{j \neq i} \varphi(r_{ij}). \tag{11}$$

Starting from Eqs. (1) and (4) and making use of Eqs. (5a) and (5b), it is straightforward to derive the expressions for the low-order frequency moments (up to $n=4$) of the spectral functions of the current correlations.[8,9] But the results for the sixth frequency moments of the longitudinal and transverse current correlations are not known as yet. The calculation of these frequency moments is straightforward but tedious. Therefore, we state here few relevant steps. The sixth frequency moment of the spectral function of the longitudinal current density correlation function can be written as

$$\begin{aligned}\langle \omega_l^6\rangle = \frac{M}{k_BT}\sum_{j=1}^{N} \langle (&q^6 v_{1x}{}^4 v_{jx}{}^4 + 36q^4 v_{1x}{}^2 v_{jx}{}^2 \dot v_{1x}\dot v_{jx} - 6q^4 v_{1x}{}^4 \dot v_{jx}{}^2 - 8q^4 v_{1x}{}^4 v_{jx}\ddot v_{jx} + 9q^2 \dot v_{1x}{}^2 \dot v_{jx}{}^2 \\ &+16q^2 v_{1x} v_{jx}\ddot v_{1x}\ddot v_{jx} + 24q^2 \dot v_{1x}{}^2 v_{jx}\ddot v_{jx} - 12q^2 v_{1x}{}^2 \dot v_{1x}\dddot v_{jx} + \dddot v_{1x}\dddot v_{jx})\cos q(x_1-x_j) \\ &-(12q^5 v_{1x}{}^4 v_{jx}{}^2 \dot v_{jx} + 36q^3 v_{1x}{}^2 \dot v_{1x}\dot v_{jx}{}^2 + 48q^3 v_{1x}{}^2 v_{jx}\dot v_{1x}\ddot v_{jx} + 2q^3 v_{jx}{}^4 \dddot v_{1x} \\ &+6q\dddot v_{jx}\dot v_{1x}{}^2 + 8q\, v_{1x}\ddot v_{1x}\dddot v_{jx})\sin q(x_1-x_j)\rangle ,\end{aligned} \tag{12}$$

where

$$\dot v_{jx} = -M^{-1}\frac{\partial\Phi(r)}{\partial x_j}, \tag{13a}$$

$$\ddot v_{jx} = -M^{-1}\frac{\partial^2\Phi(r)}{\partial x_j\,\partial r_{k\alpha}} v_{k\alpha}, \tag{13b}$$

$$\dddot v_{jx} = -M^{-1}\left(\frac{\partial^2\Phi(r)}{\partial x_j\,\partial r_{k\alpha}}\dot v_{k\alpha} + \frac{\partial^3\Phi(r)}{\partial x_j\partial r_{k\alpha}\partial r_{l\beta}} v_{k\alpha}v_{l\beta}\right). \tag{13c}$$

Here $k, l, \ldots$ run from 1 to N; $\alpha, \beta, \ldots$ denote the Cartesian components x, y, z, and summations over doubly occurring indices are implied. We then calculate each term on the right-hand side of Eq. (12) using Eq. (13). Calculations are further simplified because of the facts that the position and velocity, velocity and acceleration, and position and rate of change of acceleration are not correlated in classical systems. We thus obtain the expression for the sixth frequency moment of the longitudinal current correlation function [i.e., eighth frequency moment of $S(q,\omega)$] which on introducing the notation, $U_\alpha(r)=\partial\varphi(r)/\partial r_\alpha$ $U_{\alpha\beta}(r)=\partial^2\varphi(r)/\partial r_\alpha\partial r_\beta, \ldots,$ etc., can be written concisely as

$$\begin{aligned}\langle\omega_l^6\rangle = {}&105\left(\frac{q^2k_BT}{M}\right)^3 + \frac{n}{M^3}\int d\vec r\, g_2(\vec r)[210(q^2k_BT)^2 U_{xx}(r) + (39\cos qx - 21)(qk_BT)^2 U_{xxxx}(r) \\ &+35(1+\cos qx)(q^2k_BT)U_{xx}^2(r) + 56(q^2k_BT)U_{x\alpha}^2(r) + 72(qk_BT)\sin qx\, U_{x\alpha}(r)U_{xx\alpha}(r) \\ &+4(1-\cos qx)U_{\alpha\beta}(r)U_{x\alpha}(r)U_{x\beta}(r) + 12(k_BT)(1-\cos qx)U_{x\alpha\beta}^2(r)] \\ &+\frac{n^2}{M^3}\int\!\!\int d\vec r\, d\vec r\,'\, g_3(\vec r,\vec r\,')\{7(q^2k_BT)[5U_{xx}(r)U_{xx}(r') + 4U_{x\alpha}(r)U_{x\alpha}(r')] + 6(qk_BT) \\ &\times[6\sin qx + \sin qx' - \sin q(x-x')]U_{xx\alpha}(r)U_{x\alpha}(r') + 3(k_BT)[\cos q(x-x') - 2\cos qx + 1]U_{x\alpha\beta}(r)U_{x\alpha\beta}(r') \\ &+4[1+\cos q(x-x') - \cos qx' - \cos qx]U_{\alpha\beta}(r)U_{x\alpha}(r)U_{x\beta}(r') + 2(1-\cos qx)U_{x\alpha}(r)U_{x\beta}(r)U_{\alpha\beta}(r') \\ &+(2\cos qx - 1)U_{x\alpha}(r)U_{x\beta}(r')U_{\alpha\beta}(\vec r-\vec r\,') - \cos qx\, U_{\alpha\beta}(r)U_{x\alpha}(r')U_{x\beta}(\vec r-\vec r\,')\} \\ &+\frac{n^3}{M^3}\int\!\!\int\!\!\int d\vec r\, d\vec r\,'\, d\vec r\,''\, g_4(\vec r,\vec r\,',\vec r\,'')\{[1+\cos q(x-x') - 2\cos qx]U_{x\alpha}(r)U_{x\beta}(r')U_{\alpha\beta}(r'') \\ &\qquad +[2\cos qx'' - \cos qx - \cos q(x'-x'')]U_{\alpha\beta}(r)U_{x\alpha}(r')U_{x\beta}(\vec r\,''-\vec r)\},\end{aligned} \tag{14}$$

