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Sum rules and atomic correlations in classical liquids. III. Numerical estimates and an application*

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The expressions for the fourth and sixth frequency moments of current correlation functions are simplified by performing the angular integrations associated with the three-body contributions to these moments. The resultant expressions are applicable both in the long-wavelength limit as well as for any momentum transfer. These expressions are then numerically evaluated for a liquid-argon-like system near its triple point using the molecular dynamics data of Verlet for the static pair-correlation function. We have used Kirkwood superposition approximation for the triplet correlation function and a low-order decoupling approximation for the quadruplet correlation function. The Maxwell relaxation time for the longitudinal mode is calculated using our computed numbers for the fourth and sixth moments. The results for the relaxation time are compared with those of other authors as well as with the experimental observations. It is concluded that the approach of Machida and Murase is comparatively adequate and has to be modified in order to get a better wave-number dependence of the relaxation time.

I. INTRODUCTION

In an earlier paper,[1] we derived explicit expressions for the sixth frequency moments of both the longitudinal and transverse current correlation functions for a classical system of particles interacting through a two-body potential. The results for the low-order moments (up to the fourth) were previously known.[2,3] But until now only the long-wavelength limit of the fourth moment was possible to estimate.[3] For general wave vectors, it was not possible to compute the expressions of the fourth and sixth frequency moments. This is because these moments involve multiple integrations, the numerical evaluation of which is very difficult and expensive. However, in the long-wavelength limit, the expressions for these moments become simplified and Forster *et al.*[3] could then perform all except one angular integration involved in the three-body integrals of the fourth moments.

Another difficulty in estimating these moments is the lack of experimental information about the triplet and quadruplet correlation functions. From the last few years, a considerable effort is being made to get an information about the triplet correlation function in simple liquids. The measurement of pressure dependence of $g_2(r)$ makes it possible to test different expansions for $g_3(\vec{r}, \vec{r}')$ but its direct determination is not possible in this way.[4-6] Although in principle some molecular dynamics and Monte Carlo calculations about g_3 do exist in the literature,[7-9] the data are not sufficient enough to be used in the above mentioned multiple integrals. To our knowledge, no attempt has been made so far to understand the behavior of quadruplet correlations.

In the past, some authors have included the higher-order moments in their theoretical models[10-13] in order to see their effects. But in view of the above mentioned difficulties, they have been determining these moments either through some other physical property of the system[10,11] or in a very approximate manner.[12,13] We estimated these higher-order moments in paper II of this series[14] using approximate theoretical models[15-17] of the spectral function of longitudinal current correlation function.

In this paper, we have been able to integrate exactly all except one of the angular integrations involved in the three-body integrals of both the fourth and sixth moments for all momentum transfers. For this, we made use of a symmetric property of the triplet correlation function.[18] However, it was not possible for us to perform an exact analytical calculation of the multiple integrals associated with the four-body contributions of the sixth moment. Therefore, we have evaluated these four-body contributions by using a low-order decoupling approximation discussed by Machida and Murase (MM).[13] These results are presented in Sec. 2. To achieve a uniform presentation, we have described some steps of calculation and the notation used in the appendices. Results for the self parts of the sixth frequency moments of the current correlations and the sixth frequency moment of the velocity auto-correlation function obtained after carrying out angular integrations are also given in Appendix C.

In Sec. 3, we give some simplified expressions for the sixth moments which are applicable in the long-wavelength limit. The long-wavelength limit results for the fourth moments are not included here because these have already been given by Forster *et al.*[3] and our results reduce to their expressions in this limit.

In Sec. 4, we present the results of our numerical calculations for the fourth and sixth frequency moments of liquid argon for momentum transfers in the range 0–5 $\mathrm{\AA}^{-1}$. Our numerical calculations correspond to a temperature of 86.136 °K and density $0.021\,53\times10^{24}$ atoms/cm^3, which is close to the triple point of argon. Therefore, we feel that our results can also be used in analyzing the experimental data on liquid argon.

Our own motivation of performing these calculations was to estimate the Maxwell relaxation time for the longitudinal mode in liquid argon, an approximate microscopic expression for which has been derived by MM. This expression involves the moments of the longitudinal current correlation function up to the sixth. Using the numerical results for the various moments described above, we calculated the relaxation time from the expression of MM. These results are discussed and compared with other possible estimates[11,19-22] in Sec. 4. It is found that the present results are different from the original estimates of MM are in improvement. A summary and conclusions are given in Sec. 5.

II. EXPRESSIONS FOR SUM RULES

We define the nth frequency moment of the spectral function of the current correlation function as

$$\langle\omega^n_{l,t}\rangle = K^{l,t}_n + \sum_{i=2} I^{l,t}_{ni}\,, \tag{1}$$

where the subscripts l and t denote, respectively, the longitudinal and transverse current. $K^{l,t}_n$ denotes the kinetic part. $I^{l,t}_{n2}, I^{l,t}_{n3}, \ldots$ etc. represent the contributions due to static pair and triplet correlation functions, respectively. Explicit expressions for both $\langle\omega^4_{l,t}\rangle$ and $\langle\omega^6_{l,t}\rangle$ are given in Refs. 3 and 1.

We now describe the results obtained after performing the various possible angular integrations involved in the expressions for the fourth and sixth moments. It is trivial to carry out the angular integrations involved in two-body terms, i.e., $I^{l,t}_{n2}$. We, therefore, state here only the results.

$$I^{l}_{42} = (4\pi nk_BT/3m^2)\int_0^\infty dr\, r^2 g_2(r)\{15q^2V_4 + 18q[3j_1W_3 + (j_1 - 2J_2)W_4] + (2/k_BT)[3W_1^2(1-j_0) + V_1(1-3\theta_1)]\}\,, \tag{2a}$$

$$I^{t}_{42} = (2\pi nk_BT/3m^2)\int_0^\infty dr\, r^2 g_2(r)[29q^2V_4 + 18qj_1(W_4 + 5W_3) + (6/k_BT)(3W_1^2 + V_1)(1-j_0)] - \tfrac{1}{2}I^{l}_{42}\,, \tag{2b}$$

$$\begin{aligned} I^{l}_{62} = \left(\frac{4\pi nk_BT}{m^3}\right)\int_0^\infty dr\, r^2 g_2(r)\Bigg\{&\left(\frac{7q^2k_BT}{5}\right)(50q^2V_4 - 3V_3) + \left(\frac{7q^2}{3}\right)(2V_2 + 11V_1 + 37W_1^2) + \left(\frac{39q^2k_BT}{r}\right) \\ &\times\left[3j_0(W_4 + rW_6) + J_1(6W_3 - 6rW_6 - 3W_4 - rW_5) + j_2\left(1 - \frac{8}{q^2r^2}\right)(3W_4 - rW_5)\right] \\ &+ 35q^2\left[j_0V_2 - J_1(V_1 + 2W_2W_1) - j_2W_2^2\left(1 - \frac{8}{q^2r^2}\right)\right] \\ &+ 72q[j_1W_3V_4 + (j_1 - 2J_2)(W_4W_2 + W_4W_1 + 2W_3W_2)] + \left(\frac{4}{k_BT}\right) \\ &\times\left[(1-j_0)(W_1^3 + 6k_BTW_3^2) + (\tfrac{1}{3} - \theta_1)[W_2^2V_4 + 3W_1^2W_2 + 3k_BT(W_4^2 + 9W_3^2 + 6W_3W_4)]\right]\Bigg\}\,, \end{aligned} \tag{3a}$$

