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Thermotransport coefficients of a classical binary ionic mixture by non-equilibrium molecular dynamics

Carlo Pierleoni and Giovanni Ciccotti

Dipartimento di Fisica, Università 'La Sapienza', P. le Aldo Moro, 2-00185 Roma, Italy

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Abstract. We present a non-equilibrium molecular dynamics (NEMD) computation of both direct and cross thermotransport coefficients of a strong coupled binary mixture of positive charges in a negative neutralising background (binary ionic mixture) in the special case in which the charge and mass ratios of the mobile species are the same. We use a modified version of the MacGowan–Evans NEMD algorithm. We find that the direct coefficients qualitatively agree with the predictions of the one-fluid approximation. We show that the cross properties depend mainly on the relative interaction energy of the two different species in the mixture, while the range of interaction gives a small correction.

1. Introduction

Recently, the inter-diffusion in dense binary ionic mixtures has been extensively studied by both theoretical and molecular dynamics methods [1–3]. This phenomenon is of interest in some astrophysical problems to explain the composition of fluid planets [4] or the distribution of heavy elements in the atmosphere of white dwarfs [3, 5].

Little attention has been given to the computation of cross thermotransport coefficients of dense plasmas mainly because the cross properties, being rather weak effects, are difficult to reveal and reliable calculation of cross coefficients is a heavy computational task. Further, an estimation of the thermal diffusion ratio based on kinetic theory, performed in [3], has shown that in the intermediate-coupling regime the thermal diffusion effect can be negligible when compared with ordinary diffusion. Nevertheless, it is known that the kinetic theory fails when the density increases (or the temperature decreases), i.e. in the strong-coupling regime.

In this paper we present a computation of direct (inter-diffusion and thermal conductivity) and cross (thermal diffusion and diffusion thermo-effect) coefficients by non-equilibrium molecular dynamics (NEMD), for a binary ionic mixture (BIM) [1, 2] at a thermodynamic point in a very dense fluid phase of the mixture (strong-coupling regime), in the special case in which the charge and mass ratios between the two species are the same.

We obtain the direct and cross coefficients of the BIM with statistical error less than 5% and 10%, respectively. As expected, we find the behaviour to be dominated by the plasma oscillations which is typical in the homogeneous ($k = 0$) Coulomb systems with rigid background, for both the direct and the cross dynamical responses. Our results show that the direct transport properties can be predicted, in a very reasonable way, by the one-fluid approximation [6] based on a one-component plasma (OCP) with *effective*

valence $Z_{\text{eff}}^2 = (x_1 Z_1 + x_2 Z_2)^{1/3} (x_1 Z_1^{5/3} + x_2 Z_2^{5/3})$ [7, 8] where x_α is the number concentration of species α . As for the cross properties, we find that the relative weight of cross to direct dynamical response (equation (5.3)) is about 30%. This corresponds to a value of the phenomenological dimensionless cross coefficient k_T , appearing in the diffusion Fick's law (equation (3.7)), of -1.4 . This result shows the failure of kinetic theory predictions [3] for the strong-coupling regime in which we have to consider both direct and cross contributions to the diffusion. Finally, comparing this dynamical result with the corresponding one for the Lennard-Jones (L-J) equimolar binary mixture with the same mass ratio, recently studied by one of us [9], we find that the ratio between the relative weights of cross to direct response in the inter-diffusion currents of the BIM, and of the L-J mixture, is nearly the same as the ratio $\nu^{\text{BIM}}/\nu^{\text{L-J}}$ where $\nu^{\text{L-J}} = (\varepsilon_{12}/\varepsilon_{11})^2 = \varepsilon_{22}/\varepsilon_{11}$ (for Lorentz–Berthelot mixtures) and $\nu^{\text{BIM}} = (e_2/e_1)^2$ (note that the Coulomb interaction follows the Lorentz–Berthelot rule). This result shows that, in spite of the very different interaction laws and the plasma-oscillation-dominated behaviour of the Coulomb system, the cross properties depend mainly on the ratio between the interaction energies of the two different species in the mixture. This means that, in a qualitative sense, all the results on the cross properties of L-J mixtures [9–11] can be used to predict the BIM results.

