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# Energy current density correlation function: I. Frequency sum rules

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**Abstract.** Expressions for zeroth-, second- and fourth-frequency sum rules of energy current density correlation function have been derived. These exact expressions involve static correlation functions of up to five particles. Because of the non-availability of any information about triplet and higher-particle correlation functions, we use a low-order decoupling approximation for these. The resulting expressions for the frequency sum rules, which now contain only a static pair correlation function and an inter-atomic potential, are suitable for applications. Numerical results for these frequency sum rules have been obtained for Lennard-Jones fluids over a wide range of densities and temperatures. The density and temperature dependence and the relative importance of higher-particle correlation contributions to the frequency sum rules have been discussed.

## 1. Introduction

It is well known that dynamical and transport properties of physical systems are embodied in the time correlation functions (TCFs). Although significant progress has been made in calculating the TCFs at a microscopic level, as yet there is no dynamical theory for a realistic potential which can readily be used to calculate the TCF for any thermodynamic state of fluids. However, it has been recognised that the frequency sum rules or moments of TCF play an important role in the analysis of TCF and in the calculation of the transport coefficients. These sum rules can be directly formulated in terms of static correlation functions (SCFs) and the inter-atomic potential. Since relatively reliable interaction potentials for fluids of rare-gas atoms and for simple metals are known, SCFs can easily be calculated using either some established theory or the computer simulation method. This in turn enables us to obtain reliable results for frequency sum rules for any density and temperature of fluids.

One theoretical approach for calculating the transport coefficients of dense fluids is through the Green–Kubo integral of the TCF of appropriate dynamical variables. For example the thermal conductivity is related to the TCF of energy current density (ECD). The time evolution of TCFs can be expressed in terms of a relaxation kernel or memory function. Thus the problem of calculation of the transport coefficients reduces to the calculation of an appropriate memory function. The memory function has in it all contributions to dynamics of a many-body system—uncorrelated and correlated binary and higher-order collisions. So far there is no first-principles method which can be

applied to calculate the memory function for any arbitrary density and temperature of fluid. Therefore, one often assumes a phenomenological form (Boon and Yip 1980, Hansen and McDonald 1986) for it. The parameter introduced therein are determined by frequency sum rules. Although it does not provide a microscopic theory for the memory function, it does enable one to make acceptable predictions of the transport coefficients of fluids (Tankeshwar *et al* 1987, 1988).

In view of the above, we derive in this paper explicit molecular expressions for zeroth-, second- and fourth-frequency sum rules of the ECD correlation function. The expressions for the zeroth-, second- and fourth-frequency sum rules involve SCFs of up to three, four and five particles, respectively. Since nothing is known yet about four- and five-particle SCFs, we therefore use a low-order decoupling approximation (Tankeshwar *et al* 1987, 1988) for four- and five-particle contributions to the second and fourth moments. It enables us to write higher-particle contributions in terms of two- and three-particle correlation functions. Exact expressions for two- and three-particle contributions and an approximate expression for higher-particle contributions (in terms of two- and three-particle SCFs) are given in § 2. The exact expressions for four- and five-particle contributions together with some steps to simplify these, are given in Appendices 1 and 2. For the static triplet correlation function, we use the superposition approximation. Our final expressions involve only the static pair correlation function and the inter-atomic potential. After performing angular integration analytically, we have computed these expressions for Lennard-Jones (LJ) fluids over a wide range of densities and a wide range of temperatures. The numerical results are given in § 3. In § 4, we discuss the relative importance of two-, three-, four- and five-particle correlation function contributions. In the following paper, we use the results for frequency sum rules to calculate the thermal conductivity and ECD correlation function of LJ fluids over a wide range of densities and a wide range of temperatures.

## 2. Expressions for the frequency sum rules of the ECD correlation function

For a system interacting via pairwise central forces, we define the ECD variable as

$$J_x^e(t) = \sum_l \left( \frac{v_{lx}^2 p_l}{2m} + \frac{1}{2} \sum_{l'}' u_{ll'} v_{lx} - \frac{1}{2} \sum_{l'}' \frac{\partial u_{ll'}}{\partial r_{ll'}} \hat{r}_{ll'x} \cdot v_l \right) \quad (1)$$

where

$$U = \frac{1}{2} \sum_{ll'}' u_{ll'} = \frac{1}{2} \sum_{ll'}' u(|r_l - r_{l'}|)$$

is the potential energy. The prime on the summation denotes that  $l = l'$  terms are excluded.  $r_{lx}$  and  $v_{lx}$  are the  $x$  components of position and velocity, respectively, and  $p_l$  is the momentum of the  $l$ th particle. Further  $r_{ll'} = r_l - r_{l'}$ , and  $\hat{r}_{ll'} = r_{ll'}/r_{ll'}$  is the unit vector in the direction of  $r_{ll'}$ . The associated dynamical quantity of interest is the ECD correlation function

$$E(t) = \langle J_x^e(t) J_x^e(0) \rangle \quad (2)$$

with the short-time expansion given by

$$E(t) = E_0 - E_2 t^2/2! + E_4 t^4/4! + \dots \quad (3)$$

where  $E_0$ ,  $-E_2$  and  $E_4$  are the zeroth-, second- and fourth-frequency sum rules or

moments of the spectral function of the ECD correlation function. The angular brackets in equation (2) represent an ensemble average.

The expression for  $E_0$  has been obtained by putting  $t = 0$  in equation (2) and evaluating equilibrium averages. The method of calculation has been described by Bansal and Pathak (1974). This gives

$$E_0 = \frac{35}{4} \left( \frac{k_B T}{M} \right)^3 M^2 + \frac{k_B T}{M} n \int d\mathbf{r}_1 g(r_1) \times [U_1^2 + U_{1x}^2 r^2 + 10k_B T(U_1 - U_{1x}x_1) - 2UU_{1x}x_1] + \frac{n^2}{4} k_B T \times \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) [U_1 U_2 + 2U_{1x} U_{2x} \mathbf{r}_1 \cdot \mathbf{r}_2 - 2U_1 U_{2x} x_2] \quad (4)$$

where  $g(r_1)$  and  $g_3(\mathbf{r}_1, \mathbf{r}_2)$  are the static pair and triplet correlation functions. From the expression for  $J_x^c(t)$  it is obvious that  $E_0$  should involve a four-particle correlation, but four-particle terms vanish in the pair potential approximation.

