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Energy current density correlation function: II. Thermal conductivity

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Abstract. Expressions for the energy current density correlation function and the thermal conductivity have been derived using a continued-fraction representation of correlation function. A secant hyperbolic, a Gaussian and an exponential form of the memory function have been used. The parameters appearing in the memory function are determined from the zeroth-, second- and fourth-frequency sum rules of the energy current density correlation function. For the time dependence of the energy current density correlation function and the thermal conductivity, the results obtained for the Lennard-Jones fluids, have been compared with recent computer simulation data. Overall good agreement has been obtained over a wide range of densities and a wide range of temperatures.

1. Introduction

One of the most successful statistical mechanical theories of dynamical and transport properties of fluids is due to Boltzmann. For dilute gases the linearised Boltzmann equation provides a very good description of dynamical and transport phenomena. The Boltzmann equation does not account for the strong inter-particle correlations in dense media. For such dense fluids, where imperfect gas behaviour cannot be ignored, a more general kinetic equation is required. For hard-sphere fluids, Enskog extended the theory including the excluded volume effects. From comparison with computer simulation results for hard-sphere fluids, the Enskog theory has been found to be valid up to quite high densities (twice the critical density of fluids). Systematic generalisations of the Boltzmann equation have been studied recently. However, it has been possible to solve such an equation only for hard-sphere fluids (Boon and Yip 1980, Yip 1979). For realistic fluids there is no tractable kinetic equation which can readily be solved to predict the transport properties.

The other theoretical approach for calculating the transport coefficients is through the Green–Kubo formalism. Here the transport coefficients are related to the time integrals of the time correlation functions (TCFs) of appropriate fluxes. The TCFs are calculated using the Mori–Zwanzig formalism which provides the continued-fraction representation for the TCF in terms of the memory function (MF). The MF can be obtained using either a microscopic approach or some phenomenological arguments. Using this approach, we have calculated the diffusion coefficients (Tankeshwar *et al* 1987) and the shear viscosity (Tankeshwar *et al* 1988) of Lennard-Jones (LJ) fluids in our earlier work. In this paper, we calculate the thermal conductivity of the LJ fluids. Recently, exhaustive molecular dynamics (MD) data on the thermal conductivity of the LJ system have been reported (Heyes 1984, Vogelsang *et al* 1987) over a wide range of densities and a wide range of temperatures. The availability of these data has also been one of the motivating factors for undertaking the present work. It should be noted that very little theoretical work on the thermal conductivity and the energy current density (ECD) correlation function of LJ fluids has been done so far.

In the preceding paper, we have derived the expressions for the zeroth-, second- and fourth-frequency sum rules of the ECD correlation function which involve only the static correlation function and the inter-atomic potential. In this paper, the numerical results for these sum rules and the phenomenological forms for the MF have been used to study the time evolution of ECD correlation function and the thermal conductivity of the LJ fluids over a wide range of densities and a wide range of temperatures. The results for the ECD correlation function have been compared with the very recent MD data of Vogelsang *et al* (1987) at the triple point. On the other hand, the results obtained for the thermal conductivity are compared with the MD data of Heyes (1984). The predicted results are found to be in reasonably good agreement with computer simulation data.

In § 2, we obtain expressions for the ECD correlation function. The expressions for the thermal conductivity are obtained in § 3. In § 4, we present the numerical results for ECD correlation function and the thermal conductivity. A comparison of our results with MD data and discussion of results are also given in § 4.

2. Time evolution of the energy current density correlation function

We define the ECD correlation function $E(t)$ as

$$E(t) = \langle J_x^e(t) J_x^e(0) \rangle \tag{1}$$

where $J_x^e(t)$ is the ECD variable defined in the preceding paper. The time evolution of $E(t)$ is of fundamental importance in the study of the relaxation of heat current fluctuations and in determining the thermal conductivity of fluids. It can be expressed via the generalised Langevin equation

$$\frac{\mathrm{d}E(t)}{\mathrm{d}t} + \int_0^t \mathrm{d}\tau\, M_1(t-\tau)E(\tau) = 0 \tag{2}$$