We used a modified version of the MacGowan–Evans NEMD algorithm [10] to cope with the long-range Coulomb potential. This is a NEMD algorithm belonging to the class of so-called *synthetic* algorithms [12, 13] that allow us to excite a current into a system while preserving its translational invariance. This property is required from the periodic boundary conditions used in molecular dynamics. The main advantage of NEMD techniques with respect to the equilibrium molecular dynamics (EMD) method is the possibility of exploring the non-linear regime (see, e.g., [14]). Further, for short-range potential systems, the NEMD method is shown more efficient, in terms of computer time, than the equilibrium one. The last advantage is lost in Coulomb systems [15]. Finally, the subtraction NEMD technique that we use [16] needs also the equilibrium trajectory of the system. Therefore the equilibrium results are also obtained as a byproduct of the method. This is an important test in high-density systems where most of the theories fail.

To assure the linear behaviour of the system, we used impulsive perturbations in the framework of the subtraction technique [16]. The thermal conductivity of a OCP has been already computed in an analogous way [15].

2. The model

The BIM is a theoretical model for ion mixtures that consist of N_1 classical point ions of charge $Z_1 e$ and mass m_1 , and N_2 classical point ions of charge $Z_2 e$ and mass m_2 , immersed in a uniform neutralising background, e being the elementary charge. The independent thermodynamic variables of the system are the concentration of one species given by $x_1 = N_1/N$ with $N = N_1 + N_2$, and the coupling parameter $\Gamma = (e^2/ak_B T)$, where $a = (3/4\pi n)^{1/3}$ is the *ion-sphere radius*, $n = N/V$ is the total number density, V is the total volume, k_B is the Boltzmann constant and T is the temperature. Other useful quantities to define are: (i) $n_\alpha = N_\alpha/V$, $\rho_\alpha = m_\alpha n_\alpha$, the number and mass densities of species α ; (ii) $x_\alpha = n_\alpha/n$, $c_\alpha = \rho_\alpha/\rho$, the number and mass concentrations species α ; (iii) $\langle m \rangle = x_1 m_1 + x_2 m_2$, $\langle Z \rangle = x_1 Z_1 + x_2 Z_2$, the mean mass and mean valence of the ions; (iv) $\omega_p = (4\pi n \langle Z \rangle^2 e^2 / \langle m \rangle)^{1/2}$ the hydrodynamical plasma frequency, whose inverse we choose as time unit.

As pointed out elsewhere [1], in the special case in which the condition $Z_1/Z_2 = m_1/m_2$ is fulfilled, the electric current, defined in the centre-of-mass framework, and the corresponding electric conductivity of the BIM vanish and the phenomenological transport laws reduce to those of a mixture of simple liquids. We choose such a BIM, firstly, because it is the simplest ionic mixture† and, secondly, because we want to compare the present results with the corresponding L-J mixtures so that we can avoid phenomena, such as the electric current, lacking in mixtures of simple fluids. We choose $Z_1 = 1$, $Z_2 = 2$, $m_1 = 2$ au, $m_2 = 4$ au, $x_1 = 0.5$ and $\Gamma = 40$ that represent an equimolar mixture of deuterium and helium ($D^+ - He^{2+}$) in the fluid phase, not far from the fluid–solid transition [8]. The latter, in the framework of a one-fluid model, can be estimated to occur at $\Gamma \approx 75$. In [8, 18] it was shown that a BIM with no responding background is miscible under all the thermodynamic conditions.

3. Phenomenological laws and Green–Kubo relations

With reference to previous NEMD work on cross coefficients [9, 10] we adopted the following phenomenological laws to describe the transport of matter and heat in a binary mixture:

$$\mathbf{J}_D = -(L_{DQ}/T)\nabla(\ln T) - (L_{DD}/T)\nabla_T(\mu_1 - \mu_2) \quad (3.1)$$

$$\mathbf{J}_Q = -(L_{QQ}/T)\nabla(\ln T) - (L_{QD}/T)\nabla_T(\mu_1 - \mu_2) \quad (3.2)$$

where, as usual, the heat current \mathbf{J}_Q is defined so that, to avoid the temperature dependence in the diffusive gradient, the notation $\nabla_T \mu_\alpha$ means

$$\nabla_T \mu_\alpha = (\partial \mu_\alpha / \partial P)_T \nabla P + (\partial \mu_\alpha / \partial x_\alpha)_T \nabla x_\alpha \quad (3.3)$$

and $\mu_\alpha = \mu_\alpha(T, P, x_\alpha)$ is the specific (per unit of mass) chemical potential of species α . The quantity \mathbf{J}_D is the inter-diffusive current defined as

$$\mathbf{J}_D = x_2 \mathbf{J}_1 / m_1 - x_1 \mathbf{J}_2 / m_2 \quad (3.4)$$

where

$$\mathbf{J}_\alpha = \rho_\alpha (\mathbf{u}_\alpha - \mathbf{u}) \quad (\alpha \equiv 1, 2) \quad (3.5)$$

is the mass current of species α relative to the centre-of-mass frame, \mathbf{u}_α is the local velocity field of the component α and $\mathbf{u} = c_1 \mathbf{u}_1 + c_2 \mathbf{u}_2$ is the local velocity field of the total system.