where $g_2(\vec r)$, $g_3(\vec r,\vec r\,')$, and $g_4(\vec r,\vec r\,',\vec r\,'')$ are the static pair, triplet, and quadruplet correlation functions. The four-particle distribution function is defined as

$$n^4 g_4(\vec r,\vec r\,',\vec r\,'') = \sum_{i\neq j\neq k\neq l}\langle\delta(\vec r-\vec r_i+\vec r_j)\delta(\vec r\,'-\vec r_l+\vec r_j)\delta(\vec r\,''-\vec r_k+\vec r_j)\rangle . \tag{15}$$

The sixth frequency moment of the self-part of the spectral function of the longitudinal-current-correlation function (i.e., eighth frequency moment of the incoherent-scattering law) can be obtained by considering only the self-part of Eq. (12) and thus we obtain

$$\langle \omega_{l,s}^6 \rangle = 105\left(\frac{q^2 k_B T}{M}\right)^3 + 210\left(\frac{q^2 k_B T}{M}\right)^2 A + 28\left(\frac{q^2 k_B T}{M}\right) B + C + 7\left(\frac{q^2 k_B T}{M}\right)\frac{n}{M^2}\int d\vec{r}\, g_2(\vec{r})[5U_{xx}^2(r) - 3k_B T U_{xxxx}(r)]$$
$$+ 35\left(\frac{q^2 k_B T}{M}\right)\frac{n^2}{M^2}\int\int d\vec{r}\, d\vec{r}'\, g_3(\vec{r}, \vec{r}')\, U_{xx}(r)\, U_{xx}(r'), \tag{16}$$

where $-A$, B, and $-C$ are the second, third, and fourth coefficients in the short-time expansion of the normalized velocity autocorrelation function. The first two coefficients A and B are known.[14] We state here the result for the third coefficient,

$$C = \frac{\langle \dddot{v}_{1x}{}^2(0)\rangle}{\langle v_{1x}{}^2(0)\rangle} = \frac{4n}{M^3}\int d\vec{r}\, g_2(\vec{r})[U_{\alpha\beta}(r) U_{x\alpha}(r) U_{x\beta}(r) + 3k_B T U_{x\alpha\beta}^2(r)] + \frac{n^2}{M^3}\int\int d\vec{r}\, d\vec{r}'\, g_3(\vec{r}, \vec{r}')$$
$$\times \{3k_B T U_{x\alpha\beta}(r) U_{x\alpha\beta}(r') + U_{x\alpha}(r)[4U_{\alpha\beta}(r) U_{x\beta}(r') + 2U_{x\beta}(r) U_{\alpha\beta}(r') - U_{x\beta}(r') U_{\alpha\beta}(\vec{r} - \vec{r}')]\}$$
$$+ \frac{n^3}{M^3}\int\int\int d\vec{r}\, d\vec{r}'\, d\vec{r}''\, g_4(\vec{r}, \vec{r}', \vec{r}'')\, U_{x\alpha}(r)\, U_{x\beta}(r')\, U_{\alpha\beta}(r''). \tag{17}$$

It may be noted that the result given by Eq. (17) represents the sixth frequency moment of the spectral function of the velocity autocorrelation function.

In a similar way, we obtain for the sixth frequency moment of the spectral function of the transverse-current-correlation function, the expression

$$\langle \omega_t^6 \rangle = 15\left(\frac{q^2 k_B T}{M}\right)^3 + \frac{n}{M^3}\int d\vec{r}\, g_2(\vec{r})\{60(q^2 k_B T)^2 U_{xx}(r) + 3(q k_B T)^2(13\cos qx - 10) U_{xxyy}(r) + 32(q^2 k_B T) U_{y\alpha}^2(r)$$
$$+ 5(q^2 k_B T)(1 + \cos qx)[3U_{xx}(r) U_{yy}(r) + 4U_{xy}^2(r)] + 4(q k_B T)\sin qx\,[13U_{xy\alpha}(r) U_{y\alpha}(r)$$
$$+ 5U_{yy\alpha}(r) U_{x\alpha}(r)] + 4(1 - \cos qx) U_{\alpha\beta}(r) U_{y\alpha}(r) U_{y\beta}(r) + 12(k_B T)(1 - \cos qx) U_{y\alpha\beta}^2(r)\}$$
$$+ \frac{n^2}{M^3}\int\int d\vec{r}\, d\vec{r}' g_3(\vec{r}, \vec{r}')\{(q^2 k_B T)[15U_{xx}(r) U_{yy}(r') + 20U_{xy}(r) U_{xy}(r') + 16U_{y\alpha}(r) U_{y\alpha}(r')]$$
$$+ 2(q k_B T)[3\sin qx' + 13\sin qx - 3\sin q(x - x')] U_{xy\alpha}(r) U_{y\alpha}(r') - 2(q k_B T)\sin qx\, U_{yy\alpha}(r) U_{x\alpha}(r')$$
$$+ 3(k_B T)[\cos q(x - x') - 2\cos qx + 1] U_{y\alpha\beta}(r) U_{y\alpha\beta}(r') + 4[1 + \cos q(x - x') - \cos qx' - \cos qx]$$
$$\times U_{\alpha\beta}(r) U_{y\alpha}(r) U_{y\beta}(r') + 2(1 - \cos qx) U_{y\alpha}(r) U_{y\beta}(r) U_{\alpha\beta}(r') + (2\cos qx - 1)$$
$$\times U_{y\beta}(r) U_{y\alpha}(r') U_{\alpha\beta}(\vec{r} - \mathrm{r}') - \cos qx\, U_{\alpha\beta}(r) U_{y\alpha}(r') U_{y\beta}(\vec{r} - \vec{r}')\} + \frac{n^3}{M^3}\int\int\int d\vec{r}\, d\vec{r}'\, d\vec{r}''\, g_4(\vec{r}, \vec{r}', \vec{r}'')$$
$$\times \{[1 + \cos q(x - x') - 2\cos qx] U_{y\alpha}(r) U_{y\beta}(r') U_{\alpha\beta}(r'')$$
$$+ [2\cos qx'' - \cos qx - \cos q(x' - x'')] U_{\alpha\beta}(r) U_{y\alpha}(r') U_{y\beta}(\vec{r}'' - \vec{r})\}. \tag{18}$$

