

**Addendum to “Heat and matter transport in binary liquid mixtures”**

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We recently presented nonequilibrium molecular dynamics simulations of coupled heat and matter transport in a binary liquid mixture. While these simulations were carried out exactly as indicated, the relations given between the microscopic and macroscopic formalism were strictly wrong. Here we correct these errors and indicate how they limit the possibilities for comparison of our simulation results with experiment.

**I. INTRODUCTION**

In a recent paper<sup>1</sup> (hereinafter referred to as I), we used synthetic homogeneous nonequilibrium molecular dynamics (NEMD) to study heat and matter transport in a binary Lennard-Jones (LJ) mixture approximately representing argon-krypton near its triple point. Unfortunately, the connection between macroscopic and microscopic heat currents implied in that paper was not correct. As a result, some of the coefficients obtained in I are not directly comparable with any experimental measurements. In this Addendum we indicate which of the results of I are experimentally measurable and suggest changes to the methods of I which will lead to simulation values of other experimentally measurable quantities.

**II. FORMALISM OF LINEAR IRREVERSIBLE THERMODYNAMICS**

The standard textbooks on linear irreversible thermodynamics<sup>2-4</sup> give various forms for the equations describing coupled heat and matter transport in a binary mixture. Perhaps the clearest and most unambiguous of these is

$$\mathbf{J}_1 = L_{11}^0 \mathbf{X}_1^0 + L_{1Q}^0 \mathbf{X}_Q, \tag{1}$$

$$\mathbf{J}_Q^0 = L_{Q1}^0 \mathbf{X}_1^0 + L_{QQ}^0 \mathbf{X}_Q, \tag{2}$$

where

$$\mathbf{X}_1^0 = -\nabla[(\mu_1 - \mu_2)/T], \tag{3}$$

$$\mathbf{X}_Q = -\nabla T/T^2. \tag{4}$$

$\mathbf{J}_Q^0$ , denoted in I by  $\mathbf{J}'_Q$ , is the total energy current density excluding convection and viscous dissipation and  $\mathbf{J}_v = \rho_v(\mathbf{u}_v - \mathbf{u})$  is the diffusion current density of species  $v$  with center-of-mass velocity  $\mathbf{u}_v$  and mass density  $\rho_v$ .  $\mathbf{u}$  is the barycentric velocity and  $\mu_v$  is the specific chemical potential of species  $v$ .

Among the many transformed versions of these equations we restrict attention to a class defined by

$$\mathbf{J}_Q^v = \mathbf{J}_Q^0 - (y_1 - y_2)\mathbf{J}_1, \tag{5}$$

$$\mathbf{X}_1^v = \mathbf{X}_1^0 + (y_1 - y_2)\mathbf{X}_Q. \tag{6}$$

$\mathbf{J}_1$  and  $\mathbf{X}_Q$  remain unaltered by these transformations.  $y_v$

is any property (per unit mass) associated with species  $v$ . The new form of the transport laws is

$$\mathbf{J}_1 = L_{11}^y \mathbf{X}_1^y + L_{1Q}^y \mathbf{X}_Q, \tag{7}$$

$$\mathbf{J}_Q^y = L_{Q1}^y \mathbf{X}_1^y + L_{QQ}^y \mathbf{X}_Q. \tag{8}$$

Assuming the Onsager reciprocal relation  $L_{Q1}^0 = L_{1Q}^0$ , it is easy to see that, for any  $y_v$ ,

$$L_{11}^y = L_{11}^0, \tag{9}$$

$$L_{1Q}^y = L_{1Q}^0 = L_{1Q}^0 - (y_1 - y_2)L_{11}^0, \tag{10}$$

$$L_{QQ}^y = L_{QQ}^0 - 2(y_1 - y_2)L_{1Q}^0 + (y_1 - y_2)^2 L_{11}^0, \tag{11}$$

and

$$\Delta \equiv L_{11}^0 L_{QQ}^0 - (L_{1Q}^0)^2 = L_{11}^y L_{QQ}^y - (L_{1Q}^y)^2. \tag{12}$$

One popular choice for  $y_v$  is  $h_v$ , the specific enthalpy. This transformation removes from  $\mathbf{J}_Q^0$  the enthalpy flux contribution associated with interdiffusion of one species through the other. The corresponding diffusive driving force is the chemical potential gradient excluding the part caused purely by the temperature gradient.