where $M_1(t)$ is the first-order MF. If we define $\tilde{E}(\omega)$ as the Fourier–Laplace transform of $E(t)$ according to

$$\tilde{E}(\omega) = \mathrm{i} \int_0^\infty \exp(\mathrm{i}\,\omega t)\, E(t)\, \mathrm{d}t \tag{3}$$

equation (1) can be written as

$$\tilde{E}(\omega) = -E(t=0)/[\omega + \tilde{M}_1(\omega)]. \tag{4}$$

In equation (4), $\tilde{M}_1(\omega)$ is the Fourier–Laplace transform of $M_1(t)$. The MF $M_1(t)$ and its higher-order MF also satisfy equations similar to (2), the Fourier–Laplace transform of which can be written

$$\tilde{M}_n(\omega) = -M_n(t=0)/[\omega + \tilde{M}_{n+1}(\omega)] \qquad n = 1, 2, \ldots . \tag{5}$$

Using equations (4) and (5), one can generate a continued-fraction representation of the ECD correlation function. In the above equations, $E(t=0) = \delta_0$ and $M_n(t=0) = \delta_n$, $n = 1, 2, \ldots$, are called the damping matrices and are related to the frequency sum rules (Copley and Lovesey 1975). Here the first three δn are known, which in fact makes the continued-fraction formalism useful.

The frequency spectrum $f(\omega)$ of the ECD correlation function is given by

$$f(\omega) = \tilde{E}''(\omega) = 2\int_0^\infty \cos(\omega t)\, E(t)\, \mathrm{d}t \tag{6}$$

where $\tilde{E}''(\omega)$ is the imaginary part of $\tilde{E}(\omega)$. The ECD correlation function $E(t)$ is obtained by taking the inverse transform which is given as

$$E(t) = \frac{1}{\pi}\int_0^\infty \cos(\omega t) f(\omega)\, \mathrm{d}\omega. \tag{7}$$

In order to evaluate $\tilde{E}(\omega)$ and hence $E(t)$, it is necessary to truncate the hierarchy of the continued-fraction representation (5). Since higher-order MFs are mathematically complicated objects owing to the time evolution of fluctuating forces, one normally restricts the discussion to a first- or second-stage MF. Therefore, we truncate the hierarchy of the continued-fraction representation at the first stage. This leads to the following expression for the frequency spectrum of the ECD correlation function:

$$f(\omega) = \delta_0 \tilde{M}_1''(\omega)/[(\omega + \tilde{M}_1'(\omega))^2 + \tilde{M}_1^{2\prime\prime}(\omega)] \tag{8}$$

where $\tilde{M}_1'(\omega)$ and $\tilde{M}_1''(\omega)$ are the real and imaginary parts of $\tilde{M}_1(\omega)$.

Although we have a precise mathematical expression for $M_1(t)$, its microscopic calculation is not simple. No attempt has been made so far to calculate the MF of the ECD correlation function from first principles. In this work, we confine ourselves to only phenomenological forms of the MF. We have found that a simple sech(at) MF has given very good results for self-diffusion coefficients (Tankeshwar *et al* 1987) and the shear viscosity (Tankeshwar *et al* 1988) over a wide range of densities and a wide range of temperatures. Therefore, we assume here also that

$$M_1(t) = \delta_1 \operatorname{sech}(\sqrt{\delta_2}\, t). \tag{9}$$

It should be pointed out that the MF given by equation (9) behaves as $\exp(-\delta_2 t^2/2)$ for short times and as $\exp(-\sqrt{\delta_2}\, t)$ for long times. The Fourier–Laplace transform of equation (9) is

$$\tilde{M}_1(\omega) = M_1'(\omega) + \mathrm{i}\, M_1''(\omega) \tag{10}$$

where

$$\tilde{M}_1'(\omega) = (\pi\delta_1/2\sqrt{\delta_2}) \tanh(\pi\omega/2\sqrt{\delta_2}) + (\mathrm{i}\,\delta_1/2\sqrt{\delta_2})\{\psi[(\sqrt{\delta_2} + \mathrm{i}\omega)/4\sqrt{\delta_2}] - \psi[(\sqrt{\delta_2} - \mathrm{i}\omega)/4\sqrt{\delta_2}]\} \tag{11}$$