Its self-part is given by

$$\langle \omega_{t,s}^6 \rangle = 15\left(\frac{q^2 k_B T}{M}\right)^3 + 60\left(\frac{q^2 k_B T}{M}\right)^2 A + 16\left(\frac{q^2 k_B T}{M}\right) B + C + 5\left(\frac{q^2 k_B T}{M}\right)\frac{n}{M^2}\int d\vec{r}\, g_2(\vec{r})$$
$$\times [3U_{xx}(r) U_{yy}(r) + 4U_{xy}^2(r) - 6k_B T U_{xxyy}(r)] + 5\left(\frac{q^2 k_B T}{M}\right)\frac{n^2}{M^2}\int\int d\vec{r}\, d\vec{r}'\, g_3(\vec{r}, \vec{r}')$$
$$\times [3U_{xx}(r) U_{yy}(r') + 4U_{xy}(r) U_{xy}(r')]. \tag{19}$$

To our knowledge the results for various frequency moments obtained in this subsection have not been obtained previously.[15,16] In Sec. III we present the numerical estimates of the sixth and eighth frequency moments of the dynamical structure factor.

B. Energy-density correlations

So far we have been concerned with the calculation of the frequency-moment sum rules of the spectral functions of the current correlations. In this subsection, we calculate the frequency-moment sum rules for the correlation functions of the energy-density and KED fluctuations. We define the energy-density fluctuation operator (per particle) as

$$\epsilon(q,t)=\frac{1}{n\sqrt{N}}\sum_{i=1}^{N}\left[\frac{1}{2}\left(\frac{p_i^2}{M}+\sum_{j\neq i}\varphi(r_{ij})\right)-e\right]\exp[iqx_i(t)]\,, \tag{20}$$

where e is the mean energy per particle and is given by

$$e=\tfrac{3}{2}k_BT+\tfrac{1}{2}n\int d\vec{r}\,g_2(r)\,\varphi(r). \tag{21}$$

Let $E(q,t)$ represent the correlation of the energy-density fluctuation operator and let $E_0, -E_2, \ldots$ denote the time derivatives of $E(q,t)$ at $t=0$ [which are directly related to the moments of the spectral function of the energy-density-fluctuation-correlation function, $E(q,\omega)$]; then we obtain for E_0 the expression

$$\begin{aligned}E_0={}&\frac{1}{4n^2}\left\langle\sum_{l=1}^{N}\left[M^2\vec{v}_1^{\,2}\vec{v}_l^{\,2}+\sum_{m\neq l}\left(2M\vec{v}_1^{\,2}\varphi(r_{lm})+\varphi(r_{lm})\sum_{j\neq 1}\varphi(r_{ij})\right)\cos q(x_1-x_l)\right]\right\rangle\\&+\frac{e}{n^2}\left\langle\sum_{l=1}^{N}\left(e-M\vec{v}_1^{\,2}-\sum_{j\neq 1}\varphi(r_{1j})\right)\cos q(x_1-x_l)\right\rangle.\end{aligned} \tag{22}$$

The first average in (22) arises due to the energy density, whereas the second one is the consequence of fluctuation in energy density. E_0 can further be expressed in terms of the static correlation functions and the interparticle potential by extracting from (22) the contributions arising due to the self-term ($l=1$) and the distinct term ($l\neq 1$). Thus Eq. (22) reduces to

$$\begin{aligned}E_0={}&\frac{M^2}{4n^2}\left[\left(\frac{k_BT}{M}\right)^2[6+9S(q)]+\frac{4e}{M}S(q)\left(\frac{e}{M}-\frac{3k_BT}{M}\right)+\frac{n}{M^2}\int d\vec{r}\,g_2(\vec{r})(1+\cos qx)\,\varphi(r)[\varphi(r)+6k_BT-4e]\right.\\&+\frac{n^2}{M^2}\int\int d\vec{r}\,d\vec{r}\,'\,g_3(\vec{r},\vec{r}\,')\,\varphi(r)\{2\cos qx'[\varphi(r')+3k_BT-2e]+\varphi(r')[1+\cos q(x-x')]\}\\&\left.+\frac{n^3}{M^2}\int\int\int d\vec{r}\,d\vec{r}\,'\,d\vec{r}\,''\,g_4(\vec{r},\vec{r}\,',\vec{r}\,'')\,\varphi(r)\,\varphi(|\vec{r}\,'-\vec{r}\,''|)\cos qx''\right],\end{aligned} \tag{23}$$

