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The heat current density correlation function: sum rules and thermal conductivity

Shaminder Singh^{1,3}, K Tankeshwar^{1,4}, K N Pathak¹ and S Ranganathan²

¹ Department of Physics, Panjab University, Chandigarh-160 014, India

² Department of Physics, Royal Military College, Kingston, ON, K7K 7B4, Canada

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Abstract

Expressions for the second and fourth sum rules of the heat current density correlation function have been derived in an appropriate ensemble. The thermal conductivity of Lennard-Jones fluids has been calculated using these sum rules for the heat current density correlation function and the Gaussian form of the memory function. It is found that the results obtained for the thermal conductivity are in good agreement with the molecular dynamics simulation results over a wide range of densities and temperatures. Earlier results obtained using the energy current density correlation function are also discussed.

1. Introduction

A time correlation function (TCF) is a fundamental quantity for the study of transport properties of fluids, as all the macroscopic atomic transport coefficients can be related to the TCF of an appropriate dynamical variable through Green–Kubo expressions. Theoretically, a TCF is generally evaluated using Mori's equation of motion [1], which expresses the TCF in terms of a memory function (MF). The MF formalism reduces the problem of calculation of the TCF to that of the calculation of the corresponding MF. However, this procedure has the advantage that one can develop a phenomenological model for the calculation of the MF and still preserve the first few frequency sum rules which are exact properties of the TCF. Thus the knowledge of the frequency sum rules is of prime importance in the calculation of transport properties. In the past, the sum rules for the velocity autocorrelation function [2], transverse stress [3], longitudinal stress [4, 5] and energy current density (ECD) [6, 7] correlation functions have been derived. These sum rules have provided a reasonably good description of transport coefficients like the self-diffusion, shear viscosity, bulk viscosity and thermal conductivity of dense fluids. However, depending on the choice of ensemble there exist two different but equivalent Green–Kubo expressions for the thermal conductivity. The first expression

³ Present address: P. G. Department of Physics, Lyallpur Khalsa College, Jalandhar-144001, India.

⁴ Present address: Department of Computer Science and Applications, Panjab University, Chandigarh-160014, India.

involves a time integral over the energy current density correlation function whereas the second expression involves a time integral over the heat current density correlation (HCD) function. The second expression containing the HCD correlation function has relevance to constant temperature ensembles. Since sum rules are generally evaluated in the canonical ensemble, it is more appropriate to consider the heat current density correlation function instead of the ECD correlation function for theoretical studies which require the use of sum rules. Earlier we evaluated [6] expressions for the zeroth, second and fourth sum rules of the ECD correlation function in the canonical ensemble instead of the constant energy ensemble. MacDowell [8] has derived the zeroth sum rule of the HCD correlation function and shown that it is different from that of the ECD correlation function, when both are calculated in the canonical ensemble. He further pointed out that the remaining second and fourth order sum rules required in transport theory also need revision. In order to examine this point in the present work and to obtain sum rules for the HCD correlation function we have evaluated the second and fourth sum rules of the HCD correlation function in an appropriate ensemble. It is found after doing lengthy algebra that the second and fourth order sum rules of the HCD correlation function are exactly the same as those of the ECD correlation function when both are calculated in the canonical ensemble. In order to correct our earlier results, the thermal conductivity of Lennard-Jones (LJ) fluids over a wide range of temperature and density has been calculated using appropriate sum rules for the HCD correlation function. It is found that the present results are better than those obtained earlier using the sum rules in the canonical ensemble of the ECD correlation function instead of the constant energy ensemble.

The layout of the paper is as follows. In section 2, we present the theory involved. Section 3 contains results and discussion. Concluding remarks are given in section 4.