$$\begin{aligned} I^{t}_{62} = (4\pi nk_BT/m^3)\int_0^\infty dr\, r^2 g_2(r)[&(q^2k_BT)(-41V_3/5 + 39\{j_0(W_6 + 4W_3/r) + \theta_1[W_5 + 2W_6 + 2(W_4 - W_3)/r]\}) \\ &+ 5q^2(4W_1^2(7 + j_0) + 4V_1(7 + 3\theta_1)/3 + V_4[3W_1(1 + j_0) + W_2(1 + 3\theta_1) + 22q^2k_BT]) \\ &+ 8q\,j_1(23W_2W_3 + 9P_1(\vec{r},\vec{r})) + (4/k_BT)(1 - j_0)(P_3(\vec{r},\vec{r}) + 3k_BTP_2(\vec{r},\vec{r}))] - \tfrac{1}{2}I^{l}_{62}\,. \end{aligned} \tag{3b}$$

The various symbols used have their usual meanings and the notation used has been explained in Appendix A.

The angular integrations involved in terms like $I_{n3}^{l,t}$ are very tedious to perform and require much more complicated and lengthy algebra. Therefore, we give here few relevant steps which can help as a guideline to the readers.

The triplet correlation function $g_3(\vec{r},\vec{r}\,')$ is a function of the magnitudes of $\vec{r}$ and $\vec{r}\,'$ and β, the cosine of the angle between $\vec{r}$ and $\vec{r}\,'$. Therefore, it can be expanded in terms of spherical harmonics $Y_{lm}(\theta,\psi)$ in the following way,

$$g_3(\vec{r},\vec{r}\,')=\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\,g^{(l)}(r,r')\times Y_{lm}^{*}(\theta',\psi')Y_{lm}(\theta,\psi)\,, \qquad (4)$$

where (θ,ψ) and (θ',ψ') are the polar angles of $\vec{r}$ and $\vec{r}\,'$, respectively. The coefficients $g^{(l)}$ can be obtained from the relation

$$g^{(l)}(r,r')=\frac{2l+1}{2}\int_{-1}^{+1}d\beta\,P_l(\beta)g_3(\vec{r},\vec{r}\,')\,. \qquad (5)$$

Here $P_l(\beta)$ is a Legendre polynomial of order l. The tables for Legendre polynomials as well as spherical harmonics can be found in several standard text books.[23] Finally we use the well-known orthogonality relation

$$\int_0^{2\pi}d\psi\int_0^{\pi}d\theta\,\sin(\theta)Y_{l'm'}^{*}(\theta,\psi)Y_{lm}(\theta,\psi)=\delta_{ll'}\,\delta_{mm'}\,. \qquad (6)$$

This helps us to reduce the dimensionality of the integrals involved in $I_{n3}^{l,t}$ from six to three. It is important to note that with this procedure, the terms like

$$\int\int d\vec{r}\,d\vec{r}\,'\,g_3(\vec{r},\vec{r}\,')\{1-2\cos(\vec{q}\cdot\vec{r})\}\times(\hat{q}\cdot\vec{\nabla})(\vec{q}\cdot\vec{\nabla}')(\vec{\nabla}\cdot\vec{\nabla}')\phi(r)\phi(r') \qquad (7a)$$

(first and third terms of I_{43}^{l}, Ref. 3) can be integrated in a straightforward manner using Eqs. (4)–(6). However, the term like

$$\int\int d\vec{r}\,d\vec{r}\,'\,g_3(\vec{r},\vec{r}\,')\{\cos\vec{q}\cdot(\vec{r}-\vec{r}\,')\}\times(\hat{q}\cdot\vec{\nabla})(\hat{q}\cdot\vec{\nabla}')(\vec{\nabla}\cdot\vec{\nabla}')\phi(r)\phi(r') \qquad (7b)$$

(i.e., second term of I_{43}^{l}, Ref. 3) is difficult to handle in the present form. For this term, there is no use of expanding $g_3(\vec{r},\vec{r}\,')$ in terms of spherical harmonics because in $\cos[\vec{q}\cdot(\vec{r}-\vec{r}\,')]$, the angle between $\vec{q}$ and both $\vec{r}$ and $\vec{r}\,'$ appears. But it is possible to get rid of this difficulty with the help of a symmetric property of the triplet correlation function[18] as described below.

For $\vec{q}$ along x axis, the expression (7b) can be written as

$$I=\int\int d\vec{r}\,d\vec{r}\,'\,g_3(\vec{r},\vec{r}\,')\cos[q(x-x')]\times U_{x\alpha}(\vec{r})U_{x\alpha}(\vec{r}\,'), \qquad (7c)$$

where $U_{x\alpha}(\vec{r})=\partial^2\phi(r)/\partial x\partial r_\alpha$. α denotes the Cartesian components and summation over doubly occurring indices is implied. Using the transformation $\vec{r}\,''=\vec{r}-\vec{r}\,'$ for $\vec{r}$, Eq. (7c) becomes

$$I=\int\int d\vec{r}\,''\,d\vec{r}\,'\,g_3(\vec{r}\,''+\vec{r}\,',\vec{r}\,')\times\cos(qx'')U_{x\alpha}(|\vec{r}\,''+\vec{r}\,'|)U_{x\alpha}(\vec{r}\,')\,. \qquad (7d)$$

In this equation, we replace $\vec{r}\,''$ by $\vec{r}$, r' by $-r'$ and use the following symmetric property of the triplet correlation function[18]

$$g_3(\vec{r},\vec{r}\,')=g_3(\vec{r}-\vec{r}\,',-\vec{r}\,')\,, \qquad (8)$$

and obtain

$$I=\int\int d\vec{r}\,d\vec{r}\,'\,g_3(\vec{r},\vec{r}\,')\cos(qx)\times U_{x\alpha}(|\vec{r}-\vec{r}\,'|)U_{x\alpha}(\vec{r}\,')\,. \qquad (7e)$$

We have thus transfered the angle of $\vec{r}$ and $\vec{r}\,'$ from $\cos[q(x-x')]$ to the derivative of potential. Now we can define a new function

$$F(\beta)=g_3(\vec{r},\vec{r}\,')U_{x\alpha}(|\vec{r}-\vec{r}\,'|)\,, \qquad (9)$$

which is a function of the cosine of the angle between $\vec{r}$ and $\vec{r}\,'$, and can easily be expanded in terms of spherical harmonics.