In a binary mixture, $\sum_\alpha \mathbf{J}_\alpha = \mathbf{0}$ and equation (3.4) reduces to

$$\mathbf{J}_D = (\langle m \rangle / m_1 m_2) \mathbf{J}_1. \quad (3.6)$$

The quantities $L_{\alpha\beta}$ ($\alpha, \beta = Q, D$) appearing in equations (3.1) and (3.2) are the phenomenological transport coefficients that we have to compute.

The constitutive equation for the inter-diffusion current adopted in astrophysical problems is [3, 19]

$$\mathbf{u}_{12} = \mathbf{u}_1 - \mathbf{u}_2 = -(D_{12}/x_1 x_2) [\nabla x_1 + k_T \nabla(\ln T)] \quad (3.7)$$

in which appear two phenomenological coefficients D_{12} and k_T which are, respectively, the inter-diffusive coefficient and the thermal diffusion ratio.

† This special case presents a dynamical behaviour very similar to the OCP [17]. In particular, it has only a plasma frequency, that defined above.

The relations between these coefficients and those in equation (3.1) are

$$D_{12} = \mathcal{F}(k_B/x_1x_2)(L_{DD}/n) \tag{3.8}$$

$$k_T = (1/\mathcal{F})(x_1x_2/k_B T)(L_{DQ}/L_{DD}) \tag{3.9}$$

where \mathcal{F} is the thermodynamic factor given by

$$\mathcal{F} = (x_1 m_1 / k_B T)(\partial \mu_1 / \partial x_1)_T. \tag{3.10}$$

In an ideal mixture \mathcal{F} takes the value 1 [1]. Because the deviations from the ideality are small in the BIM model [8, 18], we assume this value.

To derive equations (3.8) and (3.9), we have used the Gibbs–Duhem relation

$$\sum_{\alpha} \rho_{\alpha} \nabla_T \mu_{\alpha} = 0. \tag{3.11}$$

The thermal conductivity λ is defined by the Fourier law. For a binary system, in the steady state defined with $\mathbf{J}_D = 0$, we have [10]

$$\lambda = (1/T_2)(L_{QQ} - L_{DQ}^2/L_{DD}). \tag{3.12}$$

The phenomenological transport coefficients are related to the microscopic dynamics of the system by the Green–Kubo relations that for the coefficients in equations (3.1) and (3.2) are [20]

$$\frac{L_{\alpha\beta}}{T} = \frac{1}{Vk_B T} \int_0^{\infty} dt C_{\alpha\beta}(t) \tag{3.13}$$

where

$$C_{\alpha\beta}(t) = \frac{1}{3} \langle \mathbf{J}_{\mathbf{k}=\mathbf{0}}^{\alpha}(t) \cdot \mathbf{J}_{\mathbf{k}=\mathbf{0}}^{\beta}(0) | f_0^{(N)} \rangle \quad (\alpha, \beta = Q, D) \tag{3.14}$$

$\mathbf{J}_{\mathbf{k}=\mathbf{0}}^{\alpha}$ is the space Fourier transform of the current α at $\mathbf{k} = \mathbf{0}$ and $f_0^{(N)}$ is the equilibrium phase space probability distribution. Between the cross coefficients the Onsager reciprocal relation $L_{QD} = L_{DQ}$ holds.

4. Microscopic currents and McGowan–Evans equations of motion

The microscopic expression of the energy current for a BIM can be easily written extending that for an OCP [15, 21] to the case of two different species. It is

$$\mathbf{J}_{\mathbf{k}=\mathbf{0}}^Q = \sum_{\alpha} \sum_i \left(\frac{\mathbf{p}_{i\alpha}}{m_{\alpha}} - \mathbf{v} \right) \cdot (E_{i\alpha} \mathbf{l} - \mathbf{S}_{i\alpha}) \tag{4.1}$$