and

$$\tilde{M}_1''(\omega) = (\pi\delta_1/2\sqrt{\delta_2}) \operatorname{sech}(\pi\omega/2\sqrt{\delta_2}) \tag{12}$$

where $\psi(x)$ is the Euler 'psi' function defined as $\psi(x) = \mathrm{d}[\ln\Gamma(x)]/\mathrm{d}x$ and $\Gamma(x)$ is the gamma function. In the above equation, δ_0, δ_1 and δ_2 are related to the frequency sum rules of the ECD correlation function up to the fourth order. These are explicitly given as

$$\begin{aligned} \delta_0 &= E_0 \\ \delta_1 &= E_2/E_0 \\ \delta_2 &= E_4/E_2 - E_2/E_0 \end{aligned} \tag{13}$$

where E_0, E_2 and E_4 are the zeroth-, second- and fourth-frequency sum rules of the ECD correlation function. The numerical results for these have already been obtained in the preceding paper.

In order to see the effect of different forms of $M_1(t)$, we assume a simple exponential form for the MF given as

$$M_1(t) = \delta_1 \exp(-\delta_2^{1/2}|t|). \tag{14}$$

It is easy to calculate the real and imaginary parts of its $\tilde{M}_1(\omega)$. Substituting these in equation (8) and the subsequent $f(\omega)$ in equation (7), one can obtain an analytical expression for the ECD correlation function. The steps of the calculation have been discussed by Denner and Wagner (1984). Therefore, we simply quote the final expression. The ECD correlation function is given by

$$E(t) = \exp(-\sqrt{\delta_2}t/2)[\cos(\omega_0\delta_2^{1/2}t) + (1/2\omega_0)\sin(\omega_0\delta_2^{1/2}t)] \qquad \text{for } \delta_2/\delta_1 < 4 \tag{15}$$

$$E(t) = \exp(-\sqrt{\delta_2}t/2)[\cosh(\gamma\delta_2^{1/2}t) + (1/2\gamma)\sinh(\gamma\delta_2^{1/2}t)] \qquad \text{for } \delta_2/\delta_1 > 4 \tag{16}$$

where

$$\omega_0 = (\delta_1/\delta_2 - \tfrac{1}{4})^{1/2} \qquad \gamma = (\tfrac{1}{4} - \delta_1/\delta_2)^{1/2}.$$

It is clear from equation (15) that $E(t)$ has an oscillating behaviour for $\delta_2/\delta_1 < 4$. On the contrary, $E(t)$ decreases monotonically with increasing time for $\delta_2/\delta_1 > 4$. We calculate in § 4 the time evolution of the ECD correlation function for the sech(at) MF as well as for the exponential MF.

3. Expressions for thermal conductivity

The Green–Kubo formula for the thermal conductivity is given by

$$\lambda = \frac{1}{Vk_B T^2} \int_0^\infty E(t)\,\mathrm{d}t. \tag{17}$$

Using equation (3) the above equation can alternatively be written as

$$\lambda = -(\mathrm{i}/Vk_B T^2)\tilde{E}(0). \tag{18}$$

Here, V is the volume of the system, and k_B and T are the Boltzmann constant and temperature. For the model sech(at) of the MF, $E(0)$ is easily obtained from equations (11), (12) and (4) and is given by

$$\tilde{E}(0) = \mathrm{i}(2/\pi)(\delta_0\delta_2^{1/2}/\delta_1). \tag{19}$$

Substituting the above equation into equation (18) and writing δ_n in terms of the frequency sum rules (equation (13)), we obtain the following expression for the thermal conductivity:

$$\lambda = (2/\pi)(E_0^2/E_2)(n/k_BT^2)(E_4/E_2 - E_2/E_0)^{1/2}. \qquad (20)$$

However, if we use $M_1(t) = \delta_1 \exp(-\delta_2 t^2/2)$ and follow the above procedure, the expression for λ is obtained to be

$$\lambda = (2/\pi)^{1/2}(n/k_BT^2)(E_0^2/E_2)(E_4/E_2 - E_2/E_0)^{1/2}. \qquad (21)$$

For the simple exponential MF $M_1(t)$ (equation (14)), the thermal conductivity is $\pi/2$ times that in equation (20).