Proceeding in a manner described above and after same lengthy algebra we obtain the following results:

$$\begin{aligned}I_{43}^{l}=(8\pi^2n^2/3m^2)\int_0^{\infty}\int_0^{\infty}dr\,dr'\,r^2r'^2 &\times\int_{-1}^{1}d\beta\,g_3(\vec{r},\vec{r}\,')\{\beta^2W_{22}+2W_{21}+3W_{11}-6[\theta_1(\beta^2W_{22}+W_{21})+(\theta_2\beta^2+J_1)W_{12}+j_0W_{11}]\\ &+3[\beta_2W_2'W_2''[\theta_1\beta r-(\theta_2\beta^2+J_1)r']/r''\\ &+W_1'W_2''[\theta_1 r(r-2\beta r')+(\theta_2\beta^2+J_1)r'^2]/r''^2\\ &+(\theta_2\beta^2+J_1)W_2'W_1''+j_0W_1'W_1'']\}\,,\end{aligned} \qquad (10a)$$

$$I_{43}^{t}=(4\pi^2 n^2/m^2)\int_0^\infty\int_0^\infty dr\,dr'\,r^2 r'^2\int_{-1}^{1}d\beta\, g_3(\vec{r},\vec{r}')[(1-2j_0)(\beta^2 W_{22}+W_{21}+W_{12}+3W_{11}) + j_0(\beta_2^2 W_2' W_2''+3W_1'W_1''+W_1'W_2''+W_2'W_1'')]-\tfrac{1}{2}I_{43}^{l}\,, \tag{10b}$$

$$\begin{aligned}I_{63}^{l}=(8\pi^2 n^2/m^3)\int_0^\infty\int_0^\infty dr\,dr'\,r^2 r'^2\int_{-1}^{1}d\beta\, g_3(\vec{r},\vec{r}')\\
\times\{(k_BT)[7q^2P_4(\vec{r},\vec{r}',\beta)+3P_5(\vec{r},\vec{r}',\beta)]+6P_6(r,r',\beta)-P_7(r,r',\beta)\\
+6(qk_BT)[Q_1(\vec{q},\vec{r},\vec{r}',\beta)+Q_2(\vec{q},\vec{r},\vec{r}',\beta)-Q_6(\vec{q},\vec{r},\vec{r}',\beta)-Q_7(\vec{q},\vec{r},\vec{r}',\beta)]\\
-3(k_BT)[2Q_3(\vec{q},\vec{r},\vec{r}',\beta)+Q_8(\vec{q},\vec{r},\vec{r}',\beta)+Q_9(\vec{q},\vec{r},\vec{r}',\beta)]\\
-4[Q_4(\vec{q},\vec{r},\vec{r}',\beta)-Q_{10}(\vec{q},\vec{r},\vec{r}',\beta)]-6Q_5(\vec{q},\vec{r},\vec{r}',\beta)+Q_{11}(\vec{q},\vec{r},\vec{r}',\beta)\}\,,\end{aligned} \tag{11a}$$

and

$$\begin{aligned}I_{63}^{t}=(4\pi^2 n^2/m^3)\int_0^\infty\int_0^\infty dr\,dr'\,r^2 r'^2\int_{-1}^{1}d\beta\, g_3(\vec{r},\vec{r}')((5q^2k_BT/3)(75W_{11}+50W_{12}+(3+16\beta^2)W_{22})+2(qk_BT)\\
\{3P_1(\vec{r},\vec{r}',\beta)(6j_1+\beta j_1')+W_{32}(6\beta j_1'+51\beta^2 j_1-5j_1)\\
-3j_1[\beta_1P_1(\vec{r}'',\vec{r}',\beta)+2\beta\beta_2W_2'W_3'']\}\\
+3(k_BT)[(1-2j_0)P_2(\vec{r},\vec{r}',\beta)-j_0P_2(\vec{r}'',\vec{r}',\beta)]+2(3-3j_0-2j_0')\\
\times P_3(\vec{r},\vec{r}',\beta)+4j_0P_3(\vec{r}'',\vec{r}',\beta)+3(j_0-1)P_7(\vec{r},\vec{r}',\beta))-\tfrac{1}{2}I_{63}^{l}\,.\end{aligned} \tag{11b}$$

Here $\vec{r}''=\vec{r}-\vec{r}'$ and the other quantities are described in Appendix A (see also Ref. 24).

Within the scheme described above, it could not become possible to integrate the angles involved in the integrals of the terms $I_{64}^{l,t}$. In this case, the symmetric property of the quadruplet correlation function[25]; namely

$$g_4(\vec{r},\vec{r}',\vec{r}'')=g_4(-\vec{r},\vec{r}'-\vec{r},\vec{r}''-\vec{r}) \tag{12}$$

again helps to transfer the relative angles of $\vec{r},\vec{r}'$ and $\vec{r}''$ from the cosine arguments to the potential arguments. But g_4 being a function of β, β_1, and β_2 (relative angles of $\vec{r}$, $\vec{r}'$, and $\vec{r}''$, defined in Appendix A), when expanded contains six spherical harmonics, which can be seen to be of no help in carrying out the angular integrations of $I_{64}^{l,t}$. Therefore, we approximated these terms in a way similar to MM and obtained

$$I_{64}^{l}=\{(4\pi n/m)\int_0^\infty dr\,r^2 g_2(r)[(1-j_0)W_1+(\tfrac{1}{3}-\theta_1)W_2]\}^3 \tag{13a}$$

and

$$I_{64}^{t}=\{(4\pi n/m)\int_0^\infty dr\,r^2 g_2(r)[(1-j_0)W_1+(\tfrac{1}{3}-J_1)W_2]\}^3. \tag{13b}$$

It is interesting to note that the right-hand sides of Eqs. (13a) and (13b) are, respectively, the cubes of potential parts of the second frequency moments of longitudinal- and transverse-current correlation functions.

For the sake of completeness, we also integrated the angles involved in the expressions for $\langle\omega_{l,s}^6\rangle$ and $\langle\omega_{t,s}^6\rangle$ and the sixth frequency moment of the velocity autocorrelation function. These results are given in Appendix C.

III. RESULTS IN THE LONG WAVELENGTH LIMIT

In the limit of long wavelengths, the expressions obtained in the previous section become simplified. The long-wavelength limit results for the fourth moments have already been given by Forster *et al.*[3] We wish to point out that the $q\to 0$ limit of our expressions for $I_{43}^{l,t}$ (Eqs. 10a and 10b) may at first look somewhat different from the results of Forster *et al.* But it is identical to their results as shown in Appendix B. Therefore, we state here the long-wavelength limit results for the sixth moments only.

$$\lim_{q\to 0} I_{62}^{l}\omega_0^{-2} = (8\pi n/15m^2)\int_0^\infty dr\, r^2\, g_2(r)(27(k_BT)V_3 + 35(25W_1^2 + 7V_1 + 2V_2) + 36r(11W_3W_2 + 15W_3W_1 + 3W_4W_2^{\prime\prime} + 3W_4W_1) + (r^2/k_BT) \times \{5W_1^3 + 3(W_2^2V_4 + 3W_1^2W_2) + 3k_BT[10W_3^2 + 3(W_4^2 + 9W_3^2 + 6W_3W_4)]\}), \tag{14a}$$

and

$$\lim_{q\to 0} I_{62}^{t}\omega_0^{-2} = (8\pi n/m^2)\int_0^\infty dr\, r^2 g_2(r)\{12k_BTV_3/5 + 5(16W_1^2 + 16V_1/3 + V_4^2) + 4r[23W_2W_3 + 9P_1(\vec{r},\vec{r})]/3 + (r^2/3k_BT)[P_3(\vec{r},\vec{r}) + 3k_BTP_2(\vec{r},\vec{r})]\} - \tfrac{1}{2}\lim_{q\to 0} I_{62}^{l}\omega_0^{-2}, \tag{14b}$$

where $\omega_0^2 = q^2k_BT/m$.