2. Theory

The Green–Kubo expression for the thermal conductivity in the constant temperature ensemble can be written [1] as

$$\lambda = \frac{1}{k_B T^2 V} \int_0^\infty H(t) dt, \quad (1)$$

where $H(t)$ is called the HCD correlation function and is defined as

$$H(t) = \langle J_x^q(t) J_x^q(0) \rangle. \quad (2)$$

On the other hand, in the constant energy ensemble one has an equivalent expression [1] given as

$$\lambda = \frac{1}{k_B T^2 V} \int_0^\infty E(t) dt, \quad (3)$$

where $E(t)$ is called the ECD correlation function and is defined as

$$E(t) = \langle J_x^e(t) J_x^e(0) \rangle. \quad (4)$$

The angular brackets in equations (2) and (4) represent corresponding ensemble averages. V , k_B and T are the volume of the system, Boltzmann's constant and the temperature, respectively. For a system interacting through central forces, the HCD variable $J_x^q(t)$ can be written as

$$J_x^q(t) = J_x^e(t) - \frac{(e + P)}{n} \sum_k v_{kx}(t), \quad (5)$$

where $J_x^e(t)$ is the energy current density given by the following expression:

$$J_x^e(t) = \sum_i \left[v_{ix}(t) \frac{p_i^2}{2m} + \frac{1}{2} \sum_j' u_{ij} v_{ix}(t) - \frac{1}{2} \sum_j' \frac{\partial u_{ij}}{\partial r_{ij}} \hat{r}_{ijx} \mathbf{r}_{ij} \cdot \mathbf{v}_i \right]. \quad (6)$$

Here

$$U = \frac{1}{2} \sum'_{i,j} u_{ij} = \frac{1}{2} \sum_{i,j} u(|\mathbf{r}_i - \mathbf{r}_j|), \quad (7)$$

is the potential energy and m represents the mass of each particle. The prime on the summation denotes that $i = j$ terms are excluded. r_{ix} and v_{ix} are the x components of position and velocity, respectively. p_i is the momentum of the i th particle. Further, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}$, and $\hat{r}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is a unit vector in the direction of \mathbf{r}_{ij} . The internal energy density, e , and pressure, P , in terms of the pair potential, can be written as

$$e = \frac{3}{2}nk_B T + 2\pi n^2 \int_0^\infty dr u(r)r^2 g(r), \quad (8)$$

and

$$P = nk_B T - \frac{2\pi n^2}{3} \int_0^\infty dr \frac{du(r)}{dr} r^3 g(r), \quad (9)$$

where $g(r)$ and n are the static pair correlation function and number density, respectively. Thus we see that $J_x^q(t)$ and $J_x^e(t)$ differ in the presence of the last term in equation (5) representing the enthalpy (average) current.

The short time expansions of $H(t)$ and $E(t)$ are given as

$$H(t) = H_0 - H_2 \frac{t^2}{2!} + H_4 \frac{t^4}{4!} + \dots, \quad (10)$$

and

$$E(t) = E_0 - E_2 \frac{t^2}{2!} + E_4 \frac{t^4}{4!} + \dots, \quad (11)$$

where H_{2n} and E_{2n} are the $2n$ th order sum rules and are also known as the frequency moments of the spectral function for the HCD and ECD correlation functions, respectively.

The ensemble average involved in equation (2) can be written as

$$\begin{aligned} \langle J_x^q(t) J_x^q(t) \rangle &= \langle J_x^e(t) J_x^e(t) \rangle + \left(\frac{e+P}{n} \right)^2 \left\langle \sum_k \sum_{k'} v_{kx}(t) v_{k'x}(t) \right\rangle \\ &\quad - 2 \left(\frac{e+P}{n} \right) \left\langle \sum_{k'} J_x^e(t) v_{k'x}(t) \right\rangle. \end{aligned} \quad (12)$$

The expression for H_0 can be obtained from the above equation and equation (2) by putting $t = 0$ and evaluating the equilibrium average in the canonical ensemble. The method used in the evaluation of the sum rules is the same as that used in [6], and gives

$$H_0 = \langle \dot{J}_x^e(0) \dot{J}_x^e(0) \rangle - \frac{k_B T}{m} (e+P)^2. \quad (13)$$

The above expression for H_0 is essentially the same as that obtained by MacDowell [8].