Instead of assuming some phenomenological forms for $M_1(t)$, Joslin and Gray (1986) proposed an alternative procedure for truncating the continued fraction given by equations (4) and (5). In this method, one takes the geometric mean of two consecutive terms of the continued fraction. Following the same procedure (Tankeshwar *et al* 1987), we obtain the following expression for the thermal conductivity:

$$\lambda = (n/k_BT^2)(E_0^{3/2}/E_2)(E_4/E_2 - E_2/E_0)^{1/4}. \qquad (22)$$

It should be noted that the above three expressions (20), (21) and (22) involve the same number of frequency sum rules but the structure of equations (20) or (21) and (22) are quite different.

4. Results and discussion

We present here numerical results for the ECD correlation function and thermal conductivity of LJ fluids for several densities and temperatures. These are obtained using the results for the zeroth-, second- and fourth-frequency sum rules of the ECD correlation function obtained in the preceding paper.

The time evolution of the ECD correlation function is calculated from equation (7) using equations (8), (11) and (12). The results are presented as full curves in figure 1 for six arbitrarily chosen thermodynamic states. The results for the exponential MF are obtained from the analytic expressions (15) or (16) and are also plotted in the same figure as broken curves. Very recent computer simulation data (Vogelsang *et al* 1987) have been obtained for $E(t)$, but only at the triple point. These are shown by the full circles in figure 1. It can easily be seen from the figure that the decrease in the ECD correlation function with increasing time obtained in the computer simulation data lies in between the results obtained from the sech(at) MF and the simple exponential MF. On the whole, the MD data are closer to the theoretical results obtained using the sech(at) MF. It has also been found that $E(t)$ decreases with increasing time more rapidly when the sech(at) MF is used than when the exponential MF is used. No significant backscattering effects in $E(t)$ have been found even at the triple point. This may be one of the important results of the present investigation.

We now calculate the thermal conductivity using equations (20)–(22) and the numerical values of the sum rules. The results for $\lambda^* = \lambda(\sigma^2/k_B)(M/\varepsilon)^{1/2}$ are presented in figure 2 for four isotherms. Here σ and ε are the two parameters of the LJ potential, having dimensions of length and energy, respectively. In figure 2 the full, broken and chain curves are the results obtained from the sech(at) MF, the Gaussian MF and the model of Joslin and Gray (1986) respectively. The MD data of Heyes (1984) are represented by the full circles. It can be seen from the figure that the results for the sech(at) MF and from