**III. THE MACROSCOPIC-MICROSCOPIC CONNECTION**

We consider a system of  $N$  particles,  $N_1$  of mass  $m_1$  and  $N_2$  of mass  $m_2$ , contained in a box of volume  $V$ . For brevity we adopt the notation that  $\sum$  represents a sum over all particles and  $\sum^v$  represents a sum only over particles of species  $v$ .  $\mathbf{r}_i$  denotes the position of particle  $i$  and  $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ . The interaction energy of the pair  $(i, j)$  is  $\phi_{ij}$  and the force on  $i$  due to  $j$  is  $\mathbf{F}_{ij}$ .

Irving and Kirkwood<sup>5</sup> have shown that the microscopic instantaneous expression

$$\mathbf{J}_Q^0 = \frac{1}{2} \sum_v \sum_i \left[ (\dot{\mathbf{r}}_i - \mathbf{u}) \left[ m_v (\dot{\mathbf{r}}_i - \mathbf{u})^2 + \sum_j \phi_{ij} \right] - (\dot{\mathbf{r}}_i - \mathbf{u}) \cdot \sum_j \mathbf{r}_{ij} \mathbf{F}_{ij} \right] \tag{13}$$

gives the macroscopic heat current  $\mathbf{J}_Q^0$  when ensemble averaged. In molecular dynamics (MD), the ensemble average is replaced by a time average. Bearman and Kirkwood<sup>6</sup> gave the expression

$$\mathbf{J}_Q^h = \mathbf{J}_Q^0 - \sum_v \mathbf{J}_v [h_v + \frac{1}{2}(J_v/\rho_v)^2], \quad (14)$$

where  $\mathbf{J}_Q^0$  is obtained from Eq. (9) and the mass currents are defined microscopically by

$$V\mathbf{J}_v = N_v m_v (\mathbf{u}_v - \mathbf{u}), \quad (15)$$

where

$$N_v \mathbf{u}_v = \sum_i^v \dot{\mathbf{r}}_i, \quad (16)$$

$$(N_1 m_1 + N_2 m_2) \mathbf{u} = \sum_v m_v \sum_i^v \dot{\mathbf{r}}_i. \quad (17)$$

However, no microscopic expressions are given for the  $h_v$  (specific enthalpies in the comoving species frame). In fact, we know of no such expression; obtaining one is made very difficult by the entropic contribution to

$$h_v = m_v^{-1} (\partial H / \partial N_v), \quad (18)$$

where  $H$  is the total enthalpy of the mixture. The last term in Eq. (14) is negligible in the linear transport regime.

A third heat current

$$V\mathbf{J}_Q^a = \frac{1}{2} \sum_v \sum_i^v \left[ (\dot{\mathbf{r}}_i - \mathbf{u}_v) \left[ m_v (\dot{\mathbf{r}}_i - \mathbf{u}_v)^2 + \sum_j \phi_{ij} \right] - (\dot{\mathbf{r}}_i - \mathbf{u}_v) \cdot \sum_j \mathbf{r}_{ij} \mathbf{F}_{ij} \right] \quad (19)$$

was introduced in I (denoted there simply by  $\mathbf{J}_Q$ ) for the following reasons: First, it proved possible to obtain a NEMD algorithm with adiabatic dissipation  $V\mathbf{J}_Q^a \cdot \mathbf{F}_{\text{ext}}$  satisfying momentum conservation and adiabatic incompressibility. Second, the lack of an instantaneous microscopic definition of  $h_v$  renders  $V\mathbf{J}_Q^h$  inconvenient for MD simulation. Third, it was believed that  $V\mathbf{J}_Q^a$  removed all the diffusive contribution to  $V\mathbf{J}_Q^0$ . This belief was based on the relation

$$\mathbf{J}_Q^a = \mathbf{J}_Q^0 - \sum_v \mathbf{J}_v \cdot [\underline{a}_v + \frac{1}{2}(J_v/\rho_v)^2 \mathbf{1}] \quad (20)$$

where

$$N_v m_v \underline{a}_v = \frac{1}{2} \sum_i^v \left[ m_v (\dot{\mathbf{r}}_i - \mathbf{u}_v)^2 + \sum_j \phi_{ij} \right] \mathbf{1} + \sum_i^v \left[ m_v (\dot{\mathbf{r}}_i - \mathbf{u}_v) (\dot{\mathbf{r}}_i - \mathbf{u}_v) - \frac{1}{2} \sum_j \mathbf{r}_{ij} \mathbf{F}_{ij} \right]. \quad (21)$$

[The tensorial character of  $\underline{a}_v$  is easily incorporated into the general equations (5)–(8) by regarding each of the  $L_{ab}$  as a tensor. The usual case is where each of these tensors is just a multiple of  $\mathbf{1}$ . At any rate, the tensorial character of  $\underline{a}_v$  is irrelevant in the linear transport regime.]