The expression for  $E_2$  is obtained by evaluating the thermodynamic average

$$E_2 = \langle \dot{J}_x^c(t) \dot{J}_x^c(t) \rangle_{t=0}$$

where  $\dot{J}_x^c(t)$  is the single time derivative of  $J_x^c(t)$ . From the expression for  $\dot{J}_x^c(t)$ , one expects that the expression for  $E_2$  should contain static correlation up to six particles. However, it has been found that five- and six-particle contributions turn out to be zero in the pair potential approximation and successive application of the Yvon theorem (Bansal and Pathak 1974). The final expression for  $E_2$  involves a SCF only up to four particles. The expression for  $E_2$  involving two- and three- particle contributions is

$$E_{22} = \left( \frac{k_B T}{M} \right)^2 n \int d\mathbf{r}_1 g(r_1) \left[ \left( \frac{43}{4} U_{1xx} + 2U_{1\beta\beta} + \frac{5}{2} U_{1xx\beta} \beta_1 + \frac{1}{2} U_{1x\beta\beta} x_1 \right) k_B T + \frac{1}{4} U_{1x\beta}^2 r_1^2 - \frac{1}{2} U_{1x}^2 - \frac{1}{2} U_{1\beta} U_{1xx} \beta_1 - \frac{3}{4} U_{1\beta} U_{1x\beta} x_1 + \frac{1}{4} (U_{1x\beta} \beta_1)^2 \right] \quad (5)$$

and

$$E_{23} = \frac{k_B T n^2}{M^2} \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) [U_1 (U_1 U_{2xx} + U_2 U_{2xx} - U_2 U_{12xx} - 2U_{1x} U_{2x\beta} \beta_2 + 2U_{1x} \beta_2 U_{12x\beta}) + U_{1x} \alpha_1 (2U_{2x} \beta_2 U_{1\alpha\beta} + U_{2x} \beta_2 U_{12\alpha\beta} + U_{1x} \beta_1 U_{2\alpha\beta}) + k_B T (U_{1x\beta} U_{2x} \beta_1 - U_{1x} U_{2x} - 2U_{1\beta} U_{2xx} \beta_2 + U_{1x\beta} \alpha_1 \beta_1 U_{2x\alpha} + U_{1x\beta} U_{2x\beta} \mathbf{r}_1 \cdot \mathbf{r}_2)] \quad (6)$$

where  $\alpha_1$  and  $\beta_1$  are Cartesian components of  $r_1$  and summation over repeated indices  $\alpha, \beta$  is implied. Here, and in what follows,  $E_{nm}$  represents an  $m$ -body contribution to  $n$ th-frequency sum rules. We also use the notation

$$U_{1\alpha_1\alpha_2\dots\alpha_n} = \partial^n u(r_1) / \partial r_{1\alpha_1} \partial r_{1\alpha_2} \dots \partial r_{1\alpha_n} \quad (7)$$

and  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ ,  $\alpha_1, \alpha_2, \dots, \alpha_n$  denote the Cartesian components, and subscripts 2 and 12 on  $U$  and on  $\alpha, \beta$  in equations (4)–(6) represent the fact that the argument of the potential is changed to  $r_2$  and  $r_{12}$ . In the above equations,  $n, k_B, T$  and  $M$  are the density, the Boltzmann constant, the temperature and the atomic mass, respectively.

The exact expression for the four-particle contribution to the second-frequency sum rule is given in Appendix 1. Since no information about static four-particle correlation is available, therefore the exact expression is of only formal interest. In order to have it in usable form, we approximate this contribution using a low-order decoupling approximation. This has been explained in Appendix A. The resulting expression now only involves the static pair and triplet correlation functions. It is explicitly given as

$$E_{24} = (k_B T/4M^2)[G_3^2 G_1 + G_2(G_3 - 2G_5) + G_5 G_1(G_5 - 2G_3) - G_5 G_4]. \quad (8)$$

Here

$$G_1 = n \int d\mathbf{r}_1 g(r_1) U_{1xx} \quad (9)$$

$$G_2 = n^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) U_{1x\beta} U_{2xx} \beta_2 \quad (10)$$

$$G_3 = n \int d\mathbf{r}_1 g(r_1) U_{1x} x_1 \quad (11)$$

$$G_4 = n^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) U_1 U_{2xx} \quad (12)$$

and

$$G_5 = n \int d\mathbf{r}_1 g(r_1) U_1. \quad (13)$$

The fourth-frequency sum rule of ECD correlation function is defined as

$$E_4 = \langle \check{J}_x^e(t) \check{J}_x^e(-t) \rangle_{t=0}. \quad (14)$$

It can be written as the sum of two-, three-, four- and five-particle contributions. We explicitly write it as

$$E_4 = E_{42} + E_{43} + E_{44} + E_{45}. \quad (15)$$

It is straightforward to obtain the two-particle contribution which is given as

$$\begin{aligned} E_{42} = & \frac{n(k_B T)^2}{M^3} \int d\mathbf{r}_1 g(r_1) [U(3U_{1xx}^2 + \frac{17}{4} U_{1x\beta}^2 + 2U_{1x\alpha\beta} U_{1x\beta} \alpha_1) \\ & + U_\beta(4U_{1x\alpha}^2 \beta_1 - \frac{9}{2} U_{1x\beta} U_1 + U_{1\beta} U_{1xx} + U_{1x\alpha} U_{1x\beta} \alpha_1 \\ & + \frac{1}{2} U_{1\alpha} U_{1\alpha\beta} + 2U_{1x} U_{1x\alpha\beta} \alpha_1 - U_{1x\alpha} U_{1\alpha\beta} x_1) + U_{1x}(U_{1x} U_{1\alpha\alpha} \\ & + U_{1\beta\beta} U_{1\alpha\alpha} \alpha_1 + \frac{1}{2} U_{1x\beta} U_{1\alpha\beta} \alpha_1) + \frac{3}{4} U_{1x\beta} U_{1x\alpha} U_{1\alpha\beta} r_1^2 \\ & + U_1(k_B T)^{-1}(U_{1x\alpha} U_{1x} U_{1\alpha\beta} \beta_1 - U_1 U_{1x\beta}^2) + k_B T(\frac{223}{4} U_{1x\beta}^2 \\ & + \frac{57}{2} U_{1\beta} U_{1xx\beta} - 11U_{1x} U_{1x\beta\beta} + \frac{53}{2} U_{1\beta\beta} U_{1xx} + \frac{3}{2} U_{1\alpha\beta\beta} U_{1\alpha} \\ & + 3U_{1\alpha\beta}^2 - \frac{1}{2} U_{1\beta\beta}^2 + 29U_{1xx}^2 + 4U_1 U_{1xx\beta\beta} - 12U_{1x} U_{1xxx} \\ & - U_{1\alpha\alpha} U_{1\beta\beta} + 4U_{1x\beta\beta} U_{1x\alpha\alpha} r_1^2 + 9U_{1x\alpha\beta}^2 r_1^2 + 11U_{1x\beta\gamma} U_{1x\alpha\beta} \beta_1 \gamma_1 \\ & + 4U_{1x\beta\gamma} \beta_1 \gamma_1 + U_{1x\alpha\alpha}^2 r_1^2 + 2U_{1x\beta\beta} U_{1x\alpha\alpha} \beta_1^2 + 4U_{1x\alpha\beta}^2 \beta_1^2 \\ & - 40U_{1x\beta\beta}^2 \beta_1^2 - 13U_{1\alpha\beta\beta} U_{1xx} \alpha_1 + U_{1\beta\beta\alpha} U_{1x\alpha} x_1 + 4U_{1\alpha\beta} U_{1x\alpha\beta} x_1 \\ & + 5U_{1\beta} U_{1x\beta\alpha\alpha} x_1 + \frac{5}{2} U_{1xx\beta} U_{1\alpha\beta} \alpha_1 - \frac{19}{2} U_{1\alpha\beta} U_{1x\beta} \alpha_1 \end{aligned}$$