where $S(q)$ is the static structure factor. Note that this expression for E_0, the zeroth frequency moment of the spectral function of the energy-density-fluctuation-correlation function, involves the static quadruplet correlation function which is not yet known. Thus it seems difficult to obtain any further information about the short-time expansion of the energy-density correlation function. But it is interesting to note that the expression for the second frequency moment of the spectral function of the energy-density-fluctuation-correlation function contains correlations only up to three particles, and it can be written as

$$\begin{aligned}E_2={}&\frac{1}{4n^2}\left\langle\sum_{l=1}^{N}\left[\left(4M^2(\vec{v}_1\cdot\vec{a}_1)(\vec{v}_l\cdot\vec{a}_l)+q^2M^2v_{1x}v_{lx}\vec{v}_1^{\,2}\vec{v}_l^{\,2}+q^2Mv_{1x}v_{lx}\vec{v}_l^{\,2}\sum_{j\neq 1}\varphi(r_{1j})+q^2v_{1x}v_{lx}\sum_{j\neq 1}\sum_{m\neq l}\varphi(r_{1j})\varphi(r_{lm})\right.\right.\right.\\&\left.+4M(\vec{v}_1\cdot\vec{a}_1)\sum_{k}\sum_{m\neq l}v_{k\alpha}\frac{\partial\varphi(r_{lm})}{\partial r_{k\alpha}}+\sum_{k,n}\sum_{j\neq 1}\sum_{m\neq l}v_{k\alpha}v_{n\beta}\frac{\partial\varphi(r_{1j})}{\partial r_{k\alpha}}\frac{\partial\varphi(r_{lm})}{\partial r_{n\beta}}\right)\cos q(x_1-x_l)\\&-\left(4qM^2v_{1x}\vec{v}_1^{\,2}(\vec{v}_l\circ\vec{a}_l)+4qMv_{1x}(\vec{v}_l\cdot\vec{a}_l)\sum_{j\neq 1}\varphi(r_{1j})+2qMv_{1x}\vec{v}_1^{\,2}\sum_{k}\sum_{m\neq l}v_{k\alpha}\frac{\partial\varphi(r_{lm})}{\partial r_{k\alpha}}\right.\\&\left.\left.\left.+2qv_{1x}\sum_{k}\sum_{j\neq 1}\sum_{m\neq l}v_{k\alpha}\varphi(r_{1j})\frac{\partial\varphi(r_{lm})}{\partial r_{k\alpha}}\right)\sin q(x_1-x_l)\right]\right\rangle\\&+\frac{e}{n^2}\left\langle\sum_{l=1}^{N}\left[q^2v_{1x}v_{lx}\left(e-M\vec{v}_1^{\,2}-\sum_{j\neq 1}\varphi(r_{1j})\right)\cos q(x_1-x_l)\right.\right.\\&\left.\left.+qv_{1x}\left(2M(\vec{v}_l\circ\vec{a}_l)+\sum_{k}\sum_{m\neq l}v_{k\alpha}\frac{\partial\varphi(r_{lm})}{\partial r_{k\alpha}}\right)\sin q(x_1-x_l)\right]\right\rangle,\end{aligned} \tag{24}$$

where $\vec{a}=d\vec{v}/dt$ denotes the acceleration. Here also, the quantity in the second pair of angular brackets represents the contribution of the fluctuation part and in the first pair is the contribution of the energy density. Separating (24) into self- and distinct parts and performing the averages, we obtain the following result for the second frequency moment of the spectral function of the energy-density-fluctuation-correlation function,

$$E_2 = \frac{M^2}{4n^2}\left(\frac{k_BT}{M}\right)\left\{\left(\frac{k_BT}{M}\right)\left[35\left(\frac{q^2k_BT}{M}\right)+12\Omega^2(0)-40\frac{eq^2}{M}\right]+\frac{4e^2q^2}{M^2}+\frac{n}{M^2}\int d\vec{r}\,g_2(\vec{r})\{q^2\varphi(r)[\varphi(r)+10k_BT-4e]\right.$$
$$-2(1+\cos qx)(\vec{\nabla}\varphi(r))^2-2\sin qx\,(\vec{q}\cdot\vec{\nabla}\varphi(r))[\varphi(r)+3k_BT-2e]\}+\frac{n^2}{M^2}\int\int d\vec{r}\,d\vec{r}'\,g_3(\vec{r},\vec{r}')$$
$$\left.\times\{\varphi(r')[q^2\varphi(r)-2\sin qx\,(\vec{q}\cdot\vec{\nabla}\varphi(r))]-(\vec{\nabla}\varphi(r))\cdot(\vec{\nabla}\varphi(r'))[4+3\cos qx-\cos q(x-x')]\}\right\}, \qquad (25)$$

where

$$\Omega^2(q)=\frac{n}{M}\int d\vec{r}\,g_2(\vec{r})\cos qx\,U_{xx}(r). \qquad (26)$$

As one expects the expression (25) should contain correlations up to four and five particles. But it has been found that the terms which involve four and five particles are zero within the assumption of pair potential. Further, as is clear from the definition of the energy-density fluctuation, one can obtain the frequency moments of the energy-density correlation function by substituting $e=0$ in the expressions for E_0 and E_2. We have found that the expression for the fourth frequency moment of the spectral function of the energy-density-fluctuation-correlation function is difficult to handle, and it seems that it will contain correlations up to five particles. Therefore, it is difficult to obtain any further information about the short-time behavior of the energy-density-fluctuation-correlation function.