where

$$E_{i\alpha} = \frac{m_{\alpha}}{2} \left(\frac{\mathbf{p}_{i\alpha}}{m_{\alpha}} - \mathbf{v} \right)^2 + \frac{4\pi e^2 Z_{\alpha}}{V} \sum_{\beta} \sum_{(j,\beta) \neq (i,\alpha)} j Z_{\beta} \sum_{q \neq 0} \frac{\exp[i\mathbf{q} \cdot (\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})]}{q^2} \tag{4.2}$$

is the energy of particle i of species α , and

$$\mathbf{S}_{i\alpha} = \frac{4\pi e^2}{V} Z_{\alpha} \sum_{\beta} \sum_{(j,\beta) \neq (i,\alpha)} Z_{\beta} \sum_{q \neq 0} \frac{\exp[i\mathbf{q} \cdot (\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})]}{q^2} \hat{\mathbf{q}} \cdot \hat{\mathbf{q}}. \tag{4.3}$$

In the above expressions, $\mathbf{r}_{i\alpha}$ and $\mathbf{p}_{i\alpha}$ are the coordinates and momenta, respectively, of

particle i of species α , \mathbf{l} is the unit tensor, \mathbf{q} is a vector in Fourier space and $\hat{\mathbf{q}}$ is a unit vector defined as $\hat{\mathbf{q}} = \mathbf{q}/q$. The quantity \mathbf{v} is the microscopic centre-of-mass velocity

$$\mathbf{v} = \sum_{\alpha} m_{\alpha} N_{\alpha} \mathbf{v}_{\alpha} / \sum_{\alpha} m_{\alpha} N_{\alpha} \tag{4.4}$$

with

$$\mathbf{v}_{\alpha} = \frac{1}{N_{\alpha}} \sum_i \frac{\mathbf{p}_{i\alpha}}{m_{\alpha}}. \tag{4.5}$$

According to [10], in the limit of an ideal mixture (e.g. an isotopic mixture) and for linear order in $(\mathbf{v}_{\alpha} - \mathbf{v})$, the microscopic expression for the heat current (3.2) is obtained from the energy current (4.1) removing all of the terms proportional to $(\mathbf{v}_{\alpha} - \mathbf{v})$. The resulting current \mathbf{J}_Q is

$$\mathbf{J}_{k=0}^Q = \sum_{\alpha} \sum_i \left(\frac{\mathbf{p}_{i\alpha}}{m_{\alpha}} - \mathbf{v}_{\alpha} \right) (\tilde{E}_{i\alpha} \mathbf{l} - \mathbf{S}_{i\alpha}) \tag{4.6}$$

where

$$\tilde{E}_{i\alpha} = \frac{m_{\alpha}}{2} \left(\frac{\mathbf{p}_{i\alpha}}{m_{\alpha}} - \mathbf{v}_{\alpha} \right)^2 + \frac{4\pi e^2 Z_{\alpha}}{V} \sum_{\beta} \sum_{i(j,\beta) \neq (i,\alpha)} Z_{\beta} \sum_{q \neq 0} \frac{\exp[i\mathbf{q} \cdot (\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})]}{q^2} \tag{4.7}$$

is the energy of particle i of species α measured in the comoving frame. Deviations from the ideality are small in a BIM and we do not discuss them. The problem is treated in [9].

The microscopic expression of the inter-diffusive current \mathbf{J}_D can be easily obtained by its definition (3.4) and (3.5) noting that $\mathbf{u}_{\alpha} = \langle \mathbf{v}_{\alpha} \rangle$ where the symbol $\langle \dots \rangle$ denotes a statistical mechanical average. We have

$$\mathbf{J}_{k=0}^D = x_2 \sum_i \frac{\mathbf{p}_{i1}}{m_1} - x_1 \sum_j \frac{\mathbf{p}_{j2}}{m_2}. \tag{4.8}$$

The equations of motion for a system forced by an external perturbation $\mathbf{F}_{\text{ext}}(t)$, not necessarily Hamiltonian, are

$$\dot{\mathbf{r}}_{i\alpha} = \mathbf{p}_{i\alpha} / m_{\alpha} + \mathbf{C}_{i\alpha} \cdot \mathbf{F}_{\text{ext}}(t) \tag{4.9}$$

$$\dot{\mathbf{p}}_{i\alpha} = \mathbf{F}_{i\alpha} + \mathbf{D}_{i\alpha} \mathbf{F}_{\text{ext}}(t) \tag{4.10}$$