$$\begin{aligned}
 & - \frac{41}{2} U_{1x\beta\beta} \alpha_1 U_{1x\alpha} - 7U_{1x} U_{1x\beta\beta\alpha} \alpha_1 - 8U_{1\beta\beta} U_{1x\alpha\alpha} x_1 \\
 & + 4U_{1xxx} U_{1x\beta} \beta_1 - 2U_{1x\alpha} U_{1x\alpha\alpha} \alpha_1 + 2U_{1\beta\beta} U_{1xxx} \alpha_1 \\
 & + 3U_{1xx} U_{1x\alpha\alpha} x_1 + 2U_{1xx\alpha} U_{1x\alpha} x_1 - U_{1\beta\beta} U_{1xxx} x_1 \\
 & - 6U_{1xx} U_{1xx\beta} \beta_1 - 3U_{1\beta\beta} U_{1\beta\beta x} x_1 - 2U_{1\beta\beta} U_{1xx\beta} \beta_1 \\
 & - 34U_{1xx} U_{1xxx} x_1 + (k_B T)^2 (\frac{127}{2} U_{1xx\beta\beta} + 3U_{1x\alpha\alpha\beta\beta} x_1 \\
 & - \frac{27}{2} U_{1xx\beta\beta\alpha} \alpha_1 - U_{1\alpha\alpha\beta\beta})]. \tag{16}
 \end{aligned}$$

The notation used here is the same as that in equation (6). It should be noted that  $E_{42}$  involves up to the fifth derivative of inter-atomic potential. This, therefore, contains the highly anharmonic motion of atoms in the fluids. The calculation of the triplet contribution is also straightforward but lengthy. It is

$$\begin{aligned}
 E_{43} = & \left(\frac{k_B T}{M}\right)^2 \frac{n^2}{M} \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) \{k_B T (\frac{241}{4} U_{1x\beta} U_{2x\beta} - \frac{75}{2} U_{1xx} U_{2xx} \\
 & + \frac{17}{2} U_{1xx} U_{2\beta\beta} + \frac{9}{2} U_{1\alpha\beta} U_{2\alpha\beta} + 10U_{1x\beta\beta} U_{2x} \\
 & + \frac{1}{2} U_{1x\beta\alpha} U_{2x\beta} \alpha_2 - 5U_{2x\alpha} U_{1x\alpha\alpha} \alpha_1 + 2U_{1x\beta\beta} U_{2x\alpha} \alpha_1 \\
 & - U_{1x\beta\alpha} U_{2x\beta} \alpha_1 + 13U_{1xx\beta} U_{2\beta} - 5U_{2\beta\beta} U_{1xx\alpha} \alpha_1 \\
 & - 12U_{1xx\alpha} U_{2\alpha\beta} \beta_1 - U_{1\alpha\alpha} U_{1\beta\beta} - 7U_{1x\alpha\beta} x_1 U_{2\alpha\beta} \\
 & - 3U_{2x} U_{1\alpha\beta\beta x} \alpha_2 - 2U_{2\alpha\beta} U_{1x\beta x} \alpha_1 + 2U_{1\alpha\beta\beta} U_{2\alpha} \\
 & - U_{2xx} U_{1x\alpha\alpha} x_1 - 14U_{1\alpha xx} U_{2x\alpha} x_2 + U_{\alpha xx} \alpha_1 U_{2\beta\beta} \\
 & - 8U_{2\beta\beta} U_{1x\alpha\alpha} x_1 - 40U_{1x\beta\beta} U_{2x\beta\beta} \beta_1 \beta_2 + 8U_{1x\beta\gamma} U_{2\beta\gamma x} \alpha_1 \alpha_2 \\
 & + 4U_{1\alpha\beta x} U_{2\alpha\beta x} \beta_1 \beta_2 + 2U_{1x\beta\beta} U_{2x\alpha\alpha} \beta_1 \beta_2 + 4U_{1x\beta\beta} U_{2x\beta\alpha} \alpha_1 \beta_2 \\
 & + U_{1x\alpha\alpha} U_{2x\alpha\alpha} \mathbf{r}_1 \cdot \mathbf{r}_2 + 11U_{1x\beta\gamma} U_{2x\alpha\alpha} \beta_1 \gamma_2 + 5U_{1x\beta\beta} U_{2x\gamma\gamma} \alpha_1 \alpha_2 \\
 & - 3U_{2x\beta} U_{2x\alpha\alpha} \beta_2 - 2U_{2x\beta} \alpha_2 U_{1x\alpha\gamma\gamma} \beta_1 + 2U_{1xx\beta\alpha} U_{2\beta} \alpha_1 \\
 & - 3U_{2\beta\beta} U_{1\beta\beta x} x_1 - 2U_{2\beta\beta} U_{1xx\beta} \beta_1 + 54U_{xxx} U_{2xx} x_1 \\
 & - 18U_{1xx\beta} U_{2xx} \beta_1 - 4U_{2x\beta} U_{1xxx} \beta_1 - U_{2\beta\beta} U_{1xxx} x_1 \\
 & + 3U_1 U_{2xx\beta\beta} + U_{1\alpha\alpha} U_{2\beta\beta} - 12U_{2xx} U_{1xx\alpha} \alpha_1 - 2U_{1\beta\beta\alpha} U_{2xx} \alpha_2 \\
 & + 4U_{1x\beta\alpha} U_{1x\beta} \alpha_1 + \frac{1}{4} U_{1x\beta\gamma} U_{2x\gamma\beta} \alpha_1 \alpha_2) + \frac{21}{2} U_{1x\alpha}^2 U_2 \\
 & + \frac{5}{2} U_{1x\alpha} U_{2x\alpha} U_2 + \frac{11}{2} U_{1x\alpha} U_{2x\alpha} U_{12} + 5U_{1xx} U_{1\beta\beta} U_2 \\
 & + 4U_{1xx} U_{2\beta\beta} U_2 + 3U_2 U_{1xx}^2 + 6U_{1xx} U_{2xx} U_2 + 2U_{1\beta\beta} U_{2xx} U_{12} \\
 & - U_{2x} U_{1x\beta\beta} U_2 - 2U_2 U_{1x\beta\beta} U_{1x} + U_{12} U_{1x\beta\beta} U_{2x} - \frac{1}{2} U_{1\beta} U_{1xx} U_{2\beta} \\
 & - U_{1\beta} U_{2\alpha} U_{12\alpha\beta} + 2U_{2\beta} U_{1\alpha} U_{1\alpha\beta} + U_{1\beta} (U_{1\alpha} U_{2\alpha\beta} - U_{1x} U_{2x\beta} \\
 & + 2U_{2x} U_{2x\beta} + 2U_{2x\beta} U_{12x} + \frac{1}{2} U_{1\beta} U_{2xx} + 2U_{2x} U_{1x\beta} \\
 & - U_{1\alpha\beta} U_{2xx} \alpha_2 - U_{2xx} U_{12\alpha\beta} \alpha_2 - 2U_{1\alpha\beta x} U_{2x} \alpha_2 - 2U_{1x\alpha} U_{2x\beta} \alpha_2 \\
 & - 2U_{2x\alpha} U_{12\alpha\beta} x_2 - \frac{1}{2} U_{1x\alpha} x_1 U_{2\alpha\beta} + U_{2x\beta} \alpha_2 U_{12x\beta} + U_{1x\alpha} U_{2\alpha x\beta} \\
 & + U_{2x\alpha} U_{12x\alpha} \beta_{12} - \frac{9}{2} U_{2x\alpha} U_{1x\beta} \alpha_1 - \frac{5}{2} U_{1x\alpha} U_{2x\beta} \alpha_1)
 \end{aligned}$$