The expression for the second frequency sum rule of the HCD correlation function can be obtained by evaluating the ensemble averages

$$H_2 = \langle \dot{J}_x^q(0) \dot{J}_x^q(0) \rangle. \quad (14)$$

The ensemble averages involved in equation (14) can be written as

$$\begin{aligned} \langle \dot{J}_x^q(0) \dot{J}_x^q(0) \rangle &= \langle \dot{J}_x^e(0) \dot{J}_x^e(0) \rangle + \left(\frac{e+P}{n} \right)^2 \left\langle \sum_k \sum_{k'} \dot{v}_{kx} \dot{v}_{k'x} \right\rangle \\ &\quad - 2 \left(\frac{e+P}{n} \right) \left\langle \sum_{k'} \dot{J}_x^e(0) \dot{v}_{k'x} \right\rangle. \end{aligned} \quad (15)$$

Using equations (14) and (15) we get the expression for H_2 . The first term, $\langle \dot{J}_x^e(0)\dot{J}_x^e(0) \rangle$, in the above expression has already been calculated earlier [6]. We have calculated the last two terms of equation (15) by using Yvon's theorem and exploring the various combinations of the indices involved in the expression. We have observed that in this way some of the terms become zero and others corresponding to different combination of the indices cancel with each other. This is demonstrated for a few terms in the appendix. Therefore, H_2 becomes equal to $\langle \dot{J}_x^e(0)\dot{J}_x^e(0) \rangle$, which has already been evaluated in the canonical ensemble.

The expression for the fourth frequency sum rules of the HCD correlation function can be obtained as

$$H_4 = \langle \ddot{J}_x^q(0)\ddot{J}_x^q(0) \rangle. \quad (16)$$

The ensemble average involved in equation (16) can be written as

$$\begin{aligned} \langle \ddot{J}_x^q(0)\ddot{J}_x^q(0) \rangle &= \langle \ddot{J}_x^e(0)\ddot{J}_x^e(0) \rangle + \left(\frac{e+P}{n} \right)^2 \left\langle \sum_k \sum_{k'} \ddot{v}_{kx}\ddot{v}_{k'x} \right\rangle \\ &\quad - 2 \left(\frac{e+P}{n} \right) \left\langle \sum_{k'} \ddot{J}_x^e(0)\ddot{v}_{k'x} \right\rangle. \end{aligned} \quad (17)$$

In this case also, after following the same procedure as was used in the calculations of second sum rule and after lengthy algebra, it has been found that all such terms cancel with each other under the pair potential approximation except that of $\langle \ddot{J}_x^e(0)\ddot{J}_x^e(0) \rangle$. Thus, it is noted that the second and fourth sum rules are the same as those obtained for $E(t)$ in the canonical ensemble earlier by us [6]. However, the change involved in the zeroth sum rule will affect the values of the thermal conductivity obtained earlier. The theory adopted to calculate the thermal conductivity in our earlier work is therefore briefly explained below.

The time evolution of $H(t)$ can be expressed through the generalized Langevin equation as

$$\frac{dH(t)}{dt} + \int_0^t d\tau M_1(t-\tau)H(\tau) = 0, \quad (18)$$

where $M_1(t)$ is the first order MF. Defining the Fourier-Laplace transform of $H(t)$ as

$$\tilde{H}(\omega) = i \int_0^\infty \exp(i\omega t)H(t) dt, \quad (19)$$

equation (1) can be written as

$$\lambda = -(i/Vk_B T^2)\tilde{H}(0). \quad (20)$$

$\tilde{H}(0)$ can be obtained from equation (18) once we know the form of the MF. To compare the present results with our earlier results [7], we prefer to use the Gaussian form of the MF given as

