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# Addendum to "Sum rules and atomic correlations in classical liquids"*

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An explicit expression for the fourth frequency moment of the spectral function of the energy-density fluctuation correlation function, and hence for the energy-density correlation function, has been derived for a classical system of particles interacting through a two-body potential. It has been found to contain correlations up to four particles only. An expression in the long-wavelength limit for the eighth frequency moment of $S(q, \omega)$ has also been given.

In a recent paper[1] (hereafter referred to as I), explicit expressions for the sixth frequency moments of the current correlations along with their self-parts, the first four frequency moments of the kinetic-energy-density (KED) fluctuation correlation function and the first two frequency moments of the energy-density fluctuation (EDF) correlation function, were derived for a classical system of particles interacting through a two-body potential. These moment relations were found to contain correlations up to a maximum of four particles. In this addendum, we extend our sum-rule calculation for the fourth frequency moment of the EDF correlation function. This completes the derivation up to fourth frequency moments of both the KED fluctuation and EDF correlation functions. It is interesting to note that the fourth frequency moment of the EDF correlation function also involves up to a maximum of a quadruplet correlation function.

Since the details of the method of calculation have been discussed in I, we briefly present here the result. Following the definition and notation of I and differentiating the EDF operator $e(q, t)$ twice with respect to time, we obtain

$$\ddot{e}(q, t) = \frac{1}{n\sqrt{N}} \sum_j \left[\tfrac{1}{2}(e_1 + iqe_2 - q^2 e_3) - e\, e_4\right] e^{iqx_j}, \tag{1}$$

where

$$e_1 = 2M(\vec{v}_j \cdot \vec{a}_j) + (2M)\vec{a}_j^2 + \sum_{m\neq j} \sum_k \left( \sum_l \frac{\partial^2 \varphi(r_{jm})}{\partial r_{k\alpha} \partial r_{l\beta}} v_{k\alpha} v_{l\beta} + \frac{\partial \varphi(r_{jm})}{\partial r_{k\alpha}} \mathring{v}_{k\alpha} \right), \tag{2}$$

$$e_2 = Ma_{jx} \vec{v}_j^2 + 4Mv_{jx}(\vec{v}_j \cdot \vec{a}_j) + \sum_{m\neq j} \left( a_{jx} \varphi(r_{jm}) + 2v_{jx} \sum_k \frac{\partial \varphi(r_{jm})}{\partial r_{k\alpha}} v_{k\alpha} \right), \tag{3}$$

$$e_3 = Mv_{jx}^2 \vec{v}_j^2 + v_{jx}^2 \sum_{m\neq j} \varphi(r_{jm}), \tag{4}$$

$$e_4 = iqa_{jx} - q^2 v_{jx}^2, \tag{5}$$

and

$$E_4 = \langle \ddot{e}(q, t) \ddot{e}(-q, 0) \rangle_{t=0}. \tag{6}$$

Using Eqs. (9) and (13) of I, it is straightforward to derive the result for $E_4$. We omit the detailed algebra involved in the derivation of $E_4$ and state here only the result:

$$E_4 = H_4 + (M^2/4n^2)(C_2 + C_3 + C_4 + C_F). \tag{7}$$

Here $H_4$ represents the fourth frequency moment of the KED correlation function and can be obtained by substituting the mean kinetic energy $T_0 = 0$ in Eq. (34) of I. $C_2$ represents the two-particle contribution to $E_4$ and is given by

$$\begin{aligned} C_2 = {} & -2q^2 \left(\frac{k_B T}{M}\right)^3 [63\Omega^2(0) + \Omega^2(q)] + n \left(\frac{k_B T}{M^2}\right)^2 \int d\vec{r}\, g_2(\vec{r}) \\ & \times \Big( U_{\alpha\alpha}(r) U_{\beta\beta}(r)(3\cos qx - 5) - 4(k_B T) U_{\alpha\alpha\beta\beta}(r) + 2q^2 \varphi(r)[2q^2(\varphi(r) + 14k_B T) + U_{\alpha\alpha}(r) + 2U_{xx}(r)(4 - 3\cos qx)] \\ & + 18q^2 U_\alpha^2(r) - 8U_{\alpha\alpha\beta}(r) U_\beta(r)(2 + \cos qx) + 2(1 + \cos qx) U_{\alpha\beta}(r) \{2[U_\alpha(r) U_\beta(r)/k_B T] - 7U_{\alpha\beta}(r)\} \\ & + q^2(1 - \cos qx)\{6U_x^2(r) + [U_{xx}(r)\varphi^2(r)/k_B T]\} + 4q \sin qx \, \{2k_B T[U_{x\alpha\alpha}(r) + 2U_{xxx}(r)] + U_{x\alpha\alpha}(r)\varphi(r) \\ & - 5U_{x\alpha}(r) U_\alpha(r) - [U_{x\alpha}(r) U_\alpha(r) \varphi(r)/k_B T]\}\Big), \end{aligned} \tag{8}$$

where $\Omega^2(q)$ has been defined in I. $C_3$ represents the contribution to $E_4$ arising due to correlations between three particles only and it is given by