where $\mathbf{F}_{i\alpha}$ is the total internal force acting on particle i of species α and $\mathbf{D}_{i\alpha} = \mathbf{D}_{i\alpha}(\{\mathbf{r}_j, \mathbf{p}_j\}_{j=1,N})$, $\mathbf{C}_{i\alpha} = \mathbf{C}_{i\alpha}(\{\mathbf{r}_j, \mathbf{p}_j\}_{j=1,N})$ are phase space functions that describe the coupling of the perturbation to the system. If the strength of the perturbation is not very high, we can use the non-Hamiltonian version of the linear response theory [13], to obtain the response of an arbitrary phase space $B \equiv B(\{\mathbf{r}_j, \mathbf{p}_j\}_{j=1,N})$ observable to the perturbation contained in equations (4.9) and (4.10) in terms of equilibrium ensemble averages:

$$\langle B \rangle_t = \langle B | f_0^{(N)} \rangle + \frac{1}{k_B T} \int_{t_{\text{on}}}^t dt' \langle B(t) \dot{H}_0(t') | f_0^{(N)} \rangle \tag{4.11}$$

where

$$\dot{H}_0 = \sum_{\alpha} \sum_i \left(\nabla_{\mathbf{r}_{i\alpha}} H_0 \cdot \dot{\mathbf{r}}_{i\alpha} + \nabla_{\mathbf{p}_{i\alpha}} H_0 \cdot \mathbf{p}_{i\alpha} \right) = \mathbf{J}_{\text{ext}} \cdot \mathbf{F}_{\text{ext}}(t) \tag{4.12}$$

$$\mathbf{J}_{\text{ext}} = \sum_{\alpha} \sum_i \left(\frac{\mathbf{p}_{i\alpha}}{m_{\alpha}} \mathbf{D}_{i\alpha} - \mathbf{F}_{i\alpha} \cdot \mathbf{C}_{i\alpha} \right). \tag{4.13}$$

\dot{H}_0 is the rate of energy dissipation due to the external force and t_{on} is the switching-on time of the perturbation. Equation (4.11) is valid if the phase space compressibility factor is zero, i.e. if

$$\Lambda = \sum_{\alpha} \sum_i^{\alpha} (\nabla_{r_{i\alpha}} \cdot \dot{r}_{i\alpha} + \nabla_{p_{i\alpha}} \cdot \dot{p}_{i\alpha}) = 0. \quad (4.14)$$

The symbol $\langle \dots \rangle_t$ in equation (4.11) denotes a statistical average on the non-equilibrium ensemble at time t .

Fixing $\mathbf{J}_{\text{ext}} = \mathbf{J}_{k=0}^{\alpha}$ ($\alpha = D, Q$), the linear response (4.11) of the current $\mathbf{J}_{k=0}^{\beta}$ is simply related to the corresponding Green–Kubo formula (3.13) and (3.14).

To excite both the diffusive and the heat current, we need to simulate two differently perturbed systems. Following the McGowan–Evans prescription, we assume $\mathbf{C}_{i\alpha} = 0$ for both systems and

$$\mathbf{D}_{i1}^D = x_2 \quad \mathbf{D}_{i2}^D = -x_1 \quad (4.15)$$

$$\mathbf{D}_{i\alpha}^Q = \left(\bar{E}_{i\alpha} - \frac{1}{N_{\alpha}} \sum_j^{\alpha} \bar{E}_{j\alpha} \right) \mathbf{l} - \left(\mathbf{s}_{i\alpha} - \frac{1}{N_{\alpha}} \sum_j^{\alpha} \mathbf{s}_{j\alpha} \right). \quad (4.16)$$

Substituting these expressions in (4.9), (4.10), (4.6), (4.8), (4.13) and (4.14) we obtain, respectively

$$\sum_{\alpha} \sum_i^{\alpha} \dot{p}_{i\alpha} = 0 \quad \text{conservation of total momentum}$$

$$\mathbf{J}_{k=0}^{\gamma} = \sum_{\alpha} \sum_i^{\alpha} \frac{p_{i\alpha}}{m_{\alpha}} \cdot \mathbf{D}_{i\alpha}^{\gamma}$$

$$\dot{H}_0^{\gamma} = \mathbf{J}_{k=0}^{\gamma} \cdot \mathbf{F}_{\text{ext}}^{\gamma}$$

$$\Lambda^{\gamma} = 0 \quad (\gamma = Q, D).$$

The external fields $\mathbf{F}_{\text{ext}}^{\alpha}(t)$ ($\alpha = D, Q$) used by us had an impulsive time behaviour and were along the z direction

$$\mathbf{F}_{\text{ext}}^{\alpha}(t) = (0, 0, P_{\alpha})\delta(t) \quad (\alpha = D, Q). \quad (4.17)$$