$$M_1(t) = \delta_1 \exp(-\delta_2 t^2/2). \quad (21)$$

In the above equations δ_1 and δ_2 are related to the frequency sum rules of the HCD correlation function up to the fourth order and are given as

$$\delta_1 = H_2/H_0, \quad \delta_2 = H_4/H_2 - H_2/H_0. \quad (22)$$

The choices of the parameters of the MF are such that the sum rules up to fourth order are exactly satisfied. The expression for λ thus obtained can be written as

$$\lambda = \left(\frac{2}{\pi} \right)^{1/2} \left(\frac{n}{k_B T^2} \right) \left(\frac{H_0^2}{H_2} \right) \left(\frac{H_4}{H_2} - \frac{H_2}{H_0} \right)^{1/2}. \quad (23)$$

Table 1. Comparison of values of purely kinetic and two body contributions of the ECD correlation function and the HCD correlation function to the zeroth sum rule at various T^* ($=k_B T/\epsilon$) and n^* ($=n\sigma^3$) in units of $\epsilon^3/m\sigma^3$. E_0 (MD) and H_0 (MD) represent MD results [8] for the zeroth sum rule calculated using the ECD correlation function and HCD correlation function, respectively.

T^*	n^*	E_0 (MD)	E_0	H_0 (MD)	H_0
0.730	0.844	33.03	30.33	16.27	13.70
0.856	0.844	53.67	51.23	42.67	40.73
1.143	0.844	131.0	125.53	130.0	124.80
1.812	0.500	138.66	137.83	136.33	135.40
1.812	0.700	281.67	276.90	275.0	269.90
1.817	0.600	196.67	193.50	193.67	190.60
1.913	0.801	489.67	485.37	455.0	447.63
1.921	0.188	81.0	82.23	61.33	62.73
1.931	0.560	208.0	205.2	202.0	199.37
2.490	0.500	385.33	382.10	341.66	338.93
3.476	0.500	1079.33	1072.0	838.66	829.16
4.496	0.500	2318.33	2323.96	1623.0	1616.46

3. Results and discussion

In order to calculate the thermal conductivity from equation (23), we require numerical values of H_0 , H_2 and H_4 . We follow the Gauss quadrature method for computing the integrals involved in H_0 , e and P . For the pair distribution function we have used optimized cluster theory [9] for a fluid of particles interacting via a LJ potential. A comparison of the values obtained for H_0 (excluding triplet contribution) with those obtained using molecular dynamics (MD) simulation [8] is presented in table 1. For the sake of completeness, we have also presented corresponding results for E_0 . It can be seen from the table that there is good agreement between simulation results and our results for H_0 . It is also noted that there is a significant difference between E_0 and H_0 at thermodynamic states close to the triple point. Therefore, in order to make the required changes in the results on the thermal conductivity, we use values of H_0 obtained by including the triplet contribution also and evaluated using the superposition approximation. The values of H_0 (including the triplet contribution) are given in table 2. For H_2 and H_4 we use our earlier results for E_2 and E_4 given in [6], as the expressions are exactly the same. The results obtained for the thermal conductivity, λ^* ($=\lambda(\sigma^2/k_B)(m/\epsilon)^{1/2}$), where σ and ϵ are parameters of the LJ potential, are shown in table 2. It can be seen from the table that the results obtained by using the Gaussian form of the memory function corresponding to the HCD correlation function are in reasonably good agreement with the MD results of Heyes [10, 11]. Earlier results obtained using the ECD correlation function are also shown in brackets. It is noted that use of the appropriate expression obviously provides better results for the thermal conductivity over a wider range of densities and temperatures. This further implies that the zeroth sum rule of $E(t)$ should have been calculated using the appropriate ensemble. In fact it was already known [14] that expressions (equations (1) and (3)) are equivalent provided appropriate ensembles are used.

