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Cross thermotransport in liquid mixtures by nonequilibrium molecular dynamics

G. V. Paolini and G. Ciccotti
Dipartimento di Fisica, Università degli Studi di Roma "La Sapienza," piazzale Aldo Moro 2, I-00185 Roma, Italy

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We performed a nonequilibrium molecular-dynamics (MD) study of thermodiffusive cross coupling in an argon-krypton liquid mixture, near the krypton's triple point. We carried out nonequilibrium MD simulations, employing the MacGowan-Evans algorithm and subtraction technique with two sets of values for the external fields, to locate the onset of the nonlinear region. We also checked consistency with our equilibrium Green-Kubo calculations. Our results are in reasonably good agreement with previous MD computations and show that nonequilibrium and Green-Kubo methods have comparable efficiency, both yielding the same values for the cross phenomenological coefficients, as in the direct transport case.

I. INTRODUCTION

In a binary mixture thermal and diffusive transport properties are described by three independent phenomenological coefficients. Two of them govern direct transport—i.e., particle flow induced by a diffusive gradient and heat flow caused by a thermal gradient—as in simple fluids. The third one is connected to the cross coupling of diffusive and thermal phenomena.

In this work we are particularly concerned with this cross-coupling property, which is generally somewhat difficult to reveal, being a rather weak effect. In a recent paper[1] MacGowan and Evans presented a generalization of the Evans-Gillan thermal-conductivity algorithm[2–4] to the case of a binary liquid mixture. Such an extension exploits a new microscopic definition of the heat current $\tilde{J}_Q$, obtained by subtracting off the "trivial" diffusive part from the total energy flux. This current satisfies a good microscopic requirement, but it is not clear whether or not $\tilde{\mathbf{J}}_Q$ is equivalent to the macroscopic heat flux $\mathbf{J}_Q$ which is found in literature. The problem arises due to the presence of partial enthalpy h_α—which has no obvious microscopic counterpart—in the definition of $\mathbf{J}_Q$. In the present case of an equimolar Lennard-Jones (LJ) mixture, however, the possible numerical discrepancy is likely to be negligible.

The form of $\tilde{\mathbf{J}}_Q$ makes it possible to write down equations of motion perturbing $\tilde{\mathbf{J}}_Q$ which preserve total momentum and adiabatic phase-space incompressibility (AIΓ),[5] while this is not achievable using $\mathbf{J}_Q$.

Taking the MacGowan-Evans definition of the microscopic heat current, we have explored the possibility to detect cross correlations by subtraction technique[6] in nonequilibrium molecular dynamics (NEMD). In the present paper we report a NEMD study of thermal and diffusive transport properties of a Lennard-Jones equimolar liquid mixture of argon and krypton near the triple point of krypton. Our results are compared with known data. This comparison proves good for direct properties and satisfactory for cross properties. We checked consistency with our own equilibrium results as well, finding that equilibrium Green-Kubo (GK) technique is appropriate for cross properties, too.

The plan of the paper is as follows. In Sec. II we discuss the connection between macroscopic and microscopic definitions and the MacGowan-Evans extension of the thermal-conductivity algorithm to binary liquid mixtures. We present our model and our implementation of NEMD in Sec. III. Section IV reports our results for two sets of values for the perturbing fields as well as our equilibrium results.

II. FORMALISM

A. Phenomenological relations

The macroscopic relations describing the transport of matter and heat in a two-component mixture can be expressed in the following way:

$$\begin{aligned}\mathbf{J}_\alpha &= -\tilde{L}_{\alpha Q}\frac{\nabla T}{T^2} - \frac{1}{T}\sum_{\beta=1}^{2}\tilde{L}_{\alpha\beta}T\nabla\left[\frac{\mu_\beta}{T}\right],\\ \mathbf{J}'_Q &= -\tilde{L}_{QQ}\frac{\nabla T}{T^2} - \frac{1}{T}\sum_{\beta=1}^{2}\tilde{L}_{Q\beta}T\nabla\left[\frac{\mu_\beta}{T}\right],\end{aligned} \tag{2.1}$$

where $\mathbf{J}_\alpha$ is the flux of particles of species α relative to the center-of-mass frame, J'_Q is the total energy flow excluding convection and viscous dissipation, μ_β is the chemical potential of species β and the $\tilde{L}_{ij}$'s are connected to the phenomenological coefficients of energy and particle transport in a mixture.

Equations (2.1) correspond to the following expression for the entropy production,[7,8] excluding the transport of momentum:

$$s = -\mathbf{J}'_Q\cdot\frac{\nabla T}{T^2} - \frac{1}{T}\sum_{\beta=1}^{2}\mathbf{J}_\beta\cdot T\nabla\left[\frac{\mu_\beta}{T}\right]. \tag{2.2}$$

However, we can redefine the heat current in a more convenient way, in order to get rid of the temperature dependence in the diffusive gradient,

$$\mathbf{J}_Q = \mathbf{J}'_Q - \sum_\alpha h_\alpha \mathbf{J}_\alpha, \tag{2.3}$$

h_α being the specific partial enthalpy of component α.