$$\begin{aligned}
& + U_{1x} [3U_{2\beta\beta} U_{1x\alpha} \alpha_1 - \frac{9}{2} U_{1\beta\alpha} U_{2x\alpha} \beta_1 + 4U_{2x\alpha} U_{2\alpha\beta} \beta_1 \\
& + \frac{5}{2} U_{1x\alpha} U_{12\alpha\beta} \beta_1 - 2U_{1\beta\beta\alpha} U_{2x\alpha} - 2U_{2\beta\beta} U_{2\alpha\alpha} \alpha_1 \\
& + 7U_{2xx} U_{1x\alpha} \alpha_1 + 7U_{2xx} U_{1x\alpha} \alpha_1 + 6U_{2xx} \alpha_1 U_{1x\alpha} \\
& - 2U_{1x\beta} \alpha_1 U_{2\alpha\beta} + \frac{1}{2} U_{2\alpha\beta\beta} U_{12x\alpha} + \frac{3}{2} U_{2\alpha\beta\gamma} U_{1x\beta} \alpha_1 \gamma_1 \\
& + \frac{3}{2} U_{1\alpha\beta\gamma} U_{12x\beta} \alpha_1 \gamma_{12} - U_{1\alpha\beta} U_{2x\beta} \alpha_1 + U_{1\alpha\beta} U_{12x\beta} \alpha_1 \\
& + \frac{1}{2} U_{2\alpha\beta} U_{2x\beta} \alpha_2 + \frac{3}{2} U_{2\alpha\beta} U_{1x\beta} \alpha_1 + U_{1\alpha\beta} U_{2x\beta} \alpha_1 + \frac{1}{2} U_{1\alpha\beta} U_{2x\beta} \alpha_2 \\
& - \frac{1}{2} U_{2\alpha\beta} U_{12x\beta} \alpha_{12} + \frac{1}{2} U_{1\alpha\beta} U_{2x\beta} \alpha_2 - \frac{1}{2} U_{2\alpha\alpha} U_{12x} + \frac{3}{2} U_{2x} U_{2\alpha\alpha} \\
& - 3U_{1\beta\beta} U_{2x\alpha} \alpha_1 + U_{2\alpha\beta} U_{12x\beta} \alpha_1 - U_{1\alpha\beta} U_{2\alpha\beta} \alpha_1 + \frac{1}{2} U_{1x} U_{12\alpha\alpha} \\
& - U_{1x} U_{2\alpha\alpha} + 2U_{2\beta\alpha} (U_{12x\gamma\gamma} \beta_2 \alpha_{12} - U_{1x\gamma\gamma} \alpha_1 \beta_1 + 3U_{12x\alpha\alpha} \beta_1 \alpha_{12} \\
& - 3U_{1x\alpha\alpha} \alpha_1 \beta_1) + U_{2\alpha\beta\beta} (U_{2\alpha} x_2 + \frac{1}{2} U_{12x} \alpha_1 + U_{1x} \alpha_1) \\
& + U_{1\alpha\beta\beta} U_{2x} \alpha_2 - U_{2x\beta} U_{1\alpha\beta} \alpha_2 + 2U_{2x\alpha\beta} U_{1\beta\alpha 1} + U_{2x\alpha} U_{2xx} \alpha_1 \\
& + \frac{1}{2} U_{1x\alpha} [U_{2\alpha\beta} (U_{2x} \beta_1 - U_{12x} \beta_1 + 4U_{2x} \beta_2) - \frac{1}{2} U_{2x\alpha} U_{12\alpha\beta} \beta_1 \alpha_2 \\
& + 2U_{1\alpha\beta} U_{2x} \beta_2 + \frac{5}{2} U_{1x\gamma} U_{2\alpha\beta} \gamma_1 \beta_1 + 4U_{2x\gamma} U_{2\beta\gamma} \beta_1 \alpha_2 - 2U_{2x} U_{12\alpha\beta} \beta_1] \\
& + U_1 [U_{2x\beta} (U_{1\beta} - \frac{3}{2} U_{2\beta} + U_{12\beta}) - \frac{3}{2} U_{1x\beta} U_{2\beta} - \frac{1}{2} U_{2x\beta\alpha} \\
& \times (U_{1x\beta} \alpha_1 - 3U_{12x\beta} \alpha_2) + 2U_{1x\beta\alpha} U_{2x\beta} \alpha_2 - U_{2x\alpha} U_{1x\beta\beta} \alpha_1 \\
& + U_{2x\alpha} U_{12x\beta\beta} \alpha_{12}] + (k_B T)^{-1} [\frac{1}{4} U_2^2 U_{1x\beta} (U_{1x\beta} + U_{2x\beta}) \\
& + \frac{3}{4} U_1 U_2 U_{1x\beta} [U_{1x\beta} + U_{2x\beta} - 3U_{12x\beta} - (3U_{1x\beta} U_{12}/U_1)] \\
& + \frac{1}{4} U_{1x} U_{1\alpha\gamma} (U_{1x} U_{2\beta\gamma} \alpha_1 \beta_1 + 2U_{2x} U_{2\beta\gamma} \alpha_1 \beta_2 + 5U_{2x} U_{1\beta\gamma} \alpha_1 \beta_2 \\
& - U_1 U_{2x\alpha} (U_{1x} U_{2\alpha\beta} \beta_1 + U_{2x} U_{1\alpha\beta} \beta_2 - U_{2x} U_{2\alpha\beta} \beta_2 + 2U_{1x} U_{12\alpha\beta} \beta_1 \\
& - 2U_{2x} U_{12x\alpha} \beta_2 - U_{2x\alpha} U_{12x} \beta_{12}) - U_1 U_{1x\alpha} (2U_{2x} U_{1\alpha\beta} \beta_2 \\
& + U_{2x} U_{2\alpha\beta} \beta_2 + U_{12x} U_{2\alpha\beta} \beta_{12}) - \frac{1}{4} U_{1x} U_{2x} U_{2\alpha\beta} U_{12\beta\gamma} \alpha_1 \beta_2 \}. \quad (17)
\end{aligned}$$

The above expression for  $E_{43}$  represents the contribution due to simultaneous correlations between the position of three arbitrary atoms in fluids at equilibrium. It involves up to the fourth derivative of the inter-atomic potential.