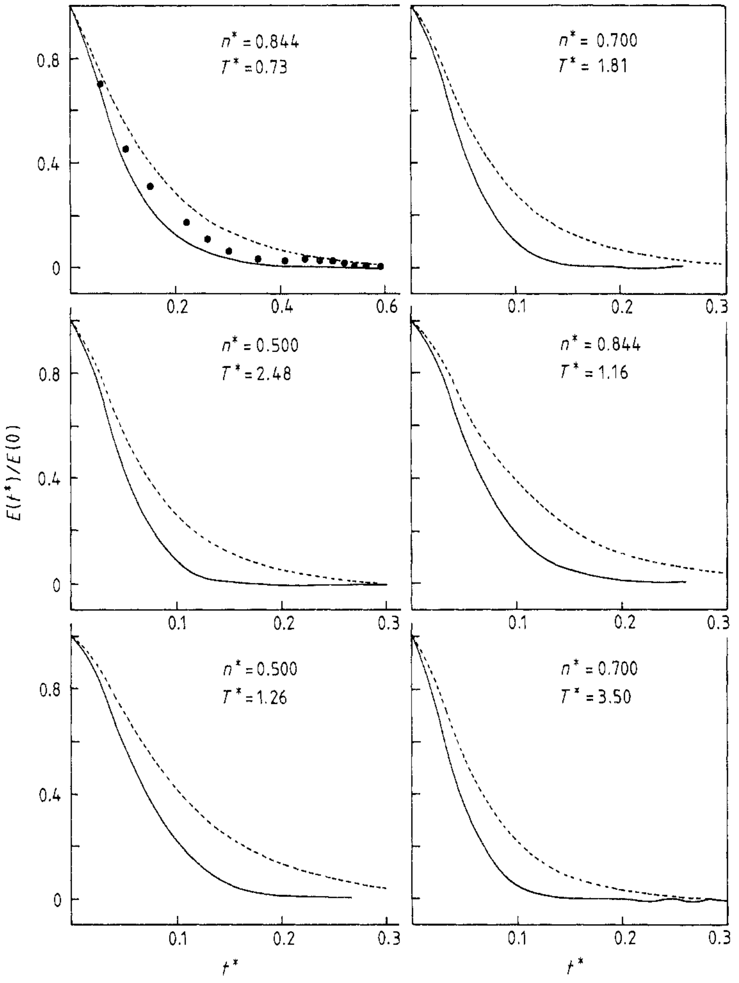

Figure 1. Variation in normalised ECD correlation function $E(t^*)/E(0)$ with time $t^* = t(\varepsilon/m\sigma^2)^{1/2}$ obtained for six thermodynamic states: ———, results obtained from equation (7) for a sech(at) MF; – – –, results from equation (15) or (16); ⊙, MD data.

the model of Joslin and Gray (1986) overlap for three of the isotherms ($T^* = (k_B T/\varepsilon) =$ 1.85, 2.5 and 3.5) for densities $n^* = n\sigma^3$ less than 0.8. The results obtained using the Gaussian MF for $T^* = 1.23$ and 1.85 are in overall good agreement with the MD results of Heyes. On the contrary, the results for λ^* obtained for the sech(at) MF are found to be good for $T^* = 2.5$ and 3.5. From this it can be concluded that the Gaussian and sech(at) model reproduce the MD data for the entire ranges of densities and temperatures investigated. A similar conclusion has also been drawn for the shear viscosity. From our earlier work (Tankeshwar *et al* 1987, 1988) as well as from the present work, it is found for LJ fluids that the thermal conductivity show a stronger temperature dependence than do the diffusion coefficients and shear viscosity.

In order to see the importance of three-, four- and five-particle contributions in estimating the thermal conductivity, we calculate λ from equations (20) and (21) including and not including the contributions to the frequency sum rules. These are denoted

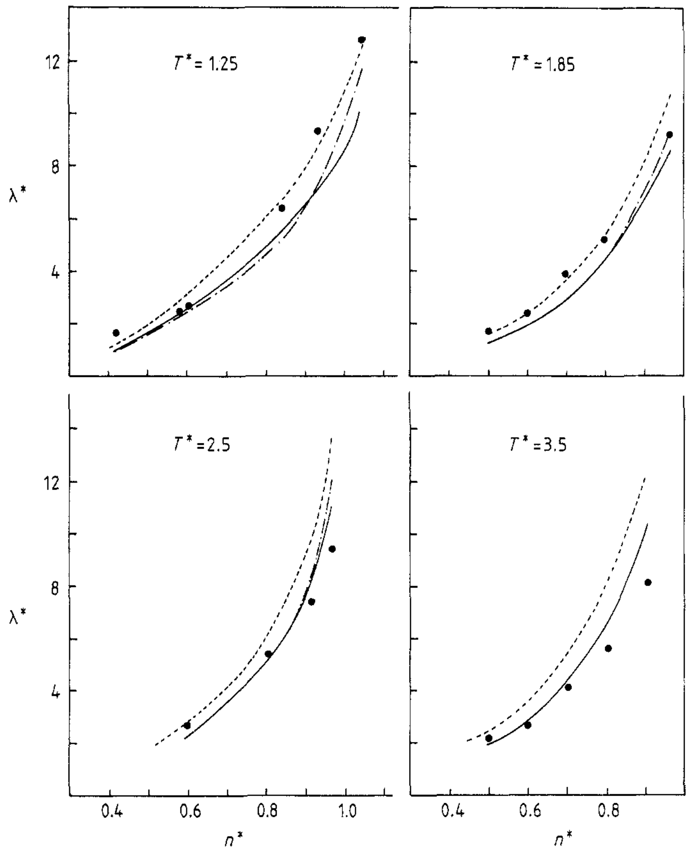

Figure 2. Variation in the thermal conductivity λ^* with density at various temperatures: ———, results obtained from equation (20); – – –, results obtained from equation (21); – · –, results obtained from equation (22); ●, MD data.