In effect,  $\mathbf{J}_Q^a$  was wrongly identified with  $\mathbf{J}_Q^h$ . It is now realized, however, that it was wrong to assume that diffusive contributions could be unambiguously removed from  $V\mathbf{J}_Q^0$ . The removal depended on splitting the energy

of each pair interaction equally between the two particles involved and there is no macroscopic justification for this. (Similarly, there is ambiguity in the definition of the macroscopic heat current.<sup>6</sup> Should enthalpy diffusion or internal energy diffusion be subtracted from  $\mathbf{J}_Q^0$ ?)

It is not at all clear how to relate the microscopic expression  $\mathbf{J}_Q^a$  to any macroscopically measurable current. Equally, it is not possible to write down a microscopic and instantaneous definition of any of the macroscopic heat currents (e.g.,  $\mathbf{J}_Q^h$ ) other than  $\mathbf{J}_Q^0$ . Thus we can only advocate, for comparison between simulation and experiment, that  $\mathbf{J}_Q^0$  should be monitored for mutual diffusion dynamics in order to obtain  $L_{Q1}^0$ . We still have no NEMD algorithm of Evans's<sup>7</sup> type which will give dissipation proportional to  $V\mathbf{J}_Q^0 \cdot \mathbf{F}_{\text{ext}}$  for mixtures and so there will be no way of confirming the Onsager reciprocal relation

$$L_{1Q}^0 = L_{Q1}^0, \quad (22)$$

since we cannot obtain  $L_{1Q}^0$ .

It is, however, possible to obtain a Gillan-type<sup>8</sup> NEMD thermal conduction algorithm (violating momentum conservation and adiabatic incompressibility of phase space<sup>9</sup> with the desired adiabatic dissipation [apart from  $O(1/N)$  differences]). The Gillan algorithm<sup>8</sup> does not appear to need any modification for mixtures. Unfortunately, it would require the evaluation of  $H/N$  which will be obtained in a separate equilibrium simulation. Since momentum is not conserved, care must be taken to include  $\mathbf{u}$ , which would be zero in an Evans-type algorithm, in Eq. (15). For future determinations of  $L_{1Q}^0$ , we advocate the use of the mutual diffusion algorithm of I but monitoring the appropriate heat current which, regrettably, was not done in I.

#### IV. IMPLICATIONS FOR RESULTS IN I

No transformation of the type represented by Eqs. (5)–(8) causes any change to  $L_{11}^0$ , as indicated by Eq. (9). Therefore, the results of I for isothermal mutual diffusion are totally unaffected by the considerations of this Addendum. More surprisingly, the *steady-state* thermal conductivity is given correctly by the coefficients  $L_{ab}$  and Eq. (21) in I. This is easily seen from our Eqs. (9) and (12). On the other hand, the thermal diffusion ratio given by Eq. (19) of I is quite clearly altered by the new corrected interpretation of  $\mathbf{J}_Q^0$ . In fact, we now have no way to get from the results of I any property which is strictly related to the experimental thermal diffusion ratio. However, we believe that the error in the results obtained by using the slightly wrong interpretation of I is likely to be small.

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<sup>1</sup>D. MacGowan and D. J. Evans, *Phys. Rev. A* **34**, 2133 (1986).

<sup>2</sup>S. R. deGroot and P. Mazur, *Nonequilibrium Thermodynamics* (Dover, New York, 1984).

<sup>3</sup>D. D. Fitts, *Nonequilibrium Thermodynamics* (McGraw-Hill, New York, 1962).

<sup>4</sup>*Transport Phenomena in Fluids*, edited by H. J. M. Hanley

(Dekker, New York, 1969), Chaps. 1–3.

<sup>5</sup>J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.* **18**, 817 (1950).

<sup>6</sup>R. J. Bearman and J. G. Kirkwood, *J. Chem. Phys.* **28**, 136 (1958).

<sup>7</sup>D. J. Evans, *Phys. Lett.* **91A**, 457 (1982).

<sup>8</sup>M. J. Gillan and M. Dixon, *J. Phys. C* **16**, 869 (1983).

<sup>9</sup>D. MacGowan and D. J. Evans, *Phys. Lett.* **117A**, 414 (1986).