The exact expressions for  $E_{44}$  and  $E_{45}$  which involve four- and five-particle SCFs are given in Appendices 1 and 2, respectively for completeness. Because no information is available about four- and five-particle SCFs, expressions for  $E_{44}$  and  $E_{45}$  are simplified using a low-order decoupling approximation. This is explained in Appendices 1 and 2 and final approximate expressions are as follows:

$$\begin{aligned}
E_{44} = & \left(\frac{k_B T}{M}\right)^2 \frac{1}{4} \left[ G_5 G_1 \left( 20G_1 + \frac{1}{4} (k_B T)^{-1} G_9 - n \int d\mathbf{r}_1 g(r) (U_{1x\beta} \beta_1 - U_{1x\beta\beta} x_1 \right. \right. \\
& \left. \left. + \frac{1}{2} (k_B T)^{-1} U_{1x} U_{1x\beta} \beta_1) \right) - G_3 \left( 6G_1^2 + (k_B T)^{-1} (\frac{1}{3} G_9 - G_{10}) \right. \right. \\
& \left. \left. + n \int d\mathbf{r}_1 g(r_1) U_{1xxx} x_1 - n^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) [U_{1x\beta\beta} U_{2x} \right. \right. \\
& \left. \left. + U_{1x\beta} U_{2x\beta\alpha} \alpha_2 + 4(k_B T)^{-1} (U_{1x} U_{1x\beta} U_{2\alpha\beta} \alpha_1 - 3\beta_1 U_{1x} U_{12x\alpha} U_{2\alpha\beta} \right. \right.
\end{aligned}$$

$$\begin{aligned}
 & + 2U_{1x}U_{2x\alpha}U_{2\alpha\beta}\beta_1 + 2U_{1x}U_{2x\alpha}U_{1\alpha\beta}\beta_1] - G_1(k_B T)^{-1}G_{10} \\
 & + \frac{1}{2}(k_B T)^{-1}(G_3G_7 - G_9G_1) - G_5 \left( n^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) [U_{1x\alpha}U_{2x\alpha} \right. \\
 & - 2U_{1xx}U_{2xx} + U_{1x\beta}(2U_{2x\alpha\beta}\alpha_2 - U_{2x\alpha\alpha}\beta_2) \\
 & - (k_B T)^{-1}(U_{1x}\beta_1U_{2x\alpha}(U_{1x\alpha} + \frac{1}{2}U_{12x\alpha}) + \frac{1}{4}U_{1x\beta}^2U_2)] \\
 & - (k_B T)^{-1}G_7(G_5 - \frac{1}{2}G_3) \left. \right) + G_1 \left( (k_B T)^{-1}\frac{1}{4}G_1G_8 - 6(G_2 + G_4) \right. \\
 & + \frac{1}{2}(k_B T)^{-1}n^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2) [U_1U_2U_{1x\alpha} - U_1U_{12}U_{2xx} \\
 & - \frac{3}{4}U_{1x}(U_{12x}\beta_1U_{2\alpha\beta}\alpha_{12} + U_{2x}U_{1\alpha\beta}\alpha_{12}\beta_2)] \\
 & - n \int d\mathbf{r}_1 g(r_1)U_1U_{1x}x_1 + (k_B T)^{-1}\frac{1}{4}(\frac{1}{3}G_9G_4 + 2G_{10}G_2 \\
 & \left. + 2G_4n^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2)U_{1x}x_1U_{2xx}) \right] \tag{18}
 \end{aligned}$$

and

$$E_{45} = (k_B T/12M_3)G_1\{G_3[G_1(G_5 - 2G_3) + G_4] + G_3(G_1G_3 - 2G_2)\} \tag{19}$$

where

$$G_6 = n^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 g_3(\mathbf{r}_1, \mathbf{r}_2)U_{1x\beta}U_{2x\alpha\beta}\alpha_2 \tag{20}$$

$$G_7 = n \int d\mathbf{r}_1 g(r_1)U_{1x\beta}^2 \tag{21}$$

$$G_8 = n \int d\mathbf{r}_1 g(r_1)U_1^2 \tag{22}$$

$$G_9 = 3n \int d\mathbf{r}_1 g(r_1)U_1U_{1xx} \tag{23}$$

$$G_{10} = n \int d\mathbf{r}_1 g(r_1)U_{1x}\alpha_1U_{1x\alpha}. \tag{24}$$

The above expressions are of practical utility as these now involve static pair and triplet correlation functions.

The expressions for frequency sum rules obtained above are new results. Luckas and Lucas (1983)<sup>†</sup> have attempted to calculate these expressions but they were unsuccessful. It should be pointed out that our expression for the fourth sum rules involve a static five-particle correlation function which has never appeared in any frequency sum rules before. Expressions obtained in this section are purely microscopic and tractable. It is expected that these would be useful in the study of an ECD correlation function and transport properties of fluids. It should be noted that very little information is known about the ECD correlation function for the fluids.

<sup>†</sup> Their expressions for the second- and fourth-frequency sum rules are incomplete and incorrect. They have ignored the four-body contribution to the second-frequency sum rule, whereas for the fourth-frequency sum rule they have calculated only two-particle contributions. Even the two-particle contribution is incomplete.



**Table 1.** Values of the various contributions to the frequency sum rules of the ECD correlation function for various densities and temperatures.