However, one can obtain much more information about the short-time behavior of another quantity called the KED fluctuation-correlation function. We have calculated here the first four frequency moments of the spectral function of the KED fluctuation-correlation function. We define the KED fluctuation operator (per particle) as

$$T(q,t)=\frac{1}{n\sqrt{N}}\sum_{i=1}^{N}\left(\frac{p_i^2}{2M}-T_0\right)\exp[iqx_i(t)], \qquad (27)$$

where $T_0=\frac{3}{2}k_BT$ is the kinetic energy per particle. KED fluctuation can also be obtained from the energy-density fluctuation by neglecting the potential-energy term in the energy-density fluctuation and e. Let $I(q,t)$ represent the correlation function of $T(q,t)$ and let I_0, $-I_2$, $I_4, \ldots$, etc. denote the time derivatives of the KED fluctuation at $t=0$; then using (1) and (7), we obtain for I_0, the expression

$$I_0=\frac{1}{n^2}\left\langle\sum_{l=1}^{N}\left(\frac{M}{2}\vec{v}_1^{\,2}-T_0\right)\left(\frac{M}{2}\vec{v}_l^{\,2}-T_0\right)\cos q(x_1-x_l)\right\rangle. \qquad (28)$$

The summation in (28) can be divided into the self- and distinct parts so as to express I_0 in terms of the static structure factor. We thus obtain

$$I_0=\frac{M^2}{4n^2}\left[\left(\frac{k_BT}{M}\right)^2[6+9S(q)]+\frac{4T_0}{M}\left(\frac{T_0}{M}-\frac{3k_BT}{M}\right)S(q)\right], \qquad (29)$$

which on substituting for the mean KE per particle, reduces to give us

$$I_0=\tfrac{3}{2}(k_BT/n)^2. \qquad (30)$$

Thus the particle interactions do not enter in the zeroth frequency moment of the spectral function of the KED fluctuation-correlation function. However, the expression for the second frequency moment includes the effect of particle interactions. This can be written as

$$I_2=\frac{M^2}{4n^2}\left\langle\sum_{l=1}^{N}\{[4(\vec{v}_1\cdot\vec{a}_1)(\vec{v}_l\cdot\vec{a}_l)+q^2v_{1x}v_{lx}\vec{v}_1^{\,2}\vec{v}_l^{\,2}]\cos q(x_1-x_l)-4qv_{1x}\vec{v}_1^{\,2}(\vec{v}_l\cdot\vec{a}_l)\sin q(x_1-x_l)\}\right\rangle$$
$$+\frac{T_0}{n^2}\left\langle\sum_{l=1}^{N}\{v_{1x}v_{lx}(T_0-M\vec{v}_1^{\,2})\cos q(x_1-x_l)-2qMv_{lx}(\vec{v}_1\cdot\vec{a}_1)\sin q(x_1-x_l)\}\right\rangle. \qquad (31)$$

In the above expression only the self-part contributes whereas the distinct part is zero. Thus it reduces to

$$I_2=\frac{M^2}{4n^2}\left[\left(\frac{k_BT}{M}\right)^2\left(12\Omega^2(0)+35\frac{q^2k_BT}{M}\right)+4\left(\frac{q^2k_BT}{M}\right)\frac{T_0}{M}\left(\frac{T_0}{M}-\frac{5k_BT}{M}\right)\right], \qquad (32)$$

which on substituting for T_0 simplifies to give us

$$I_2 = \frac{M^2}{4n^2}\left(12\Omega^2(0) + 14\frac{q^2 k_B T}{M}\right)\left(\frac{k_B T}{M}\right)^2. \tag{33}$$

Note that this result is a consequence of the self-part of Eq. (31) and the result for I_0 contains only the kinetic contribution. Therefore, the first two frequency moments of both the self- and distinct parts of the KED fluctuation-correlation function will be equal. The collective effects enter through the fourth frequency moment of the kinetic-energy-density fluctuation-correlation function. Its calculation is straightforward but lengthy. We therefore state here only the result:

$$\begin{aligned} I_4 = \frac{M^2}{4n^2}\Bigg\{ & 189q^4\left(\frac{k_B T}{M}\right)^4 + 3q^2\left(\frac{k_B T}{M}\right)^3[61\Omega^2(0) - 3\Omega^2(q)] + 48B\left(\frac{k_B T}{M}\right)^2 + \left(\frac{k_B T}{M}\right)^3 \frac{n}{M}\int d\vec{r}\, g_2(\vec{r}) \\ & \times[4\nabla^2(\nabla^2\varphi(r))(1+\cos qx) + 12(\vec{q}\cdot\vec{\nabla})\nabla^2\varphi(r)\sin qx + 12(k_B T)^{-1}(\cos qx - 1)(\vec{\nabla}\vec{\nabla}\varphi(r))^2] \\ & + \frac{4T_0}{M}\Bigg[3q^4\left(\frac{k_B T}{M}\right)^2\left(\frac{T_0}{M} - \frac{7k_B T}{M}\right) + \left(\frac{k_B T}{M}\right)\frac{n}{M}\int d\vec{r}\, g_2(\vec{r})\{(\vec{q}\cdot\vec{\nabla})^2\varphi(r)[(1-\cos qx)T_0/M \\ & - (11 - 3\cos qx)(k_B T/M)] - 2(k_B T/M)\sin qx\,(\vec{q}\cdot\vec{\nabla})\nabla^2\varphi(r)\}\Bigg]\Bigg\}, \end{aligned} \tag{34}$$