In the $q\to 0$ limit, the expressions for $I_{63}^{l,t}$ can be written concisely as

$$\lim_{q\to 0} I_{63}^{l}\omega_0^{-2} = (4\pi^2n^2/15m^2)\int_0^\infty\int_0^\infty dr\, dr'\, r^2r'^2\int_{-1}^{1} d\beta\, g_3(\vec{r},\vec{r}')[210P_4(\vec{r},\vec{r}',\beta)$$
$$+ 12\{15(W_{31} + W_{41}/5)(5r + 2\beta r') + W_{32}[22\beta r' + 5r(2 + 9\beta^2)] + \beta W_{42}[15\beta r + 2r'(1 + 2\beta^2)]\}$$
$$+ (2r/k_BT)(W_1'(5W_1^2 + 3V_1)(r + 4\beta r') + W_2'\{W_1^2[12\beta r' + r(1 + 2\beta^2)] + \beta V_1[3\beta r + 4r'(1 + 2\beta^2)]\})$$
$$+ 6rr'[W_{44}\beta^2(1 + 2\beta^2) + W_{33}(9 + 28\beta^2) + 2W_{43}(1 + 8\beta^2)]$$
$$- (1/k_BT)\{5r^2W_{111} + W_{121}[3r'^2 + r^2(1 + 2\beta^2)]$$
$$+ 3\beta^2r^2W_{221} + (\beta_2/r'')W_{122}[3(\beta r^3 - r'^3) - rr'r''(\beta_1 + 2\beta\beta_2) - 6r'^2r''\beta_2]$$
$$+ \beta\beta_1r^2W_{222}(5\beta_2 - 2\beta\beta_1) + (r^2/r''^2)W_{112}[3\beta_1^2r''^2 + r'^2(1 - \beta^2)]\}], \tag{15a}$$

and

$$\lim_{q\to 0} I_{63}^{t}\omega_0^{-2} = (4\pi^2n^2/m^2)\int_0^\infty\int_0^\infty dr\, dr'\, r^2r'^2\int_{-1}^{1} d\beta\, g_3(\vec{r},\vec{r}')(5[75W_{11} + 50W_{12} + (3 + 16\beta^2)W_{22}]/3$$
$$+ 2P_1(\vec{r},\vec{r}',\beta)(5r + 2\beta r') + 2W_{32}[5r(3\beta^2 - 1/3) + 4\beta r'] + rr'\beta P_2(\vec{r},\vec{r}',\beta)$$
$$+ (r/6k_BT)[2(r + 4r'\beta)P_3(\vec{r},\vec{r}',\beta) - 3rP_7(\vec{r},\vec{r}',\beta)]) - \tfrac{1}{2}\lim_{q\to 0} I_{63}^{l}\omega_0^{-2}. \tag{15b}$$

It may be noted from our exact expressions for the sixth moments[1] that in the long-wavelength limit, the expressions for $I_{64}^{l,t}/q^2$ should also be finite, but Eqs. (13a) and (13b) contribute zero in this limit. It can be considered as a drawback of the approximation used in writing Eqs. (13a) and (13b).

The results obtained in this section as well as in the previous section have been computed numerically for a liquid-argon-like system. These numerical results are presented below.

IV. NUMERICAL CALCULATIONS AND RESULTS

Here we describe the numerical evaluation of $\langle\omega_{l,t}^4\rangle\omega_0^{-2}$, $\langle\omega_{l,t}^6\rangle\omega_0^{-2}$ and the longitudinal relaxation time $\tau_l(q)$ for the momentum transfers in the range 0–5 Å^{-1}. We have computed the expressions for the moments described in the last two sections for a liquid-argon-like system at $T = 86.136$ °K and $n = 0.021\,53\times 10^{24}$ atoms/cm^3. We selected this temperature and density because all the neutron scattering measurements[26] and the molecular dynamics calculations[27,28] for the current correlations in liquid argon are available corresponding to these conditions. Therefore, our results can directly be used in interpreting the experimental data. In these computations, a knowledge of three-particle correlation function is needed for which we have used the well-known Kirkwood superposition approximation. Therefore, the accuracy of our results is limited by the validity of superposition approximation and the approximation which we have used for $I_{64}^{l,t}$. For $g_2(r)$, we have used the results obtained by Verlet[29] from computer simulation of a argon-like-system using a (6–12) Lennard-Jones potential.

In all the numerical integrations, we have used the method of Gaussian quadratures and the results are consistent up to at least four significant figures. In Figs. 1(a) and 1(b), we have plotted $\langle\omega_l^4\rangle\omega_0^{-2}$ and $\langle\omega_t^4\rangle\omega_0^{-2}$, respectively. To have an im-

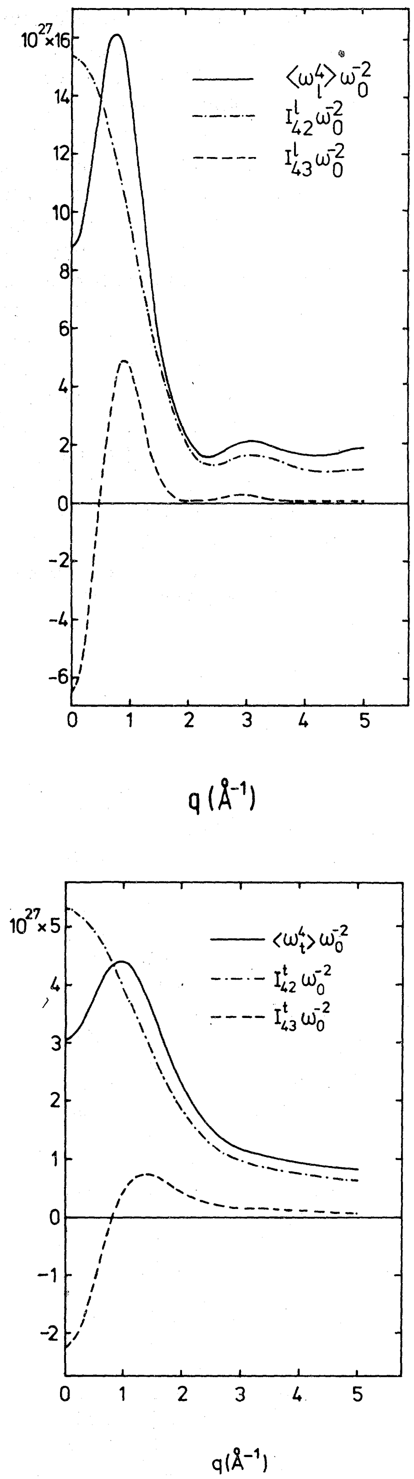

FIG. 1. (a) Fourth frequency moment of the longitudinal-current correlation function, its $g_2(r)$ and $g_3(\vec{r},\vec{r}')$ contributions versus $\vec{q}$. (b) Fourth frequency moment of the transverse-current correlation function, its $g_2(r)$ and $g_3(\vec{r},\vec{r}')$ contributions versus $\vec{q}$.