Then, the diffusive and thermal responses to both kinds of imposed perturbation are

$$\langle j_{k=0}^{\alpha} \rangle_{\beta,t} = (1/k_B T) \langle j_{k=0}^{\alpha}(t) j_{k=0}^{\beta}(0) | f_0^{(N)} \rangle P_{\beta} \quad (\alpha, \beta = Q, D) \quad (4.18)$$

where $j_{k=0}^{\alpha}$ is the z -component of the current α . Direct time integration of equations (4.18) gives the required transport coefficients:

$$\frac{L_{\alpha\beta}}{T} = \frac{1}{V} \int_0^{\infty} \frac{\langle j_{k=0}^{\alpha} \rangle_{\beta,t}}{P_{\beta}} dt \quad (\alpha, \beta = Q, D). \quad (4.19)$$

5. Implementation and results

We studied a system of $N = 250$ particles in a cubic box of edge L , with periodic boundary conditions. To deal with the long-range nature of the Coulomb potential, we used the Ewald technique. The convergence parameter and the long-range cut-off were chosen

Table 1. Results for the direct and cross responses: P_α , strength of perturbation; $(t_{\min}; t_{\max})$, time interval chosen to compute the plateau value of the integral; K_α are defined in equations (5.1) and (5.2). The reduced quantities are defined as follows: $K_Q(\text{cgs}) = K_Q^*(e^4 \omega_p^2 n)/k_B$; $K_D(\text{cgs}) = K_D^*(\omega_p^2/a k_B)$; $P_Q(\text{cgs}) = P_Q^*(m L^2 \omega_p/e^2)$; $P_D(\text{cgs}) = P_D^*(L \omega_p)$; $L_{DQ}(\text{cgs}) = L_{DQ}^*(e^4 \omega_p n)/k_B$; $L_{DD}(\text{cgs}) = L_{DD}^*(\omega_p/a k_B)$; $L_{DQ}(\text{cgs}) = L_{DQ}^*(e^2 \omega_p/a^2 k_B)$.

Coefficient	P_α	$(t_{\min}; t_{\max})$	$K_{\alpha\beta}^* \pm \Delta K_{\alpha\beta}^*$	$L_{\alpha\beta}^* \pm \Delta L_{\alpha\beta}^*$	Source
L_{QQ}	10^{-8}	(190; 300)	$(0.233 \pm 0.002) \times 10^{-3}$	$(0.43 \pm 0.02) \times 10^{-3}$	EMD results
		(210; 290)	$(0.228 \pm 0.001) \times 10^{-3}$	$(0.45 \pm 0.02) \times 10^{-3}$	NEMD results
L_{DD}	3×10^{-8}	(190; 300)	$(0.257 \pm 0.002) \times 10^{-3}$	$(0.500 \pm 0.015) \times 10^{-3}$	EMD results
		(190; 260)	0.250×10^{-3}	$(0.497 \pm 0.012) \times 10^{-3}$	NEMD results
L_{DQ}	10^{-8}	(190; 300)		$-(0.70 \pm 0.07) \times 10^{-4}$	EMD results
		(210; 280)		$-(0.65 \pm 0.05) \times 10^{-4}$	NEMD results
L_{QD}	3×10^{-8}	(190; 300)		$-(0.70 \pm 0.07) \times 10^{-4}$	EMD results
		(170; 250)		$-(0.67 \pm 0.05) \times 10^{-4}$	NEMD results

as in [15] to ensure continuous behaviour of the *mechanical* response (the response of the system as computed from a given initial condition) when the subtraction technique is used. The Verlet algorithm [22] was used to integrate the equations of motion, with the time step $h = 0.1 \omega_p^{-1}$.

For both thermal and diffusive perturbations, we performed 800 sectors (mechanical responses), each of 300 time steps, i.e. 240 000 time steps for the unperturbed system. In table 1 we collect our NEMD and EMD results for the coefficients $L_{\alpha\beta}$. The quantities K_α , which as usual represent the average initial value for the direct responses (superscript neq) or for the autocorrelation functions (superscript eq), are defined as

$$K_\alpha^{\text{neq}} = (T/V) \langle \langle j_{\mathbf{k}=0}^\alpha \rangle_{\alpha,0+} / P_\alpha \rangle \quad (5.1)$$

$$K_\alpha^{\text{eq}} = C_{\alpha\alpha}(0)/V k_B. \quad (5.2)$$

Agreement between NEMD and EMD results is excellent and the statistical uncertainties inherent to the two methods are comparable (direct coefficients, about 5%; cross coefficients, about 10%). As was expected in the linear regime, the cross coefficients L_{DQ} and L_{QD} verify the Onsager reciprocal relation. In table 2, we report the values of λ , D_{12} and k_T , obtained by (3.8), (3.9) and (3.12), and the available results for the OCP at $\Gamma = 100$.