Substituting Eq. (2.3) into (2.2) we get, exploiting the fact that $\sum_\alpha J_\alpha=0$,

$$s=-\mathbf{J}_Q\cdot\frac{\nabla T}{T^2}-\frac{1}{T}\mathbf{J}_1(\nabla_T\mu_1-\nabla_T\mu_2)\;, \tag{2.4}$$

where $\nabla_T\mu_\beta=T\nabla(\mu_\beta/T)+(h_\beta/T)\nabla T$ means the gradient of μ_β obtained by subtracting off the temperature dependence.

Thus by using (2.3) we are in principle able to separate the flux induced by the purely diffusive gradient $\nabla_T\mu_1-\nabla_T\mu_2$ from the flux driven by the thermal gradient ∇T, the thermodynamic forces in (2.4) being independent from each other.

We get the following phenomenological equations:

$$\begin{aligned}\mathbf{J}_1&=-L_{1Q}\frac{\nabla T}{T^2}-\frac{1}{T}L_{11}(\nabla_T\mu_1-\nabla_T\mu_2)\;,\\ \mathbf{J}_Q&=-L_{QQ}\frac{\nabla T}{T^2}-\frac{1}{T}L_{Q1}(\nabla_T\mu_1-\nabla_T\mu_2)\;.\end{aligned} \tag{2.5}$$

An explicit microscopic expression for (2.3), however, is still not available, since h_α is defined only in a thermodynamic way—that is, $(\partial H/\partial N_\alpha)_{P,T,N_\beta}$.

Interpreting the definition of $\mathbf{J}_Q$ as the operation of removing all of the contributions due to the interdiffusion of particles, MacGowan and Evans[1] carried out a microscopic derivation of a new heat current $\tilde{\mathbf{J}}_Q$ in which no h_α appears. This $\tilde{\mathbf{J}}_Q$ is invariant for any translation in the relative velocities of the two species. The $\mathbf{J}_\alpha$ terms which appear in such a definition are multiplied by a dynamical quantity whose average, in the thermodynamic limit, behaves like the thermodynamic quantity $\tilde{h}_\alpha$ (see Sec. II B), which is similar to—but does not coincide with—the partial enthalpy h_α.

Using such a definition it is possible to write down equations of motion which perturb $\tilde{\mathbf{J}}_Q$ and conserve both momentum and AIΓ,[5] while this is not possible using $\mathbf{J}_Q$. Gillan,[9] however, made a successful calculation of direct and cross effects for Hydrogen in Palladium—generalizing his nonequilibrium technique.[3] He employed non-AIΓ equations of motion and calculated h_α from its thermodynamic definition. This is rather a heavy task, since an accurate calculation of the partial enthalpy involves a number of runs at different concentrations and temperatures to compute numerically the various thermodynamic derivatives appearing in the definition of h_α.

Taking Evan's definition for the microscopic heat current we explored the possibility of obtaining by a dynamical NEMD simulation the cross correlations and cross coefficients in an argon-krypton mixture near the triple point of krypton. Of course, the same simulations can be used to obtain the direct-transport coefficients. Details on the dynamical variables and on the equations of motion employed are given in Secs. II B and II C.

B. Microscopic currents

We consider a system of N particles, N_1 of mass m_1 and N_2 of mass m_2, with coordinates $\mathbf{q}_{i\alpha}$ and momenta $\mathbf{p}_{i\alpha}$, where $\alpha=1,2$ runs over different substances, $i=1,2,\ldots,N_\alpha$ over all particles belonging to species α. Let $q_{i\alpha,j\beta}$ be the relative position of particles i_α and j_β, $E_{i\alpha}$ the total energy of particle i_α, and $\mathbf{F}_{i\alpha,j\beta}$ the force on j_β due to i_α, defined as follows:

$$\mathbf{q}_{i\alpha,j\beta}=\mathbf{q}_{i\alpha}-\mathbf{q}_{j\beta},\quad q_{i\alpha j\beta}=|\mathbf{q}_{i\alpha,j\beta}|\;, \tag{2.6a}$$

$$E_{i\alpha}=\frac{p_{i\alpha}^2}{2m_\alpha}+\tfrac{1}{2}\sum_\beta\sum_i{}^{\beta}\phi_{i\alpha,j\beta}\;, \tag{2.6b}$$

$$F_{i\alpha,j\beta}=-\frac{\partial\phi(q_{i\alpha j\beta})}{\partial\mathbf{q}_{i\alpha}}=-\frac{\partial\phi(q_{i\alpha,j\beta})}{\partial q_{i\alpha,j\beta}}\frac{\mathbf{q}_{i\alpha,j\beta}}{q_{i\alpha,j\beta}} \tag{2.6c}$$

where $\phi(q_{i\alpha,j\beta})=\phi_{i\alpha,j\beta}$ is the pair potential and the summation $\sum_i^\alpha$ is taken over the particles i belonging to species α.