mediate feeling about the two- and three-body correlation function contributions, we have plotted these contributions separately on the same graphs. Figures 2(a) and 2(b) contain corresponding plots for $\langle\omega_l^6\rangle\omega_0^{-2}$ and $\langle\omega_t^6\rangle\omega_0^{-2}$. In Figs. 2(a) and 2(b), we have not plotted $I_{64}^{l,t}$ because this contribution is very small and is difficult to be plotted on the same scale. However, as we stated in Sec. II $I_{64}^{l,t}$ are the cubes of the potential parts of $\langle\omega_{l,t}^2\rangle$,

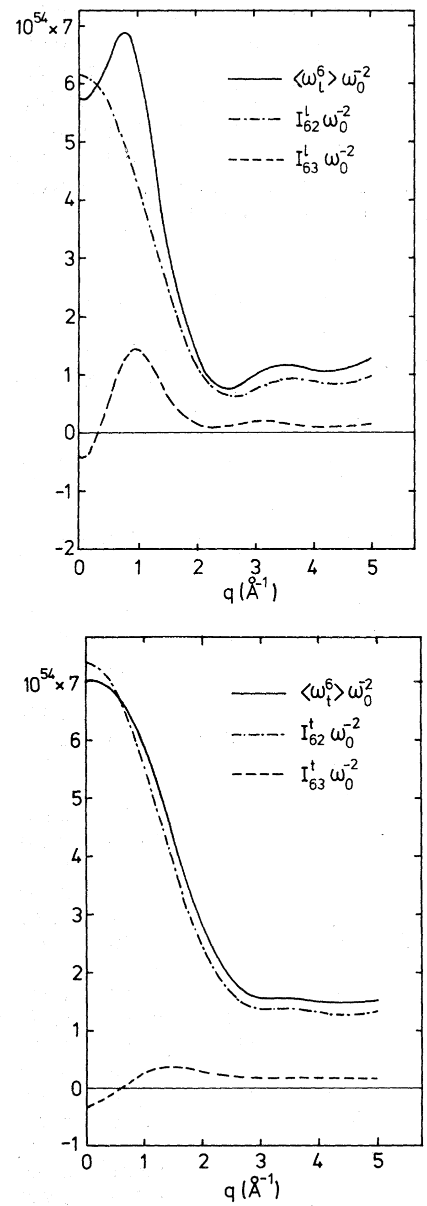

FIG. 2. (a) Sixth frequency moment of the longitudinal-current correlation function, its $g_2(r)$ and $g_3(\vec{r},\vec{r}')$ contributions versus $\vec{q}$. (b) Sixth frequency moment of the transverse-current correlation function, its $g_2(r)$ and $g_3(\vec{r},\vec{r}')$ contributions versus $\vec{q}$.

the behavior of which is already known. It may be noted that both $\langle\omega_l^4\rangle\omega_0^{-2}$ and $\langle\omega_l^6\rangle\omega_0^{-2}$ show a first maximum at momentum transfer where the static structure factor shows a sharp increase. Also the maxima and minima of these two moments are almost in phase with the minima and maxima of the static structure factor. Since it is always difficult to read the numbers from the published graphs, we have also tabulated our results in Table I for future applications.

Having calculated the moments, we use these results to estimate the Maxwell relaxation time for the longitudinal mode. MM have derived an approximate microscopic expression for the longitudinal relaxation time[13] by relating it to the second-order memory function in the continued fraction expansion of the longitudinal current correlation function. It is given by

$$\tau_l^{-1}(q) = \delta_3(\pi/2\delta_4)^{1/2}, \qquad (16)$$

where δ_3 and δ_4 are expressible in terms of the moments of the longitudinal current correlation function up to the sixth. Explicit expressions for δ_3 and δ_4 are given by Copley and Lovesey.[30] MM have instead used the abbreviation Δ^2 and σ^{-2} for δ_3 and δ_4. In their paper, MM estimated δ_3 and δ_4 by using a decoupling approximation for the higher-order static correlation functions which are involved in the expressions for the frequency moments (see Ref. 31). But we have now estimated $\tau_l^{-1}(q)$ using our computed numbers for the moments discussed above. For the static structure factor, we have used the results obtained by Yarnell *et al.*[32] The results for $\sqrt{\delta_4}$ are displayed in Fig. 3. Clearly $\sqrt{\delta_4}$ is not a constant and has a stronger wave-number dependence which is in disagreement with the result of MM who find that $\sqrt{\delta_4}$ is almost constant with a value 2×10^{13} sec^{-1}.

In Fig. 4, we have compared our results for $\tau_l^{-1}(q)$ with those of Akcasu and Daniels,[19] Lovesey,[20] and MM.[13] In this figure, we have also plotted the results of Rowe and Sköld[22] and Aila-

TABLE I. $g_2(\vec{r})$ and $g_3(\vec{r},\vec{r}\,')$ contributions to the fourth and sixth frequency moments (in units of $\omega_0^2\times10^{27}$ sec^{-2} and $\omega_0^2\times10^{54}$ sec^{-4}) of the longitudinal- and transverse-current correlation functions as a function of momentum transfer. The inverse of the Maxwell relaxation time for the longitudinal mode is also given here.

q(Å^{-1})	I_{42}^l	I_{43}^l	I_{42}^t	I_{43}^t	I_{62}^l	I_{63}^l	I_{62}^t	I_{63}^t	τ_l^{-1}
0.0	15.366	−6.527	5.296	−2.249	6.158	−0.393	7.334	−0.344	0.470
0.1	15.287	−6.196	5.277	−2.185	6.136	−0.430	7.314	−0.292	0.466
0.2	15.085	−5.169	5.230	−2.042	6.072	−0.287	7.253	−0.266	0.482
0.3	14.753	−3.571	5.154	−1.797	5.966	−0.057	7.154	−0.222	0.508
0.4	14.299	−1.615	5.048	−1.483	5.820	0.233	7.016	−0.163	0.543
0.5	13.730	0.437	4.916	−1.126	5.635	0.552	6.842	−0.095	0.588
0.6	13.057	2.305	4.760	−0.755	5.415	0.862	6.635	−0.022	0.644
0.7	12.291	3.749	4.583	−0.395	5.163	1.127	6.396	0.052	0.691
0.8	11.445	4.620	4.387	−0.069	4.882	1.318	6.131	0.123	0.747
0.9	10.536	4.887	4.177	0.208	4.577	1.418	5.842	0.187	0.814
1.0	9.582	4.625	3.956	0.425	4.252	1.422	5.533	0.242	0.882
1.2	7.616	3.150	3.494	0.679	3.566	1.200	4.875	0.319	0.943
1.4	5.722	1.531	3.030	0.731	2.868	0.829	4.197	0.353	1.041
1.6	4.066	0.535	2.590	0.660	2.206	0.491	3.536	0.352	1.177
1.8	2.776	0.157	2.191	0.541	1.625	0.271	2.932	0.329	1.247
2.0	1.910	0.078	1.848	0.421	1.165	0.157	2.414	0.296	1.209
2.2	1.451	0.082	1.567	0.321	0.845	0.104	2.004	0.262	1.084
2.4	1.314	0.127	1.348	0.247	0.668	0.090	1.707	0.231	1.010
2.6	1.376	0.205	1.183	0.196	0.617	0.108	1.518	0.207	1.060
2.8	1.508	0.267	1.064	0.164	0.658	0.146	1.417	0.190	1.175
3.0	1.607	0.265	0.979	0.146	0.747	0.180	1.376	0.180	1.278
3.2	1.621	0.206	0.918	0.136	0.842	0.189	1.368	0.175	1.372
3.4	1.545	0.135	0.870	0.127	0.911	0.175	1.369	0.173	1.465
3.6	1.410	0.086	0.830	0.117	0.938	0.149	1.363	0.171	1.543
3.8	1.265	0.064	0.792	0.105	0.925	0.125	1.344	0.168	1.555
4.0	1.152	0.059	0.757	0.093	0.890	0.109	1.318	0.165	1.504
4.2	1.093	0.064	0.723	0.082	0.855	0.101	1.293	0.161	1.464
4.4	1.086	0.074	0.693	0.072	0.839	0.102	1.279	0.157	1.472
4.6	1.112	0.082	0.666	0.065	0.854	0.109	1.282	0.153	1.537
4.8	1.144	0.081	0.644	0.060	0.901	0.118	1.304	0.150	1.621
5.0	1.160	0.070	0.626	0.056	0.968	0.123	1.341	0.148	1.710