as λ_2^*, λ_3^*, λ_4^* and λ_5^*. The subscripts 2, 3, 4 and 5 on λ represent the contributions to frequency sum rules up to two, three, four and five particles, respectively. These results are presented in table 1. It can be seen from the table that the effect of the five-particles contribution on the thermal conductivity is almost always negligible. On the contrary, the three- and four-particle contributions are quite significant. For example, the triplet and the quadruplet contributions to the thermal conductivity are found to be up to 85% and 16%, respectively, for the densities and temperatures investigated here. Further the triplet and the quadruplet contributions are insignificant at high temperatures as one would normally expect for the thermal conductivity of dilute systems. From the above, therefore, we conclude that the triplet correlation contribution plays an important role in estimating the thermal conductivity at and in the vicinity of the triple point (i.e. dense fluids).

It is also noted from figure 1 that, for the density and the temperature corresponding to the triple point, the area under the MD curve for $E(t)$ is larger than the area under the theoretical $E(t)$ curve obtained using the sech(at) MF. However, the theoretical thermal conductivity is larger than the MD value by about 15%. The absolute value of the thermal conductivity depends on the proportionality constant which in this case is the zeroth-frequency sum rule apart from the dimensional multiplying factor. Since our E_0 is

Table 1. Values of the thermal conductivity λ_2^*, λ_3^*, λ_4^* and λ_5^* obtained from equation (21) by including up to pair, triplet, quadruplet and pentuplet contributions, respectively. The values in parentheses represent the thermal conductivity obtained using the sech(at) MF whereas λ_{MD}^* represent the MD values of Heyes.

T^*	n^*	λ_2^*	λ_3^*	λ_4^*	λ_5^*	λ_{MD}^*
0.73	0.8442	0.271 (0.217)	7.76 (6.19)	9.43 (7.52)	10.07 (8.03)	5.80, 7.07[a], 6.78[b]
1.23	0.419	0.291 (0.238)	1.123 (0.896)	1.195 (0.954)	1.197 (0.955)	1.66
1.19	0.584	0.601 (0.479)	2.715 (2.166)	2.939 (2.345)	2.953 (2.356)	2.43
1.16	0.844	3.804 (3.03)	5.76 (4.59)	6.82 (5.44)	6.85 (5.46)	6.37
1.83	0.500	0.90 (0.72)	1.48 (1.18)	1.54 (1.23)	1.55 (1.23)	1.67
1.81	0.700	2.59 (2.07)	3.33 (2.65)	3.58 (2.85)	3.59 (2.86)	3.88
1.9	0.801	4.98 (3.97)	5.07 (4.04)	5.39 (4.30)	5.40 (4.31)	5.24
2.5	0.6	2.39 (1.91)	2.73 (2.18)	2.81 (2.24)	2.81 (2.24)	2.72
2.5	0.803	6.63 (5.28)	6.31 (5.03)	6.46 (5.15)	6.46 (5.15)	5.36
2.53	0.909	11.65 (9.29)	10.32 (8.23)	10.35 (8.26)	10.33 (8.24)	7.30
3.46	0.500	2.33 (1.86)	2.52 (2.01)	2.55 (2.04)	2.55 (2.04)	2.20
3.41	0.600	3.46 (2.76)	3.63 (2.86)	3.67 (2.92)	3.67 (2.93)	2.68
3.5	0.7	5.48 (4.37)	5.51 (4.40)	5.54 (4.41)	5.53 (4.41)	4.09

[a] Experimental data of Hanley *et al* (1974).
[b] MD data of Vogelsang *et al* (1984).

obtained using the superposition approximation for the triplet correlation function, we can say that the superposition approximation overestimates the triplet contribution. It should also be pointed out that the thermal conductivity obtained using the exponential MF is 57% larger than the value obtained using the sech(at) MF, implying a larger discrepancy with MD data. We also note that the initial values of the velocity and the stress autocorrelation function are exactly known, in contrast with the initial value of the ECD correlation function; the latter is known only approximately owing to the appearance of the triplet correlation function in its expression.