The *statistical* responses (average on the 800 independent initial conditions of the mechanical responses) of the heat current to the thermal perturbation and its time integral are very similar to the OCP responses reported in [15]. The value for the thermal conductivity λ is very similar to what we expect for an OCP at a coupling slightly lower than $\Gamma = 100$ [15]. In the one-fluid model for the BIM the best choice for the *effective* valence [7, 8] leads to defining the one-fluid coupling parameter as $\Gamma_{\text{eff}} = \langle Z \rangle^{1/3} \langle Z^{5/3} \rangle \Gamma_{\text{BIM}}$. In the present case it is $\Gamma_{\text{eff}} = 95$, a very reasonable value.

A similar feature is found for the other direct coefficient D_{12} . Indeed, using the relation $D_{12} \simeq x_1 D_1 + x_2 D_2$ [1], we can compare the present value of inter-diffusion with the self-diffusion coefficient of the OCP computed in [23]. As for the thermal conductivity the value achieved in a BIM is as we expect for an OCP with Γ about 100.

Table 2. Results for the direct and cross transport coefficients. The reduced quantities are defined as follows: $D_{12}(\text{cgs}) = D_{12}^*(\omega_p a^2)$; k_T dimensionless; $\lambda(\text{cgs}) = \lambda^*(k_B \omega_p a^2 n)$; PCB, EMD result for a OCP at $\Gamma = 100.9$ from [15]; B, EMD result for self-diffusion coefficient of the OCP at $\Gamma = 100.0$ from [23].

λ	D_{12}	k_T	Source
0.62 ± 0.05	$(8.4 \pm 0.3) \times 10^{-3}$	-1.39 ± 0.14	EMD results
0.66 ± 0.04	$(8.3 \pm 0.2) \times 10^{-3}$	-1.30 ± 0.10	NEMD results
0.724 ± 0.033 (PCB)	6.02×10^{-3} (B)		

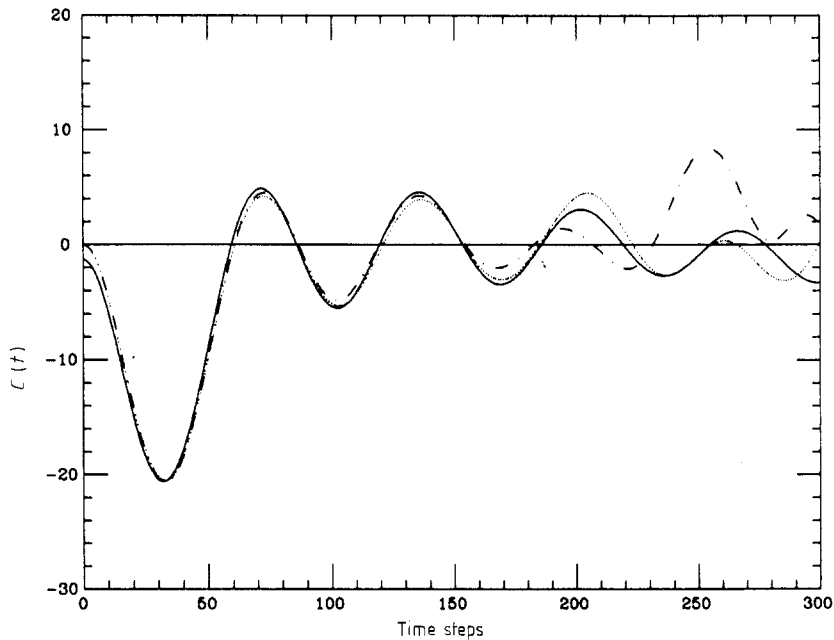


Figure 1. Equilibrium cross correlation function $C_{QD}(t)$ (—) and statistical cross responses $\langle j_{k=0}^D \rangle_{Q,i} / P_a$ (·····), $\langle j_{k=0}^Q \rangle_{D,i} / P_D$ (- - -). The ordinates are in arbitrary units.

These results show that, for the direct transport properties, our particular BIM behaves qualitatively like an OCP.