$$\begin{aligned}C_3=\left(\frac{nk_BT}{M^2}\right)^2\int\int d\vec{r}\,d\vec{r}\,'g_3(\vec{r},\vec{r}\,')\,[&4q^2\varphi(r')[q^2\varphi(r)+U_{xx}(r)(4-3\cos qx)]+2U_{\alpha\alpha}(r)[16q^2k_BT\cos qx'+U_{\beta\beta}(r')(\cos qx-7)]\\&+U_{\alpha\beta}(r)U_{\alpha\beta}(r')[3\cos q(x-x')-8\cos qx-11]-4U_{\alpha\beta\beta}(r)U_\alpha(r')\\&\times[3-\cos qx-\cos qx'-\cos q(x-x')]+2q^2U_x(r)U_x(r')[5+2\cos q(x-x')]\\&+2U_{\alpha\alpha}(r)\varphi(r')[1-\cos qx+\cos q(x-x')]+2q^2U_\alpha(r)U_\alpha(r')(4+\cos qx)\\&+4qU_{\alpha\alpha}(r)U_x(r')[4\sin qx'+3\sin qx+2\sin q(x-x')]+16q^3k_BTU_x(r)\sin qx'\\&+2qU_{x\alpha}(r)U_\alpha(r')[\sin q(x-x')+\sin qx'-4\sin qx]+4q\sin qxU_{x\alpha\alpha}(r)\varphi(r')+(1/k_BT)\\&\times(q^2U_{xx}(r)\varphi(r')[2\varphi(r)(1-\cos qx)-\varphi(|\vec{r}-\vec{r}\,'|)\cos qx+\varphi(r')]\\&\quad+2U_{\alpha\beta}(r')U_\alpha(r)U_\beta(r)(1+\cos qx)+U_{\alpha\beta}(r)U_\beta(r')[U_\alpha(\vec{r}-\vec{r}\,')+4U_\alpha(r)]\\&\quad\times[1+\cos qx+\cos qx'+\cos q(x-x')]-2qU_{x\alpha}(r)U_\alpha(r')\\&\quad\times\{\varphi(r')\sin qx'+\varphi(r)[\sin qx+\sin qx'+\sin q(x-x')]\}-2qU_{x\alpha}(r)\varphi(r')\\&\quad\times\{\sin qx[2U_\alpha(r)-U_\alpha(\vec{r}\,'-\vec{r})]-U_\alpha(\vec{r}\,'-\vec{r})\sin qx'\})].\end{aligned}\tag{9}$$

$C_4$ and $C_F$ represent, respectively, the contributions due to the four-particle distribution function and due to the fluctuation in the energy density. These are given as

$$\begin{aligned}C_4=\frac{n^3k_BT}{M^4}\int\int\int d\vec{r}\,d\vec{r}\,'d\vec{r}\,''\,g_4(\vec{r},\vec{r}\,',\vec{r}\,'')\,(&U_{\alpha\beta}(r)U_\alpha(r')\{U_\beta(r'')[1+\cos qx'+\cos qx''+\cos q(x''-x')]\\&\qquad+U_\beta(\vec{r}-\vec{r}\,'')[2\cos qx''+\cos qx+\cos q(x-x'')]\}\\&+q\varphi(r')\{qU_{xx}(r)[\varphi(r'')-\varphi(|\vec{r}-\vec{r}\,''|)\cos qx]\\&\qquad-2U_{x\alpha}(r)[U_\alpha(r'')\sin qx''-U_\alpha(\vec{r}\,''-\vec{r})(\sin qx+\sin qx'')]\})\end{aligned}\tag{10}$$

and

$$\begin{aligned}C_F=\frac{4e}{M}\left(\frac{k_BT}{M}\right)\Bigg[3q^4\left(\frac{k_BT}{M}\right)\left(\frac{e}{M}-\frac{7k_BT}{M}\right)&+\frac{n}{M^2}\int d\vec{r}\,g_2(\vec{r})\,(q^2U_{xx}(r)\{(1-\cos qx)[e-\varphi(r)-6k_BT]-2k_BT\}\\&\qquad-4q^4k_BT\varphi(r)+2\sin qx\,[U_{x\alpha}(r)U_\alpha(r)-k_BTU_{x\alpha\alpha}(r)])\\+\frac{n^2}{M^2}\int\int d\vec{r}\,d\vec{r}\,'\,g_3(\vec{r},\vec{r}\,')\{&qU_{x\alpha}(r')U_\alpha(r)[\sin qx+\sin qx'+\sin q(x'-x)]\\&-q^2U_{xx}(r)\varphi(r')(1-\cos qx)\}\Bigg].\end{aligned}\tag{11}$$

Although one expects that higher-order correlation functions (involving more than four particles) should enter in $E_4$, yet it is interesting to note that $E_4$ contains up to four-particle correlation functions only. During the course of the calculation, we do come across certain terms containing more than four particles [which is evident from Eqs. (2) and (6)] but all these terms vanish within the assumption of pair potential. For example, in Eq. (3) the last term will contribute only for $k=j$ or $k=m$, so that $e_2$ contains at the most two particles. The case is similar with $e_1$. Therefore, only those terms involving a maximum of four particles will contribute to $E_4$. Looking at the steps of calculation and the results of the frequency moments of the EDF correlation function, we feel that the sixth frequency moment also will not involve more than four-particle correlation functions, whereas the moments higher than sixth may involve five-particle distribution function.