The overall good result in this paper for the thermal conductivity, in fact, provides *a posteriori* justification for the use of the Gaussian or sech(at) forms of the MF. It is noted that any MF of the functional form

$$M_1(t) = \delta_1 F(\sqrt{\delta_2}\, t) \tag{23}$$

gives the following expression for the inverse thermal conductivity:

$$\lambda^{-1} = \frac{k_{\mathrm{B}} T^2}{n} \frac{\delta_1}{\sqrt{\delta_2 \delta_0}} \int_0^\infty F(x)\, \mathrm{d}x \tag{24}$$

where $F(x)$ is an even function of x and we call the integral appearing in equation (24) the normalisation integral. For our models, $F(x)$ is $\exp(-x^2/2)$ or $\mathrm{sech}(x)$. Hence equations (20) and (21) differ by a factor of only $(\pi/2)^{1/2}$. From figure 2, it can be seen that both the MFs reproduce the density and temperature dependences of the thermal conductivity quite well. This implies that the density and temperature dependences of the normalisation integral are quite weak. This good agreement shows that the $\mathrm{sech}(at)$ or Gaussian form of the MF provides average behaviour of the relaxation processes in the fluids.

It is of interest to know the dilute-gas limit of the thermal conductivity. To obtain this, we use the results obtained in the $n \rightarrow 0$ limit of the frequency sum rules, namely

$$E_0 = \tfrac{35}{4}(k_B T/M)^3 M^2 + O(n) \tag{25}$$

$$E_2 = An + O(n^2) \tag{26}$$

$$E_4 = Bn + O(n^2). \tag{27}$$

Substituting these values of E_0, E_2 and E_4 into equation (20), we obtain

$$\lambda = (2/\pi)(1/k_B T^2)[\tfrac{35}{4}(k_B T)^3/M]^2(B/A^3)^{1/2} \tag{28}$$

where B and A are independent of density but depend on temperature. Equation (28) provides a finite λ in the $n \rightarrow 0$ limit. On the contrary, if we use the zeroth- and second-frequency sum rules of $E(t)$ for estimating the thermal conductivity, i.e. assuming that $E(t) = \delta_0 \exp(-\delta_1 t^2/2)$, we obtain

$$\lambda = (\pi/2)^{1/2}(n/k_B T^2)(E_0^3/E_2)^{1/2}. \tag{29}$$

In the $n \rightarrow 0$ limit, equation (29) reduces to

$$\lambda = (\pi/2)^{1/2}(n^{1/2}/k_B T^2)[(35/A)(k_B T/M)]^{1/2}\, 35(k_B T)^4/8M \tag{30}$$

which tends to zero for $n \rightarrow 0$. Further the results obtained from equation (29) are up to 40% less than those obtained from equation (21). The above points and the good agreement of results obtained from equations (20) and (21) justify the choice of MF and the truncation of the continued fraction at the first stage for the ECD correlation function. Our results are also suggestive of the small effect of the higher-frequency sum rules on thermal conductivity.

In conclusion, we find that the $\mathrm{sech}(at)$ and Gaussian forms of the MF provide good agreement of the thermal conductivity with MD data over a wide range of densities and temperatures for LJ fluids. From our earlier work on diffusion coefficients (Tankeshwar *et al* 1987) and shear viscosity (Tankeshwar *et al* 1988) as well as from the present study of the thermal conductivity, we conclude that the Green–Kubo formula coupled with the continued-fraction representation of the correlation function, MF and frequency sum rules is a workable and successful approach for calculating the transport coefficient of fluids using only the inter-atomic potential as input.

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