In figures 1 and 2 we present the cross responses and their time integrals, respectively, and we compare NEMD and EMD results. The quantity k_T computed by relation (3.9) assumes an unexpected high value (see table 2) for a cross coefficient of a system in a liquid-like state [10]. To get a better understanding of the underlying dynamical phenomenon, we have to evaluate the relative weight of cross to direct response. The latter can be represented by the dimensionless quantity

$$W = \left| \int_0^\infty \frac{C_{DQ}(t)}{[C_{DD}(0)C_{QQ}(0)]^{1/2}} dt \right| / \left| \int_0^\infty \frac{C_{DD}(t)}{C_{DD}(0)} dt \right|. \quad (5.3)$$

Using equations (3.13) and (3.14), W can be written as

$$W = (|L_{DQ}|/L_{DD})(K_D/K_Q)^{1/2}. \quad (5.4)$$

From the EMD results in table 1, we get $W^{\text{BIM}} = 0.30 = 30\%$. It is interesting to compare this quantity with the corresponding value for the L-J liquid mixture of [9]. This can be

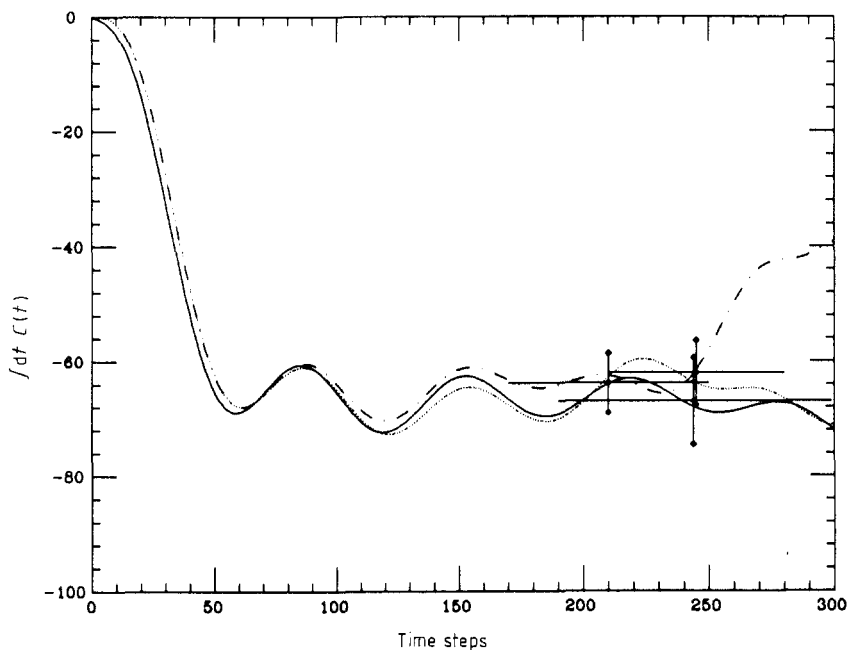


Figure 2. Integrals of the curves in figure 1. The horizontal lines with error bars mark the plateau values used for calculation of the transport coefficients.

done in spite of the different thermodynamic state point of the two systems under consideration as, roughly speaking, the cross coefficients are quite independent from the specific thermodynamic condition, provided that the system is in a liquid-like state. The L-J system of [9] is an equimolar Ar–Kr mixture for which the quantity W takes the value $W^{L-J} = 0.11 = 11\%$. Noting that the mass ratios for the two different mixtures are quite similar ($m^{Kr}/m^{Ar} \approx 2.1$), we tried to explain this difference in terms of the potential's parameters. We found $W^{BIM}/W^{L-J} = 2.73$ which should be compared with $\nu^{BIM}/\nu^{LJ} = 2.87$, where $\nu^{BIM} = (e_2/e_1)^2$, $\nu^{LJ} = (\epsilon_{12}/\epsilon_{11})^2 = \epsilon_{22}/\epsilon_{11}$. This result suggests that the quantity W depends mainly on the ratio between the interaction energy of the two different species in the mixture. The range and other details of the potential and the size of the particles should then give only small contributions to W .

6. Concluding remarks

We studied both the direct and the cross properties of thermal and diffusive transport in a BIM. We showed that the direct transport coefficients qualitatively agree with the predictions of the one-fluid approximation based on an OCP. Comparing our cross results with the L-J mixture results, we found that the relative weight of cross to direct dynamical response depends mainly on the mutual interaction between the two species in the mixture.

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