4. Conclusion

In the present work expressions for the zeroth, second and fourth sum rules of the heat current density correlation function have been derived in an appropriate ensemble. Using these expressions for the sum rules of the HCD correlation function, the thermal conductivity of LJ

Table 2. Values of H_0 in units of $\epsilon^3/m\sigma^3$, the thermal conductivity λ^* and λ_{MD}^* in reduced units for various densities and temperatures. The values in parentheses represent earlier results [7].

T^*	n^*	H_0	λ^*	λ_{MD}^*
0.73	0.844	40.35	6.191 (10.07)	5.800, 7.07 ^a , 6.78 ^b
1.23	0.419	48.91	1.492 (1.686)	1.670
1.26	0.500	62.08	1.600 (1.823)	1.784
1.28	0.600	81.64	2.558 (2.932)	2.690
1.16	0.844	127.14	6.007 (6.865)	6.370
1.83	0.500	152.28	1.479 (1.547)	1.670
1.81	0.600	192.46	2.298 (2.384)	2.400
1.81	0.700	254.47	3.428 (3.591)	3.880
1.90	0.801	382.72	4.338 (5.200)	5.240
2.48	0.500	329.09	1.475 (1.867)	1.869
2.50	0.600	438.84	2.221 (2.817)	2.720
2.50	0.803	763.98	4.173 (6.481)	5.360
3.46	0.600	1014.7	2.400 (3.569)	2.680
3.50	0.700	1360.4	3.175 (5.529)	4.090
3.54	0.803	1840.4	3.807 (7.749)	5.080
4.49	0.500	1531.5	1.739 (3.301)	1.860
4.53	0.600	2037.3	2.528 (4.733)	2.650
4.45	0.700	2518.2	3.437 (6.716)	4.290
4.45	0.803	3282.0	4.472 (9.897)	5.230

^a Experimental values of Hanley *et al* [12].

^b MD data of Vogelsang *et al* [13].

fluids has been calculated over a wide range of densities and temperatures. It is found that the Gaussian form of the MF provides a reasonably good agreement with MD simulation data. This also corrects our earlier results obtained using the ECD correlation function.

Appendix

The detailed expression for the second frequency sum rule of the HCD correlation function is obtained as

$$\begin{aligned}
 H_2 = & \langle J_x^e(0) J_x^e(0) \rangle + \left(\frac{e+P}{n} \right)^2 \left\langle \sum_k \sum_{k'} \dot{v}_{kx} \dot{v}_{k'x} \right\rangle \\
 & - \left(\frac{e+P}{n} \right) \left[\left\langle m \sum_i \sum_k \dot{v}_{ix} v_i^2 \dot{v}_{kx} \right\rangle + 2m \left\langle \sum_i \sum_k v_{ix} (\mathbf{v}_i \cdot \dot{\mathbf{v}}_i) \dot{v}_{kx} \right\rangle \right] \\
 & + \left\langle \sum_i \sum_l \sum_j \sum_k \frac{\partial u_{ij}}{\partial r_{l\beta}} v_{l\beta} v_{ix} \dot{v}_{kx} \right\rangle - \left\langle \sum_i \sum_j \sum_k \frac{\partial u_{ij}}{\partial r_{ix}} (\mathbf{v}_{ij} \cdot \mathbf{v}_i) \dot{v}_{kx} \right\rangle \\
 & + \left\langle \sum_i \sum_j \sum_k u_{ij} \dot{v}_{ix} \dot{v}_{kx} \right\rangle - \left\langle \sum_i \sum_j \sum_k \frac{\partial u_{ij}}{\partial r_{ix}} (\mathbf{r}_{ij} \cdot \dot{\mathbf{v}}_i) \dot{v}_{kx} \right\rangle \\
 & - \left\langle \sum_i \sum_l \sum_j \sum_k \frac{\partial^2 u_{ij}}{\partial r_{ix} \partial r_{l\beta}} (\mathbf{r}_{ij} \cdot \mathbf{v}_i) v_{l\beta} \dot{v}_{kx} \right\rangle. \tag{A.1}
 \end{aligned}$$