which in the long-wavelength limit reduces to

$$\lim_{q\to 0}\frac{4n^2}{M^2} I_4 = 48B\left(\frac{k_B T}{M}\right)^2 + \frac{32\pi n}{M}\left(\frac{k_B T}{M}\right)^3 \int_0^\infty dr\, g_2(r)[r^2\varphi^{\mathrm{IV}}(r) + 4r\varphi^{\mathrm{III}}(r)], \tag{35}$$

where B has been defined earlier in Sec. II A and $\varphi^{\mathrm{III}}(r) = \partial^3\varphi(r)/\partial r^3$, etc.

In Eq. (34), the second part arising due to the fluctuation in KED is zero in the long-wavelength limit. Thus the long-wavelength limits of the fourth frequency moments of both the KED and KED fluctuation-correlation functions will be equal. Further, all the first four frequency moments of the spectral function of the KED correlation function can be obtained by substituting $T_0 = 0$ in Eqs. (29), (32), and (34). The first two frequency moments of the KED correlation function agree with those obtained by Rahman.[12]

The results for the various frequency moments derived here in this section are also believed to have not appeared before. The zeroth and second frequency moments of the spectral function of the energy-density-fluctuation-correlation function involve correlations up to four particles which are not known as yet. Therefore, it is difficult to estimate these moments exactly. But the first four frequency moments of the spectral function of the KED fluctuation correlation function can be estimated, and numerical estimates for these in the long-wavelength limit have been obtained in the next section.

III. NUMERICAL ESTIMATES

In Sec. II we have been concerned with the explicit calculation of the frequency-moment sum rules of various time-correlation functions. We now estimate some of them numerically for liquid argon. Obviously, the expressions for the various frequency moments of the spectral functions of the correlation functions are quite complicated. Since no information about the static four-particle distribution function is available as yet from the computer experiments, we cannot estimate the various frequency moments involving the quadruplet correlation function directly from their expressions.

However, we have estimated the sixth and eighth frequency moments of the dynamical structure factor for liquid argon at 76°K using the results for the spectral function of the longitudinal-current correlations obtained by Rahman[10] from the molecular-dynamics calculations. Since we have Rahman's data available only in the range of momentum transfer 0.5–3.3 Å^{-1}, we have calculated the fourth and sixth frequency moments of the longitudinal current correlation function in this range. From these numbers we obtain information about the contributions of the triplet and quadruplet correlation functions to the above fourth and sixth frequency moments using the following definitions:

$$\langle\omega_l^4\rangle/\langle\omega_d^2\rangle = M_{4l}(q) + G_3(q), \tag{36}$$

$$\langle\omega_l^6\rangle/\langle\omega_d^2\rangle = M_{6l}(q) + G_{34}(q). \tag{37}$$

Here $\langle\omega_d^2\rangle = q^2 k_B T/M$ represents the second frequency moment of the dynamic structure factor. $M_{4l}(q)$ and $M_{6l}(q)$ represent the kinetic and static pair-correlation-function contributions to the above fourth and sixth frequency moments, respectively. $G_3(q)$ represents the contribution of the triplet correlation function to the fourth frequency moment, and $G_{34}(q)$ represents the combined contribution of the triplet and quadruplet correlation functions to the sixth frequency moment. We have calculated $M_{4l}(q)$ and $M_{6l}(q)$ for liquid argon at 76°K using the Lennard-Jones (6-12) potential and the results for the static-pair-correlation function obtained by Verlet[11] (at about the same temperature and density) from the molecular-dynamics calculations. Having calculated the fourth and sixth frequency moments $M_{4l}(q)$ and $M_{6l}(q)$, we estimate $G_3(q)$ and $G_{34}(q)$ from Eqs. (36) and (37).

In Fig. 1 we have plotted $\langle\omega_l^4\rangle/\langle\omega_d^2\rangle$, $M_{4l}(q)$, and $G_3(q)$ versus q, and in Fig. 2 we have plotted $\langle\omega_l^6\rangle/\langle\omega_d^2\rangle$, $M_{6l}(q)$, and $G_{34}(q)$ versus q. As is clear from the figures, both the fourth and sixth frequency moments show a minimum at about $q = 2$ Å^{-1}, which obviously is a reflection of the maximum value of the static structure factor. $G_3(q)$ and $G_{34}(q)$ have been shown by dashed curves in Figs. 1 and 2, respectively. $G_{34}(q)$ is always negative, whereas $G_3(q)$ is positive as well as negative. Further in Fig. 1, the solid triangle corresponds to the value of $\lim_{q\to 0}\langle\omega_l^4\rangle/\langle\omega_d^2\rangle$ for liquid argon obtained by Forster *et al.*[9] (at about the same temperature and density) using the superposition approximation for the static triplet correlation function. Since we do not have molecular-dynamics results for the spectral function of the longitudinal current correlation function in the hydrodynamic region ($q < 0.5$ Å^{-1}), it is difficult to point out where our curve for $\langle\omega_l^4\rangle/\langle\omega_d^2\rangle$ will cut the y axis at $q = 0$. But the shape of the curve in the hydrodynamic region clearly indicates that it will lie below the solid triangle. Perhaps this is suggestive that the superposition approximation overestimates the magnitude of the triplet correlation contributions. This is in agreement with the conclusion of Dolling and Sears.[17]