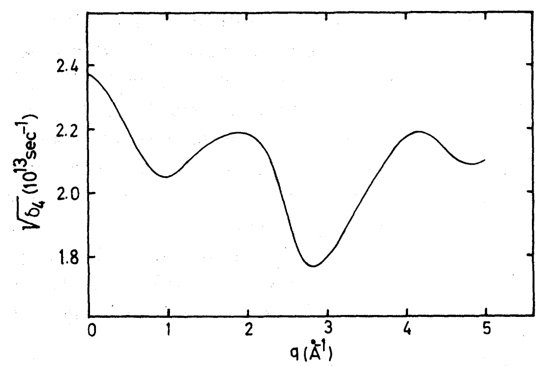

FIG 3. The wave-number dependence of $\sqrt{\delta_4}$.

wadi *et al.*[11] who treated $\tau_l^{-1}(q)$ as a free parameter and determined through the least-square fitting of the experimental data on the longitudinal current correlations in liquid argon. Rowe and Sköld fitted the expression for the spectral function of the longitudinal current correlation function to the neutron scattering data of Sköld *et al.*[26] on liquid argon. Ailawadi *et al.* also fitted the same expression but to the molecular dynamics data of Rahman.[27] The results of Rowe and Sköld and Ailawadi *et al.* are shown by crosses and solid circles, respectively. It can be seen that the present results are always somewhat higher than the experimental results. However, the maxima and minima of the results of Rowe and Sköld[22] can be considered as being exactly reproduced and in this respect the present results are definitely in improvement over the results of Lovesey[20] and Akcasu and Daniels.[19] Furthermore, the present results are different from the results of MM. This difference can be partially ascribed to our use of superposition approximation for g_3 which,

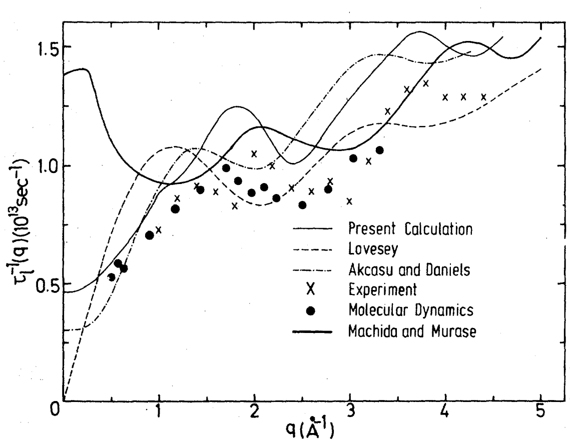

FIG. 4. The wave-number dependence of the inverse of the Maxwell relaxation time for the longitudinal mode.

of course, is comparatively better than the decoupling approximation used by MM for estimating three-body integrals. We believe that the reason of our results being consistently above the experimental results lies in the nature of the approximate theory of MM itself and the low-order approximations used for g_3 and g_4. Now we do not know how to estimate the errors involved in our calculations due to the mentioned approximations. It is, however, known that the superposition approximation for g_3 generally overestimates the magnitude of three-body correlations in liquids[4,33] and information about g_4 is not at all available. Our results are, therefore, subject to these approximations. But we feel that within this limitation, the present results can still be improved if the approach of MM is modified in a suitable manner. This is done successfully in the accompanying paper[34] where we obtain a very good agreement with the experimental results.

V. SUMMARY AND CONCLUSIONS

In this paper, we have successfully performed all except one of the angular integrations associated with the three-body integrals of both the fourth and sixth frequency moments of the current correlation functions. Our expressions are applicable for both the $q \to 0$ limit as well as the general wave vector. The complicated nature of g_4 has not allowed us to integrate analytically the angles contained in the four-body integrals of the sixth moments. Therefore, we have evaluated these contributions by using the decoupling approximation discussed by MM. This approximation has the merit of expressing four-body contributions in terms of pair correlation functions. But it has also a drawback that it gives a zero contribution in the long-wavelength limit which is wrong.

We have also computed our above mentioned expressions for a liquid-argon-like system using Kirkwood's superposition approximation for the triplet-correlation function. Since these computations are time consuming, we have been confined only to one particular set of density and temperature which is close to the triple point of argon. Our results can, therefore, be of use to other theoretical workers to interpret the experimental data on current correlation functions in liquid argon.

Utilizing the above mentioned approximate results for various moments in the expression for $\tau_l(q)$ derived by MM, we estimated the wave-number dependence of the longitudinal relaxation time for liquid argon and compared the results with other existing estimates. In regard to the positions of maxima and minima of the experimentally observed results, the present results are in improvement over the other theoretical results. In the long-wavelength limit, the approximation of Lovesey gives $\tau_l^{-1}(0)=0$ resulting in an infinite answer to the longitudinal viscosity of the liquid which is incorrect. The approximation of MM and that of Akcasu and Daniels leads to a finite value of $\tau_l^{-1}(0)$. But the approximation of Akcasu and Daniels involves an adjustable parameter. Also, our results are generally higher in magnitude than the observed results but the use of correct behavior of both g_3 and g_4 should further improve these results. In view of such results, we conclude by saying that the approach of MM, together with our estimated results for the moments, is comparatively more adequate to understand the wave-number dependence of the Maxwell time and has to be slightly modified in order to improve upon the present results. One way to do this is to look for a more suitable approximation for the second-order memory function in the continued fraction expansion of the longitudinal current correlation function. A modification along these lines is presented in the following paper.[34]

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APPENDIX A

A detailed description of the notation used in this paper is as follows. We define

$$W_1(r)=\frac{1}{r}\frac{\partial\phi(r)}{\partial r};\quad W_2(r)=r\frac{\partial W_1(r)}{\partial r};$$
$$W_3(r)=W_2(r)/r;\quad W_4(r)=\frac{\partial W_2(r)}{\partial r}-2W_3(r);\quad \text{(A1)}$$
$$W_5(r)=\frac{\partial W_3(r)}{\partial r};\quad W_6(r)=\frac{\partial W_4(r)}{\partial r},$$

where $\phi(r)$ is the interatomic potential. It is understood that W_i denotes $W_i(r)$; W_{ij} denotes $W_i(r)W_j(r')$, and W_{ijk} denotes $W_i(r)W_j(r')W_k(r'')$; and subscripts i, j, and k can run from 1 to 6. j_0, j_1, and j_2 are spherical Bessel functions of the zeroth, first, and second order; their argument is understood to be qr, i.e., $j_0=j_0(qr)$, etc. Also $J_1=j_1/qr$ and $J_2=j_2/qr$.