The fourth frequency moment of the energy-density correlation function can be obtained by substituting in (11) $e=0$, i.e., substituting the fluctuation contribution $C_F=0$. Further, in the long-wavelength limit, the fluctuation part $C_F$ vanishes. Thus, like $E_2$, the $q\to 0$ limits of the fourth frequency moments of the EDF correlation function and the energy-density correlation function will be equal.

In I, the expression for the sixth frequency moment of the longitudinal current correlation function [eighth frequency moment of the dynamical structure factor $S(q,\omega)$] for $q\to 0$ has not been given. We wish to point out that it is nontrivial to obtain this limit directly from the form of the expression given in I. We therefore state here the result:

$$\lim_{q\to 0}\frac{\langle\omega_l^6\rangle}{q^2}=\frac{n}{M^3}\int d\vec{r}\; g_2(\vec{r})[18(k_BT)^2U_{xxxx}(r)+70(k_BT)U_{xx}^2(r)+56(k_BT)U_{x\alpha}^2(r)+72(k_BT)xU_{x\alpha}(r)U_{xx\alpha}(r)$$
$$+2x^2U_{\alpha\beta}(r)U_{x\alpha}(r)U_{x\beta}(r)+6(k_BT)x^2U_{x\alpha\beta}^2(r)]+\frac{n^2}{M^3}\int\int d\vec{r}\,d\vec{r}\,'\,g_3(\vec{r},\vec{r}\,')$$
$$\times\{7(k_BT)[5U_{xx}(r)U_{xx}(r')+4U_{x\alpha}(r)U_{x\alpha}(r')]+6(k_BT)(5x+2x')U_{xx\alpha}(r)U_{x\alpha}(r')+(3k_BT/2)$$
$$\times(x^2-x'^2+2xx')U_{x\alpha\beta}(r)U_{x\alpha\beta}(r')+4xx'U_{\alpha\beta}(r)U_{x\alpha}(r)U_{x\beta}(r')+x^2U_{x\alpha}(r)U_{x\beta}(r)U_{\alpha\beta}(r')$$
$$-x^2U_{x\alpha}(r)U_{x\beta}(r')U_{\alpha\beta}(\vec{r}-\vec{r}\,')+\tfrac{1}{2}x^2U_{\alpha\beta}(r)U_{x\alpha}(r')U_{x\beta}(\vec{r}-\vec{r}\,')\}$$
$$+\frac{n^3}{2M^3}\int\int\int d\vec{r}\,d\vec{r}\,'\,d\vec{r}\,''\,g_4(\vec{r},\vec{r}\,',\vec{r}\,'')[(x^2-x'^2+2xx')U_{x\alpha}(r)U_{x\beta}(r')U_{\alpha\beta}(r'')$$
$$+(x^2+x'^2-x''^2-2x'x'')U_{\alpha\beta}(r)U_{x\alpha}(r')U_{x\beta}(\vec{r}\,''-\vec{r})]\,. \qquad (12)$$

An analogous expression for the transverse part can now be easily written.

So far no sufficient information about the triplet and quadruplet correlation functions is available from computer experiments. Therefore it seems difficult as yet to estimate the various frequency moments involving three- and four-particle correlation functions. Recently, Machida and Murase[2] have estimated the sixth frequency moment of the longitudinal current correlation function. It may be noted that their expression for the sixth frequency moment of the longitudinal current correlation function is incomplete and in error (see footnote 2). Machida and Murase have approximated the various higher-order correlation functions by the products of two-particle correlation functions, which seems to be the simplest approximation, at least initially. They have used the results of the various frequency moments (up to the sixth) of the longitudinal current correlation function to estimate the Maxwell relaxation time required in the viscoelastic theory of liquids. Thus if required the various frequency moments of the EDF correlation function can be estimated using the same kind of decoupling approximation for higher-order correlation functions as used by Machida and Murase.[2] Also, we feel that because of the possibility of using high-speed computers for numerical experiments, it may not be impossible to obtain detailed information about the triplet and quadruplet correlation functions.

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[1]R. Bansal and K. N. Pathak, Phys. Rev. A 9, 2773 (1974).

[2]M. Machida and C. Murase, Prog. Theor. Phys. 50, 1 (1973). After the publication of Ref. 1, the work of Machida and Murase came to our attention. These authors have stated the results for the fourth and sixth frequency moments of the longitudinal current correlation function. These results are incomplete in the sense that a class of terms (i.e., "sine" terms) is completely missing and there is an error of the numerical factor in one of the terms of the sixth frequency moment. Moreover, their results have not been expressed in terms of the static correlation functions. The above discrepancies have been confirmed to us by Professor Murase in a private communication. We are thankful to Professor Murase for this correspondence.