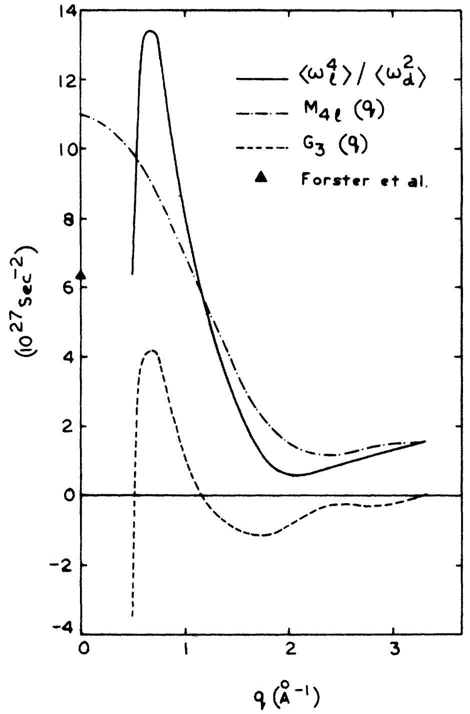

FIG. 1. Fourth frequency moment of the longitudinal current correlation function, its kinetic and $g_2(\vec{r})$ contributions and the $g_3(\vec{r}, \vec{r}')$ contribution vs q.

There may be some uncertainty in our estimates of the fourth and sixth frequency moments. This is partly due to the uncertainty in the molecular-dynamics data, the detailed analysis of which has been done by Ailawadi,[4] and partly because computer data for different q are available only up to some finite frequency. We have estimated these frequency moments from the theory of Pathak and Singwi (PS),[3] and we find that these compare reasonably well with what we obtain using the computer data. For example,[18] PS theory gives

$$\frac{\langle\omega_l^4\rangle}{\langle\omega_d^2\rangle} = 11.24\times 10^{27}\ \mathrm{sec}^{-2}\quad \text{for } q = 1\ \text{Å}^{-1}$$

$$= 1.68\times 10^{27}\ \mathrm{sec}^{-2}\quad \text{for } q = 3\ \text{Å}^{-1}$$

whereas from the molecular-dynamics data we find the corresponding numbers to be 8.56×10^{27} and 1.3×10^{27} sec^{-2}. PS theory gives

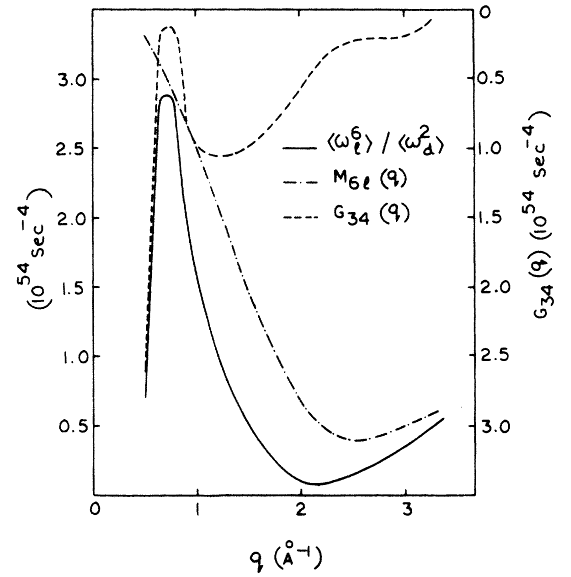

FIG. 2. Sixth frequency moment of the longitudinal current correlation function, its kinetic and $g_2(\vec{r})$ contributions and the combined contribution of $g_3(\vec{r}, \vec{r}')$ and $g_4(\vec{r}, \vec{r}', \vec{r}'')$ vs q.

$$\frac{\langle \omega_l^6 \rangle}{\langle \omega_d^2 \rangle} = 30.38 \times 10^{53}\ \text{sec}^{-4} \quad \text{for } q = 1\ \text{Å}^{-1}$$

$$= 4.93 \times 10^{53}\ \text{sec}^{-4} \quad \text{for } q = 3\ \text{Å}^{-1}$$

and molecular-dynamics data give 19.78×10^{53} and 3.32×10^{53} sec^{-4}. Since the PS model has given quantitatively good results for $q > 0.5$ Å^{-1} and for all frequencies, we feel that our results for the fourth and sixth frequency moments, obtained using the molecular-dynamics data, are at least order-of-magnitude estimates, if not better.

We have also estimated, in the long-wavelength limit, the first four frequency moments of the spectral function of the KED fluctuation-correlation function for liquid argon at 86.1°K using the molecular-dynamics data of Verlet.[11] For B, the second frequency moment of the velocity autocorrelation function, we have used the result estimated by Nijboer and Rahman[14] (at 85.5°K) through computer experiments. The estimated results for the various frequency moments of the KED fluctuation-correlation function are

$$4n^2M^{-2}I_0 = 18.9397 \times 10^{16}\ \text{cm}^4\,\text{sec}^{-4},$$

$$\lim_{q \to 0} 4n^2M^{-2}I_2 = 22.1642 \times 10^{42}\ \text{cm}^4\,\text{sec}^{-6},$$

$$\lim_{q \to 0} 4n^2M^{-2}I_4 = 1.1765 \times 10^{70}\ \text{cm}^4\,\text{sec}^{-8}.$$

Of course, the estimates of the first two frequency moments are trivial, we have quoted them only for the sake of completeness.