Further unprimed, single-primed and double-primed quantities are assumed to have arguments with respect to r, r', and r'', respectively. For example

$$W_i=W_i(r);\quad W_i'=W_i(r') \text{ and } W_i''=W_i(r'').$$

We also noted that certain combinations of spherical Bessel functions and of the derivatives of potential are appearing frequently in the results described in Secs. II and III. We, therefore, abbreviated these combinations in the following way

$$V_1=W_2(W_2+2W_1);\quad V_2=W_1(W_1+2W_2);$$
$$V_3=5W_6+W_5+2(5W_3+W_4)/r;\quad V_4=W_2+3W_1. \quad \text{(A2)}$$

And

$$\theta_1=j_0-2J_1;\quad \theta_2=\theta_1-J_1. \quad \text{(A3)}$$

Throughout the paper, we have denoted $\vec{r}''=\vec{r}-\vec{r}'$. The variables β, β_1 and β_2 are, respectively, the cosine of the angles between the vectors $\vec{r}$ and $\vec{r}'$, $\vec{r}$ and $\vec{r}''$, and $\vec{r}'$ and $\vec{r}''$.

We now give explicit expressions for the various quantities used in Eqs. (3b), (11), (14b), and (15).

$$P_1(\vec{r},\vec{r}',\beta)=\beta^2W_{42}+5W_{31}+W_{41}+W_{32}, \quad \text{(A4)}$$
$$P_2(\vec{r},\vec{r}',\beta)=\beta[\beta^2W_{44}+15W_{33}+3(W_{34}+W_{43})], \quad \text{(A5)}$$
$$P_3(\vec{r},\vec{r}',\beta)=V_1(\beta^2W_2'+W_1')+W_1^2V_4', \quad \text{(A6)}$$
$$P_4(\vec{r},\vec{r}',\beta)=3(3W_{11}+2W_{21})+W_{22}(2\beta^2+\tfrac{1}{3}), \quad \text{(A7)}$$
$$P_5(\vec{r},\vec{r}',\beta)=\beta(5W_{33}+2W_{43}+\beta^2W_{44}/3), \quad \text{(A8)}$$
$$P_6(\vec{r},\vec{r}',\beta)=[W_1^2V_4'+V_1(W_1'+\beta^2W_2')]/3, \quad \text{(A9)}$$
$$P_7(\vec{r},\vec{r}',\beta)=(\beta\beta_1\beta_2W_{222}+\beta^2W_{221}+\beta_1^2W_{212}+\beta_2^2W_{122}+W_{211}+W_{112}+W_{121}+3W_{111})/3. \quad \text{(A10)}$$

It may be noted that all these quantities are independent of q. We now introduce the q-dependent quantities.

$$Q_1(\vec{q},\vec{r},\vec{r}',\beta)=(3W_{31}+\beta^2W_{42})(6j_1+\beta j_1')+W_{41}(6j_1+\beta^3j_1')+3\beta W_{32}(6\beta j_1+j_1'), \quad \text{(A11)}$$
$$Q_2(\vec{q},\vec{r},\vec{r}',\beta)=4W_{32}(3J_2-\beta J_2'-9\beta^2J_2)+W_{41}(3\beta J_2'-12J_2-5\beta^3J_2')+\beta W_{42}(J_2'-12\beta J_2-3\beta^2J_2'), \quad \text{(A12)}$$
$$Q_3(\vec{q},\vec{r},\vec{r}',\beta)=\beta[W_{33}(11j_0-18J_1)+\theta_1\beta^2W_{44}+W_{43}(3\theta_1+j_0'+2\beta^2\theta_2')], \quad \text{(A13)}$$
$$Q_4(\vec{q},\vec{r},\vec{r}',\beta)=W_1[j_0W_1'^2+V_1'(\beta^2\theta_2+J_1)]+\theta_1W_2(W_1'^2+\beta^2V_1'), \quad \text{(A14)}$$

$$Q_5(\vec{q},\vec{r},\vec{r}',\beta)=W_1''^2[j_0W_1'+W_2'(\beta^2\theta_2+J_1)]+\theta_1V_1(W_1'+\beta^2W_2')\,,\tag{A15}$$

$$Q_6(\vec{q},\vec{r},\vec{r}',\beta)=W_3''r''^{-2}(j_1\beta_1^2r''^2(W_2'\beta\beta_2+W_1'\beta_1)+J_2\{W_2'\beta_2[\beta r^2-3\beta\beta_1^2r''^2-2\beta_1r'r''+\beta r'^2(1-2\beta^2)]$$
$$+W_1'[6\beta\beta_1^2r'r''^2+r'^2(1+\beta^2)(2r+\beta_1r'')-2(r^3+\beta r'^3)]/r''\}\,,\tag{A16}$$

$$Q_7(\vec{q},\vec{r},\vec{r}',\beta)=W_4''\{j_1[3\beta_1W_1'+\beta(2\beta\beta_1+\beta_2)W_2']+2J_2W_2'(\beta_1+2\beta\beta_2-5\beta^2\beta_1)\}\,,\tag{A17}$$

$$Q_8(\vec{q},\vec{r},\vec{r}',\beta)=j_0W_3''\beta_1[\beta\beta_2^2W_4'+(\beta+2\beta_1\beta_2)W_3']$$
$$+J_1W_4''[W_4'\beta_2^2(\beta_2-3\beta\beta_1)+W_3'(\beta_2-4\beta_1^2\beta_2-3\beta\beta_1+2r'^2\beta_2(1-\beta^2)/r''^2)]\,,\tag{A18}$$

$$Q_9(\vec{q},\vec{r},\vec{r}',\beta)=W_3''\{j_0[W_3'(2\beta_2+9\beta\beta_1)+W_4'\beta(\beta_1+2\beta\beta_2)]+3J_1[3W_3'(\beta_2-3\beta\beta_1)+W_4'(\beta_2-\beta\beta_1-2\beta^2\beta_2)]\}\,,\tag{A19}$$

$$Q_{10}(\vec{q},\vec{r},\vec{r}',\beta)=W_1''^2[j_0(W_1'+\beta^2W_2')+J_1(1-3\beta^2)W_2']+V_1''(W_2'\{\beta\beta_1\beta_2j_0+\beta_2J_1[r'(\beta^2-1)-2\beta\beta_1r'']/r''\}$$
$$+W_1'\{j_0\beta_1^2+J_1[r'^2(1-\beta^2)-2\beta_1^2r''^2]/r''^2\})\,,\tag{A20}$$

$$Q_{11}(\vec{q},\vec{r},\vec{r}',\beta)=j_0W_{111}+\theta_1(W_{211}+\beta^2W_{221}+\beta_1^2W_{212})+(\theta_2\beta^2+J_1)W_{121}+\beta_2W_{122}(\beta\beta_1\theta_2+\beta_2J_1)$$
$$+\beta\beta_1W_{222}[\theta_1(2\beta_2-\beta\beta_1)+J_1r'(1-\beta^2)/r'']+W_{112}[\theta_1\beta_1^2+J_1r'^2(1-\beta^2)/r''^2]\,.\tag{A21}$$