$T^*$	$n^*$	$E_0/(\epsilon^3/m\sigma^3)$		$E_2/(\epsilon^4/m^2\sigma^5) (10^3)$			$E_4/(\epsilon^5/m^3\sigma^7) (10^7)$			
		$E_{02}$	$E_{03}$	$E_{22}$	$E_{23}$	$E_{24}$	$E_{42}$	$E_{43}$	$E_{44}$	$E_{45}$
0.73	0.844	32.8	18.3	26.6	-5.4	-1.3	4.275	1.88	1.06	0.905
1.23	0.419	33.1	18.8	33.9	-6.1	-5.7	9.06	0.47	0.043	0.032
1.26	0.500	43.3	22.8	45.1	-8.8	-1.0	12.32	0.89	0.74	0.066
1.28	0.600	63.0	24.2	63.2	-12.9	-2.2	17.56	2.99	1.34	0.149
1.16	0.844	139.2	-3.6	107.9	-6.3	-7.5	27.89	20.94	3.51	0.586
1.83	0.500	143.1	12.5	145.4	-17.5	-2.3	57.10	8.76	1.23	0.100
1.81	0.600	190.39	5.5	193.3	-22.9	-4.6	75.41	18.68	2.15	0.221
1.81	0.700	274.8	-14.6	269.8	-23.2	-8.5	106.08	42.46	3.54	0.412
1.90	0.801	473.9	-56.7	452.6	6.0	-12.9	189.14	103.03	7.27	0.418
2.57	0.200	206.6	2.9	133.2	-5.4	-0.2	73.17	2.68	0.118	0.003
2.51	0.300	235.5	4.4	199.7	-11.4	-0.7	107.30	7.95	0.388	0.015
2.47	0.400	282.9	3.0	277.6	-19.1	-1.7	147.10	18.32	0.900	0.052
2.48	0.500	374.6	-6.2	396.5	-27.7	-4.0	211.83	40.87	1.75	0.132
2.5	0.600	520.2	-28.5	568.3	-31.3	-7.8	307.9	88.81	3.03	0.272
2.5	0.803	1052.1	-109.8	1138.0	81.8	-10.0	630.0	408.21	15.44	-0.329
3.46	0.500	1025.9	-40.92	1192.6	-35.3	-5.9	890.89	195.22	1.877	0.145
3.41	0.600	1305.3	-77.6	1593.1	-18.1	-8.9	1181.05	362.62	3.51	0.212
3.50	0.700	1906.5	-132.4	2419.6	80.6	-4.4	185.81	798.34	11.06	-0.181
3.54	0.803	2738.8	-163.5	3548.9	405.9	33.4	2791.14	1089.6	54.77	-3.16
4.49	0.500	2163.1	-76.7	2731.9	-27.2	-4.9	2631.03	608.39	1.335	0.092
4.53	0.600	2883.9	-128.5	3924.7	47.5	-0.2	3840.1	1203.1	5.51	-0.083
4.45	0.700	3644.4	-171.0	5152.8	265.2	25.3	5003.86	2107.2	28.30	-1.197
4.45	0.803	4951.1	-151.9	7217.7	893.5	126.7	7091.5	4047.4	146.08	-6.896

### 3. Numerical results

In order to obtain the numerical estimate for the frequency sum rules from the expressions obtained in § 2, we first perform the angular integration. The angular integration of the two-particle contribution is straightforward and simple. The procedure for angular integration has been described by Bansal and Pathak (1977) and, in a simplified manner, it has been recently discussed by Tankeshwar *et al* (1987). The static pair contributions involve single integration, whereas the triplet contributions involve three-dimensional integration. The resulting expressions involve only static pair and triplet correlation functions and the inter-atomic potential. For the triplet correlation function, we use the superposition approximation given as

$$g_3(\mathbf{r}_1, \mathbf{r}_2) = g(r_1)g(r_2)g(|\mathbf{r}_1 - \mathbf{r}_2|). \quad (25)$$

We use the LJ potential as interaction potential. The static pair correlation function is calculated using the method of Sung and Chandler (1974) based on optimised cluster theory. This  $g(r)$  has been found to be in good agreement (Pathak *et al* 1985) with molecular dynamics data. Numerical integration is done using the Gauss quadrature method. The accuracy of our numerical work is better than 5%. The calculation has been done over a wide range of densities and a wide range of temperatures for the LJ system. In order to see the relative importance of two-, three-, four- and five-particle contributions, we have presented these separately in table 1 for various densities  $n^* =$

$n\sigma^3$  and  $T^* = k_B T/\varepsilon$ , where  $\sigma$  and  $\varepsilon$  are two parameters of the LJ potential having the dimensions of length and energy, respectively.

#### 4. Summary and conclusion

In this paper, we have obtained the complete expressions for the zeroth-, second- and fourth-frequency sum rules of the ECD correlation function. The expressions presented here are new and are expected to be useful in the study of the ECD correlation function. Although exact expressions involve SCFs up to five particles, we have succeeded in approximating them. Final expressions now involve only  $g(r)$  and  $U(r)$ . The expressions are lengthy but simple and can be used for practical applications. We have computed these expressions for a LJ system over a wide range of densities and a wide range of temperatures.

From the numerical results, it can be seen that three-particle contributions are appreciable for all the frequency sum rules. In contrast, the four- and five-particle contributions (reduced to two-particle contributions) to the second and fourth sum rules, respectively, are quite small. At the triple point, both of these are about 10% of the two-particle contributions. The four-particle contribution to the fourth-frequency sum rule is not negligible and at the triple point it is about 25% of the pair correlation contribution. Further the triplet contribution to  $E_0$  becomes negative as the density increases for a given temperature. Finally it becomes negative at a higher temperature for any density, whereas the three-body contribution to  $E_2$  becomes positive with increasing temperature and density. The ratio of triplet contribution to pair contribution to the zeroth- and second-frequency sum rules range from  $-10$  to  $65\%$  and from  $-20\%$  to  $25\%$  for the densities and temperatures investigated here. On the contrary, the three-body contribution to  $E_4$  is positive for all the densities and temperatures. It also increases with increasing density and decreases with increasing temperature. The triplet contribution to the fourth-frequency sum rule is about  $1-70\%$  of the two-particle contribution for the range of densities and the range of temperatures considered here. It is also noted that frequency sum rules of the ECD correlation function show appreciable density and temperature dependences.

It is of interest to know the dilute-gas limit of these frequency sum rules, especially if one wishes to calculate thermal conductivity as will be done in the following paper. In the  $n \rightarrow 0$  limit we find that

$$E_0 = \frac{35}{4}(k_B T/M)^3 M^2 + O(n) \quad (26)$$

$$E_2 = An + O(n^2) \quad (27)$$

$$E_4 = Bn + O(n^2) \quad (28)$$

where  $A$  and  $B$  are independent of density and depend on temperature. Explicit expressions for  $A$  and  $B$  can be obtained from equations (5) and (16) with the understanding that  $g(r)$  will have the low-density value. It may also be noted that the first term in equation (26) is the contribution from the purely kinetic part of the ECD correlation function.

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### Appendix 1. Four-particle contributions to $E_2$ and $E_4$

Since very little is known about the static quadruplet correlation function  $g_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$  and no tractable and successful closure for it is yet available, we therefore use a low-order decoupling approximation for four-particle contributions to the second- and fourth-frequency sum rules of the ECD correlation function as explained below.