Here, we show the evaluation of the ensemble average involved in the second term of the above equation, which in terms of the potential can be written as

$$\left\langle \sum_k \sum_{k'} \dot{v}_{kx} \dot{v}_{k'x} \right\rangle = \frac{1}{m^2} \sum_k \sum_{k'} \left\langle \frac{\partial V(r)}{\partial r_{kx}} \frac{\partial V(r)}{\partial r_{k'x}} \right\rangle. \quad (\text{A.2})$$

Applying Yvon's theorem, we get

$$\left\langle \sum_k \sum_{k'} \dot{v}_{kx} \dot{v}_{k'x} \right\rangle = \frac{k_B T}{m^2} \sum_k \sum_{k'} \left\langle \frac{\partial^2 V(r)}{\partial r_{k'x} \partial r_{kx}} \right\rangle. \quad (\text{A.3})$$

Expressing $V(r)$ in terms of the pair potential and separating cases $k = k'$ and $k \neq k'$, the above equation can be written as

$$\left\langle \sum_k \sum_{k'} \dot{v}_{kx} \dot{v}_{k'x} \right\rangle = \frac{k_B T}{m^2} \sum_k \sum_{k'} \left\langle \frac{\partial^2 u_{kk'}}{\partial r_{kx}^2} \right\rangle_{k \neq k'} + \left\langle \frac{\partial^2 u_{kk'}}{\partial r_{kx} \partial r_{k'x}} \right\rangle_{k \neq k'}. \quad (\text{A.4})$$

These terms cancel with each other as the second term within the pair potential approximation is just the negative of the first term. Physically, this implies that the correlation of forces on and arising from the particle at the same time are equally balanced within the pair potential approximation. It may be noticed that the third, fourth, fifth, sixth and seventh terms in expression (A.1) involve correlation of the forces on two different particles at the same time. We have found that these terms also become zero. However, the eighth term in the expression (A.1) appears different to the other terms and is discussed here. Applying Yvon's theorem successively and expressing $V(r)$ in terms of the pair potential, the eighth term can be written as

$$\begin{aligned} \left\langle \sum_i \sum_j \sum_k \frac{\partial u_{ij}}{\partial r_{ix}} (\mathbf{r}_{ij} \cdot \dot{\mathbf{v}}_i) \dot{v}_{kx} \right\rangle &= \frac{1}{m^2} \sum_i \sum_j \sum_k \left[\left\langle \frac{\partial^3 u_{ij}}{\partial r_{ix} \partial r_{i\alpha} \partial r_{kx}} r_{ij\alpha} \right\rangle_{i \neq j} \right. \\ &\quad \left. + \left\langle \frac{\partial^2 u_{ij}}{\partial r_{ix} \partial r_{i\alpha}} \frac{\partial r_{ij\alpha}}{\partial r_{kx}} \right\rangle_{i \neq j} + \left\langle \frac{\partial^2 u_{ij}}{\partial r_{kx} \partial r_{ix}} \frac{\partial r_{ij\alpha}}{\partial r_{i\alpha}} \right\rangle_{i \neq j} + \left\langle \frac{\partial u_{il}}{\partial r_{ix}} r_{il\alpha} \frac{\partial^2 u_{ij}}{\partial r_{kx} \partial r_{i\alpha}} \right\rangle_{i \neq j, i \neq l} \right]. \end{aligned} \quad (\text{A.5})$$

Now within the pair potential approximation k could be equal either to i or to j . The two possibilities lead to two terms in each ensemble average appearing in the above equation and cancel with each other. In this way, it is noted that all terms appearing with $(e + P)/n$ as multiplier vanish in the evaluation of H_2 and H_4 .

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