IV. CONCLUDING REMARKS

In this paper we have extended the existing frequency moment calculations of the various time-correlation functions in classical liquids. Although we have not used our results for calculating any physical property of the liquids, it is tempting to speculate on some future applications of these results. For example, it is known that the dynamical structure factor, in the hydrodynamic limit, involves the ratio of two specific heats (i.e., C_p/C_v) for which it has become possible to obtain the molecular expression[19] involving the static quadruplet correlation function in addition to the interatomic potential and the low-order static-correlation functions. A successful theory for the dynamical structure factor must reduce to the hydrodynamic theory in that limit. Therefore it may be expected that a correct theory of the dynamical structure factor may involve its moments up to eight. Already the first six frequency moments have been built in some recent models[5,6] and have given better results. It appears to us a straightforward matter to extend the formalism of Nelkin and co-workers[5] to build into their model the moments of the dynamical structure factor up to eight. On the other hand, if one has a reliable theory of the dynamical structure factor, one can get information about the three- and four-particle correlation functions from the moment relations.

The various frequency-moment relations we have obtained contain the static-correlation functions only up to four particles. It seems to us that it is not yet possible to estimate the magnitude of the contributions of the quadruplet correlation functions to the respective moments directly from their expressions. However, due to the advent of high-speed computers, this may not be impossible in the near future. We have estimated the contributions of the three- and four-particle correlation functions to the respective moments in a rather indirect way using the molecular-dynamics data of Rahman.[10] Since we do not have the molecular-dynamics data for the spectral function of the transverse current correlation function, we have not been able to estimate its frequency moments.

Recently, Rahman[12] has reported the results of the molecular-dynamics calculations for the KED correlation function for liquid sodium, and he has analyzed his data using the memory-function approach and the first two frequency moments of the KED correlation function. We understand that he is in the process of calculating the KED fluctuation and energy-density-fluctuation-correlation functions through the computer experiments. Thus the various frequency-moment sum rules of the KED fluctuation and the energy-density-fluctuation-correlation functions might be helpful in analyzing the molecular-dynamics data. We are also in the process of analyzing the molecular-dynamics data of Rahman for liquid sodium using the effective mean-field approach. We have estimated in the long-wavelength limit the first four frequency moments of the KED correlation function for liquid argon. It has not become possible for us to estimate the frequency moments of the energy-density-fluctuation-correlation function.

We conclude with the remark that the frequency-moment sum rules play an important role in understanding the dynamics of atomic motions in liquids. Therefore, it is hoped that the various results obtained here will prove to be useful in both the experimental and theoretical investigations of the atomic correlations in classical liquids.

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[1] L. P. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) 24, 419 (1963).

[2] C. H. Chung and S. Yip, Phys. Rev. 182, 323 (1969).

[3] K. N. Pathak and K. S. Singwi, Phys. Rev. A 2, 2427 (1970). See also K. N. Pathak, K. S. Singwi, G. Cubiotti, and M. P. Tosi, Nuovo Cimento B 13, 185 (1973).

[4] N. K. Ailawadi, A. Rahman, and R. Zwanzig, Phys. Rev. A 4, 1616 (1971). See also N. K. Ailawadi, Ph.D. thesis (University of Maryland, 1969) (unpublished).

[5] K. Kim and M. Nelkin, Phys. Rev. A 4, 2065 (1971). See also K. Kim, Ph.D. thesis (Cornell University, 1971) (unpublished); P. Ortoleva and M. Nelkin, Phys. Rev. A 2, 187 (1970).

[6] M. I. Barker and T. Gaskell, J. Phys. C 5, 3279 (1972).

[7] K. N. Pathak and R. Bansal, J. Phys. C 6, 1989 (1973).

[8] G. Placzek, Phys. Rev. 86, 377 (1952); P. G. de Gennes, Physica 25, 825 (1959).

[9] D. Forster, P. C. Martin, and S. Yip, Phys. Rev. 170, 155 (1968).

[10] A. Rahman (private communication); also in *Neutron Inelastic Scattering* (International Atomic Energy Agency, Vienna, 1968), Vol. I, p. 561; Phys. Rev. Lett. 19, 420 (1967).

[11] L. Verlet, Phys. Rev. 165, 201 (1968); L. Verlet, Phys. Rev. 159, 98 (1967).

[12] A. Rahman, in *Statistical Mechanics*, edited by S. A. Rice, K. F. Freed, and J. C. Light (University of Chicago Press, Chicago, 1972), p. 177.

[13] H. Mori, Progr. Theor. Phys. 33, 423 (1965). See also R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Britten, B. W. Downs, and J. Downs (Interscience, New York, 1961).

[14] B. R. A. Nijboer and A. Rahman, Physica 32, 415 (1966).

[15] V. F. Sears, Phys. Rev. A 5, 452 (1972). In this paper the sum rules for the self-part of the spectral function of the longitudinal current correlation function have also been discussed, rather formally. But these have not been calculated explicitly beyond the fourth moment, i.e., the sixth moment of the self-correlation function.

[16] When we were in the process of calculating the frequency-moment sum rules, we saw a paper by P. Petalas [Helv. Physica Acta 44, 943 (1971)] where he seems to have stated the result for the eighth frequency moment of the dynamical structure factor. The expression given by him is valid only for a one-dimensional sytem and even that contains several errors. This has been confirmed to us in a private communication by Dr. Petalas. We are thankful to Dr. Petalas for this correspondence.

[17] G. Dolling and V. F. Sears, Solid State Commun. 8, 2091 (1970).

[18] R. Bansal and K. N. Pathak, reported in the Nuclear Physics and Solid State Physics Symposium, Bangalore, India, 1973.

[19] N. H. March (private communication).