The exact expression for  $E_{24}$ , the four-particle contribution to the second moment, is

$$E_{24} = \frac{k_B T}{4M^2} n^3 \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) [U_{1x} U_{2x} \alpha_1 \beta_1 U_{3\alpha\beta} + U_{1x} U_{23x} \alpha_1 \beta_{23} U_{2\alpha\beta} - 2U_1 U_{2x} \beta_2 U_{3x\beta} - 2U_1 U_{23x} \beta_{23} U_{1x\beta} + U_1 U_{2xx} (U_3 - U_{23})]. \quad (\text{A1.1})$$

Here we have used the same notation as in the text. The four-particle correlation function in equation (A1.1) is defined as

$$n^3 g_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_{k \neq l \neq m \neq n} \langle \delta(\mathbf{r}_1 - \mathbf{r}_k + \mathbf{r}_n) \delta(\mathbf{r}_2 - \mathbf{r}_l + \mathbf{r}_n) \delta(\mathbf{r}_3 - \mathbf{r}_m + \mathbf{r}_n) \rangle. \quad (\text{A1.2})$$

Here the four arbitrary atoms are labelled  $k, l, m$  and  $n$  with the  $n$ th atom at the origin. The pair potential obeys the following property:

$$\partial U(r_{kn}) / \partial r_{k\alpha} = \partial U(r_{nk}) / \partial r_{k\alpha} = -\partial U(r_{kn}) / \partial r_{n\alpha} = [\partial U(r_1) / \partial r_1] (\partial r_1 / \partial r_{k\alpha}) \quad (\text{A1.3})$$

A similar expression can be derived from these for higher derivatives of the potential. Using expressions (A1.2) and (A1.3), we can equivalently write the first term of equation (A1.1) as

$$T_1 = \sum_{k \neq l \neq m \neq n} \left\langle \frac{\partial U_{nk}}{\partial r_{nx}} \frac{\partial U_{nl}}{\partial r_{nx}} r_{nk\alpha} r_{nl\beta} \frac{\partial^2 U_{nm}}{\partial r_{n\alpha} \partial r_{n\beta}} \right\rangle. \quad (\text{A1.4})$$

We note that there is no direct coupling between the atoms labelled  $k, l$  and  $m$ ; therefore we approximate (A1.4) as

$$T_1 = \sum_{k, l, m, n} \left\langle \frac{\partial U_{nk}}{\partial r_{nx}} r_{nkx} \right\rangle \left\langle \frac{\partial U_{nl}}{\partial r_{nx}} r_{nlx} \right\rangle \left\langle \frac{\partial^2 U_{nm}}{\partial r_{nx}^2} \right\rangle. \quad (\text{A1.5})$$

It should be pointed out that, once the correlation between  $k, l$  and  $m$  is neglected, only  $\alpha = \beta$  contributes in (A1.5). Finally (A1.5) can be written as

$$T_1 = G_3^2 G_1 \quad (\text{A1.6})$$

where  $G_1$  and  $G_3$  are defined in the text.  $T_1$  is one of the terms in equation (8). Following the argument used to obtain equation (A1.4) we obtained equation (8).

The exact expression for the four-particle contribution to the fourth-frequency sum rule is

$$E_{44} = \left( \frac{k_B T}{M} \right)^2 \frac{n^3}{M} \iiint d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 g_4(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \{ U_{2x\alpha} (U_1 U_{3x\alpha} - 3U_{1\beta\beta} U_{23x} \alpha_{23} + U_{1x\alpha} U_{13} - 2U_{1\beta\alpha} U_{13x} \beta_{13}) + \frac{1}{2} U_{1x\alpha} (5U_{1x} U_{3\beta\alpha} \beta_2 - U_{2x} U_{3\alpha\beta} \beta_2 + U_{2x} U_{13\alpha\beta} \beta_2) - 6U_{1xx} (U_{2x} U_{3x\alpha} \alpha_2 + U_{2xx} U_{13}) + U_{2xx} (9U_1 U_{3xx} + 2U_1 U_{3\beta\beta}) \}$$

$$\begin{aligned}
 &+ U_{1\alpha x} U_{13x} \alpha_{13} - U_{1\beta} \alpha_2 U_{3\alpha\beta} + U_{2\alpha\beta} (4U_{1x} U_{3\alpha\alpha} \beta_1 \alpha_3 \\
 &+ 3U_{1x} U_{3x\gamma\gamma} \alpha_3 \beta_1 + U_{1x} U_{3x\beta} \alpha_3) - U_{1\alpha\beta} (3U_{2x} U_{13x\alpha\alpha} \beta_2 \alpha_{13} \\
 &+ 3U_{2x} U_{13x\gamma\gamma} \beta_2 \alpha_{13\alpha} - U_{2x} U_{13x\beta\gamma} \alpha_2 \gamma_{13} - U_{1x} U_{2x\beta} \alpha_{13}) \\
 &+ U_{1x} (U_{2\alpha\beta\gamma} U_{3x\beta} \gamma_2 \alpha_1 + U_{3\alpha\beta\beta} U_{2x} \alpha_2) + U_{2x} (U_{1\alpha\beta\beta} U_{13x} \alpha_2 \\
 &+ U_{1\alpha\beta\gamma} U_{13x\beta} \alpha_2 \gamma_{13} - 3U_{1\beta\beta} \alpha_2 U_{3\alpha x} - 2U_{1\alpha} U_{3\alpha x} + 2U_{1\beta} U_{3\alpha\beta} \alpha_2) \\
 &- U_1 (U_{2x\beta\beta} U_{3x} + U_{2x\beta} U_{3x\beta\alpha} \alpha_3 + 3U_{2x\alpha} U_{3x\beta\beta} \alpha_3 \\
 &+ \frac{1}{2} U_{2x\alpha\beta} U_{3x\beta} \alpha_3) - U_2 (2U_{1xx} U_{13xx} + U_{1x\beta\beta} U_{13x} \\
 &+ U_{1x\beta\alpha} U_{13x\beta} \alpha_{13} - 2U_{1x\beta} U_{13\alpha\beta x} \alpha_{13} + U_{1x\alpha} U_{13x\beta\beta} \alpha_{13} \\
 &+ \frac{1}{2} U_{1x\alpha\beta} U_{13x\beta} \alpha_{13}) - U_{1\beta} (U_{2x\alpha} U_{3x\alpha} \beta_3 + \frac{5}{2} U_{2x\beta} U_{3x\alpha} \alpha_2 \\
 &+ 2U_{2\alpha} U_{3\alpha\beta} + \frac{1}{2} U_{2\beta} U_{3xx}) - 2U_{2\beta} U_{1\alpha x\beta} U_{13x} \alpha_{13} \\
 &+ U_{1x\beta} (U_{3\alpha\gamma} U_{2x\beta} \alpha_2 \gamma_1 + \frac{1}{4} U_{2x\gamma} U_{3\beta\gamma} \alpha_2 \alpha_1) \\
 &+ (4k_B T)^{-1} [U_1 U_{2x\beta} (U_1 U_{3x\beta} + 3U_2 U_{3x\beta} - U_{3x\beta} U_{13} \\
 &- 2U_{1x} U_{3\alpha\beta} \alpha_1 - 2U_{2x} U_{3\alpha\beta} \alpha_2 - 2U_{3x} U_{1\alpha\beta} \beta_3 - 2U_{3x} U_{3\alpha\beta} \alpha_3 \\
 &- 2U_{3x} U_{2\alpha\beta} \alpha_3) + U_1 U_{3x\beta} (U_2 U_{3x\beta} - U_2 U_{1x\beta}) \\
 &- \frac{1}{4} U_{1x\beta}^2 (U_1 U_{23} + U_2 U_3) + U_{1x} U_{2x} (U_{1\alpha\gamma} U_{3\beta\gamma} \alpha_1 \beta_2 + 2U_{2\alpha\gamma} U_{3\beta\gamma} \alpha_1 \beta_2 \\
 &+ U_{1\alpha\gamma} U_{13\beta\gamma} \alpha_2 \beta_1 + U_{3\alpha\gamma} U_{13\beta\gamma} \alpha_2 \beta_1 + U_{1\alpha\gamma} U_{3\beta\gamma} \beta_2 \alpha_{12} \\
 &+ U_{13\alpha\gamma} U_{3\beta\gamma} \beta_2 \alpha_{12}) + \frac{1}{4} U_{1x} U_{2\alpha\gamma} (U_{1x} U_{3\beta\gamma} \alpha_1 \beta_1 - U_{13x} U_{3\beta\gamma} \alpha_1 \beta_{13}) \\
 &- U_{2x} U_{13x} (2U_{2\alpha\gamma} U_{1\beta\gamma} \alpha_2 \beta_{13} + 2U_{1\alpha\beta} U_{1\beta\gamma} \alpha_2 \beta_{13} + 2U_{3\alpha\beta} U_{1\beta\gamma} \alpha_2 \beta_{13} \\
 &- 2U_{3\alpha\beta} U_{13\beta\gamma} \alpha_2 \beta_{13}) - U_2 U_{1x\alpha} (4U_{1x} U_{13\alpha\beta} \beta_1 + U_{3x} U_{13\beta\alpha} \beta_3) \\
 &- 2U_{2x} U_{3x\alpha} U_{12} U_{13x\alpha} \beta_2] \}. \tag{A1.7}
 \end{aligned}$$