APPENDIX B

In the long-wavelength limit, the expression (10a) for I_{43}^l can be written as

$$\lim_{q\to0}I_{43}^l=\frac{n^2(I_1+I_2)}{3m^2}\,,\tag{B1}$$

where

$$I_1=8\pi^2\int_0^\infty\int_0^\infty dr\,dr'\,r^2r'^2\int_{-1}^1 d\beta\,g_3(\vec{r},\vec{r}')\{-(\beta^2W_{22}+2W_{21}+3W_{11})$$
$$+(q^2r^2/5)[3\beta^2W_{22}+3W_{21}+(2\beta^2+1)W_{12}+5W_{11}]\}\tag{B2}$$

and

$$I_2=8\pi^2\int_0^\infty\int_0^\infty dr\,dr'\,r^2r'^2\int_{-1}^1 d\beta\,g_3(\vec{r},\vec{r}')(\beta_2^2W_2'W_2''+W_1'W_2''+W_2'W_1''+3W_1'W_1''-(q^2r^2/10)$$
$$\times\{5W_1'W_1''+(2\beta^2+1)W_2'W_1''+[3r^2+r'^2(2\beta^2+1)-6\beta rr']W_1'W_2''/r''^2$$
$$+[3\beta r-r'(2\beta^2+1)]\beta_2W_2'W_2''/r''\})\,.\tag{B3}$$

In order to recover the result of Forster *et al.*,[3] we have to bring out the angle from the potential arguments in Eq. (B3). We do this with the help of a transformation and the symmetric property of g_3 defined by Eq. (8). This is shown below, but only for one term of I_2, say the first one. We denote this term by I_2' which can alternatively be written as

$$I_2'=\int\int d\vec{r}\,d\vec{r}'\,g_3(\vec{r},\vec{r}')\frac{\vec{r}'\cdot(\vec{r}-\vec{r}')}{r'|\vec{r}-\vec{r}'|}$$
$$\times W_2(r')W_2(|\vec{r}-\vec{r}'|)\,.\tag{B4}$$

In this equation, we change the variable of integration from $\vec{r}$ to $\vec{r}_1$ through the transformation $\vec{r}_1=\vec{r}-\vec{r}'$ and obtain

$$I_2'=\int\int d\vec{r}_1\,d\vec{r}'\,g_3(\vec{r}_1+\vec{r}',\vec{r}')$$
$$\times[(\vec{r}_1\cdot\vec{r}')/r_1r']^2W_2(r')W_2(r_1)\,.\tag{B5}$$

We now change r' to $-r'$, $\vec{r}_1$ to $\vec{r}$ and use Eq. (8) of the text and find that

$$I_2'=8\pi^2\int_0^\infty\int_0^\infty dr\,dr'\,r^2r'^2$$
$$\times\int_{-1}^1 d\beta\,g_3(\vec{r},\vec{r}')\beta^2W_{22}\,.\tag{B6}$$

It may be noted that (B6) directly cancels with the first term of I_1. The same procedure is applied to the other terms of I_2. The resultant expression for I_2, when added to I_1, gives

$$\lim_{q\to0}I_{43}^l\,q^{-2}=(8\pi^2n^2/15m^2)\int_0^\infty\int_0^\infty dr\,dr'\,r^3r'^3\int_{-1}^1 d\beta\,g_3(\vec{r},\vec{r}')\beta(W_{22}(1+2\beta^2)+3W_{21}+3W_{12}+5W_{11})\,.\tag{B7}$$

Now with the use of Eq. (A1), it is easy to check that (B7) reduced to the result of Forster *et al.*[3] In a similar way, the corresponding expression for the transverse case can also be reduced to the result of Forster *et al.*

APPENDIX C

In this appendix, we state the results obtained after performing the angular integrations contained in $\langle\omega_{l,s}^6\rangle$, $\langle\omega_{t,s}^6\rangle$, and C, the sixth frequency moment of the velocity autocorrelation function. Explicit expressions for these three quantities have already been obtained by us in Ref. 1. Within the notation described in Appendix A, we find that

$$C=(16\pi n/3m^3)\int_0^\infty dr\, r^2 g_2(r)[2W_1^3+(W_1+W_2)^3+3(k_BT)(W_4^2+15W_3^2+6W_3W_4)]$$
$$+(8\pi^2n^2/m^3)\int_0^\infty\int_0^\infty dr\,dr'\,r^2r'^2\int_{-1}^1 d\beta\, g_3(\vec r,\vec r')[3(k_BT)P_5(\vec r,\vec r',\beta)-P_7(\vec r,\vec r',\beta)+6P_6(\vec r,\vec r',\beta)]$$
$$+[(4\pi n/3m)\int_0^\infty dr\, r^2 g_2(r)V_4]^3 . \tag{C1}$$

For writing the last term of this equation, we have used the same approximation as for $I_{64}^{1,t}$. But here we suggest an alternative approximation for the quadruplet correlation function and assume that $\langle g_4(\vec r,\vec r',\vec r'')\rangle$ is an angular averaged quadruplet correlation function. With this approximation, the four-body contribution term of C becomes

$$(4\pi n/3m)^3\int_0^\infty\int_0^\infty\int_0^\infty dr\,dr'\,dr''\,r^2r'^2r''^2\langle g_4(\vec r,\vec r',\vec r'')\rangle\,(W_{222}+9W_{221}+27W_{112}+27W_{111}),$$

where

$$\langle g_4(\vec r,\vec r',\vec r'')\rangle=\tfrac18\int_{-1}^1\int_{-1}^1\int_{-1}^1 d\beta\,d\beta_1\,d\beta_2\, g_4(\vec r,\vec r',\vec r'') . \tag{C2}$$

The results for the self parts of the sixth frequency moments of longitudinal and transverse current correlation functions are obtained to be

$$\langle\omega_{l,s}^6\rangle=7\omega_0^2(15\omega_0^4+30\omega_0^2A+4B)+C+(28\pi n\omega_0^2/15m^2)\int_0^\infty dr\,r^2g_2(r)[5(15W_1^2+3W_2^2+10W_2W_1)-9k_BTV_3]$$
$$+(56\pi^2n^2\omega_0^2/3m^2)\int_0^\infty\int_0^\infty dr\,dr'\,r^2r'^2\int_{-1}^1 d\beta\, g_3(\vec r,\vec r')[5(3W_{11}+2W_{21})+(2\beta^2+1)W_{22}], \tag{C3}$$

and

$$\langle\omega_{t,s}^6\rangle=\omega_0^2(15\omega_0^4+60\omega_0^2A+16B)+C+(2\pi n^2\omega_0^2/3m^2)\int_0^\infty dr\,r^2g_2(r)(30W_1^2-11W_2^2+30V_2+25V_1-48k_BTV_3)$$
$$+(40\pi^2n^2\omega_0^2/m^2)\int_0^\infty\int_0^\infty dr\,dr'\,r^2r'^2\int_{-1}^1 d\beta\, g_3(\vec r,\vec r')[3W_{11}+2W_{12}+W_{22}(4+3\beta^2)/15]. \tag{C4}$$

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