We write the second term of equation (A1.7) using (A1.2) and (A1.3) as

$$T_2 = -3 \sum_{k \neq l \neq m \neq n} \left\langle \frac{\partial^2 U_{nk}}{\partial r_{n\beta}^2} \frac{\partial U_{ml}}{\partial r_{mx}} r_{ml\alpha} \frac{\partial^2 U_{nl}}{\partial r_{nx} \partial r_{n\alpha}} \right\rangle. \tag{A1.8}$$

Since there is no direct coupling between the atoms  $k$  and  $m$  or  $l$ , therefore we can decouple expressions (A1.8) as

$$T_2 = -3 \left( \sum_{k \neq n} \left\langle \frac{\partial^2 U_{nk}}{\partial r_{n\beta}^2} \right\rangle \right) \sum_{m \neq l \neq n} \left\langle \frac{\partial U_{ml}}{\partial r_{mx}} r_{mlx} \frac{\partial^2 U_{nl}}{\partial r_{nx} \partial r_{n\alpha}} \right\rangle. \tag{A1.9}$$

Here it may be noted that coupling between  $m$  and  $l$  and between  $l$  and  $n$  is not weak as it is direct.

Finally, the above expression can be written as

$$T_2 = -9G_2 G_1. \tag{A1.10}$$

Again we use the same argument to obtain the remaining terms in equation (18).

## Appendix 2. Five-particle contribution to $E_4$

Our expression for  $E_4$  involves a five-particle SCF. The static pentuplet correlation function has never appeared in any frequency sum rules so far and nothing is known

about it. In the absence of any knowledge, we decouple its contribution in terms of the static pair and triplet correlation functions. The exact expression for  $E_{45}$  is

$$E_{45} = \frac{k_B T}{4M^3} n^4 \iiint \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 g_5(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) (U_1 U_2 U_{3x\beta} U_{4x\beta} \\ + U_1 U_{2x\beta} U_{24} U_{3x\beta} - 2U_2 U_{2x\alpha} U_{3x} U_{4x\beta} \beta_3 \\ + U_{2x} U_{1x} U_{3\alpha\beta} U_{4\alpha\beta} \alpha_1 \alpha_2 - 2U_{1x} U_{23x\alpha} U_{4\alpha\gamma} U_{2\beta\gamma} \alpha_1 \beta_{23}). \quad (\text{A2.1})$$

Here we define the static pentuplet correlation function as

$$n^4 g_5(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4) = \sum_{j \neq k \neq l \neq m \neq n} \langle \delta(\mathbf{r}_1 - \mathbf{r}_k + \mathbf{r}_n) \delta(\mathbf{r}_2 - \mathbf{r}_l + \mathbf{r}_n) \delta(\mathbf{r}_3 - \mathbf{r}_m + \mathbf{r}_n) \\ \times \delta(\mathbf{r}_4 - \mathbf{r}_j + \mathbf{r}_n) \rangle. \quad (\text{A2.2})$$

Here five arbitrary atoms are labelled  $j, k, l, m$  and  $n$  with the  $n$ th particle at the origin. Using (A2.2) and (A1.3), the first term of equation (A2.1) can equivalently be written as

$$T = \sum_{j \neq k \neq l \neq m \neq n} \left\langle U_{nk} U_{nl} \frac{\partial^2 U_{nm}}{\partial r_{nx} \partial r_{n\beta}} \frac{\partial^2 U_{nj}}{\partial r_{nx} \partial r_{n\beta}} \right\rangle. \quad (\text{A2.3})$$

Since the coupling between  $k, l, m$  and  $j$  atoms is not direct, we decouple (A2.3) as

$$T = \sum_{j, k, l, m, n} \langle U_{nk} \rangle \langle U_{nl} \rangle \left\langle \frac{\partial^2 U_{nm}}{\partial r_{nx}^2} \right\rangle \left\langle \frac{\partial^2 U_{nj}}{\partial r_{nx}^2} \right\rangle \quad (\text{A2.4})$$

It should be noted that, after neglecting the coupling, only  $\beta = x$  contributes. Finally the above expression can be written as

$$T = G_2^2 G_1^2.$$

Following the above method, we obtain the remaining terms in equation (19).

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