The microscopic diffusive current of species α measured in the comoving frame is

$$\mathbf{J}_\alpha=\frac{1}{V}\sum_i{}^{\alpha}m_\alpha\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}\right]=\frac{N_\alpha m_\alpha}{V}(\mathbf{u}_\alpha-\mathbf{u})\;, \tag{2.7}$$

where $\mathbf{u}_\alpha$ is the mean velocity of species α,

$$\mathbf{u}_\alpha=\frac{1}{N_\alpha}\sum_i{}^{\alpha}\frac{\mathbf{p}_{i\alpha}}{m_\alpha}\;, \tag{2.8}$$

and

$$\mathbf{u}=\frac{\sum_\alpha N_\alpha m_\alpha\mathbf{u}_\alpha}{\sum_\alpha N_\alpha m_\alpha} \tag{2.9}$$

is the instantaneous baricentric velocity. Note incidentally that the usual Irving-Kirkwood[10] expressions for both the energy and diffusive currents contain the average value of $\mathbf{u}$.

From expression (2.7) we see that

$$\sum_\alpha\mathbf{J}_\alpha=\mathbf{0}\;. \tag{2.10}$$

Let us define the "interdiffusive current" $\mathbf{J}_D$ which we will use in our equations of motion,

$$\begin{aligned}\mathbf{J}_D&=\frac{1}{V}\left[x_2\sum_i{}^{1}\frac{\mathbf{p}_{i1}}{m_1}-x_1\sum_j{}^{2}\frac{\mathbf{p}_{j2}}{m_2}\right]\\ &=\left[\frac{x_2}{m_1}+\frac{x_1}{m_2}\right]\mathbf{J}_1\;,\end{aligned} \tag{2.11}$$

where in the last passage we have made use of (2.10).

The microscopic heat current is defined, according to Ref. 1, by removing from the total energy current

$$\begin{aligned}V\mathbf{J}'_Q=\sum_\alpha\sum_i{}^{\alpha}&\left[\frac{m_\alpha}{2}\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}\right]^2\right.\\ &\left.+\tfrac{1}{2}\sum_\beta\sum_j{}^{\beta}\phi_{i\alpha,j\beta}\right]\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}\right]\\ &+\tfrac{1}{2}\sum_\alpha\sum_\beta\sum_i{}^{\alpha}\sum_j{}^{\beta}\mathbf{q}_{i\alpha,j\beta}\mathbf{F}_{i\alpha,j\beta}\cdot\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}\right]\end{aligned} \tag{2.12}$$

all of the terms proportional to $\mathbf{u}_\alpha-\mathbf{u}$. The resulting current $\widetilde{\mathbf{J}}_Q$ is invariant for any translation in the mean velocities of the two species,

$$V\widetilde{\mathbf{J}}_Q=\sum_{\alpha}\sum_{i}{}^{\alpha}E'_{i\alpha}\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}_\alpha\right]$$

$$+\tfrac{1}{2}\sum_{\alpha}\sum_{\beta}\sum_{i}{}^{\alpha}\sum_{j}{}^{\beta}\mathbf{q}_{i\alpha,j\beta}\mathbf{F}_{i\alpha,j\beta}\cdot\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}_\alpha\right], \tag{2.13}$$

where $E'_{i\alpha}$ is the total energy of particle i_α measured in the comoving frame

$$E'_{i\alpha}=\frac{m_\alpha}{2}\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}_\alpha\right]^2+\tfrac{1}{2}\sum_{\beta}\sum_{j}{}^{\beta}\phi_{i\alpha,j\beta}\,. \tag{2.14}$$

The different between $\widetilde{\mathbf{J}}_Q$ and $\mathbf{J}'_Q$ is given by

$$\mathbf{J}'_Q-\widetilde{\mathbf{J}}_Q=\sum_{\alpha}\mathbf{J}_\alpha\cdot\frac{(E'_\alpha\overleftrightarrow{1}+V\overleftrightarrow{\mathbf{P}}_\alpha)}{m_\alpha N_\alpha}$$

$$+\frac{1}{2V}\sum_{\alpha}m_\alpha N_\alpha(\mathbf{u}_\alpha-\mathbf{u})\cdot(\mathbf{u}_\alpha-\mathbf{u})^2 \tag{2.15}$$

with

$$E'_\alpha=\sum_{i}{}^{\alpha}E'_{i\alpha}\,,$$

$$V\overleftrightarrow{\mathbf{P}}_\alpha=\tfrac{1}{2}\sum_{i}{}^{\alpha}\sum_{\beta}\sum_{j}{}^{\beta}\mathbf{q}_{i\alpha,j\beta}\mathbf{F}_{i\alpha,j\beta}$$

$$+m_\alpha\sum_{i}{}^{\alpha}\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}_\alpha\right]\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}-\mathbf{u}_\alpha\right],$$

where we can neglect quadratic terms in $\mathbf{u}$, $\mathbf{u}_\alpha$.

We expect that in the thermodynamic limit and within linear regime the average of the microscopic expression given in (2.15) will approach $\sum_\alpha \tilde{h}_\alpha \mathbf{J}_\alpha$, where

$$\tilde{h}_\alpha=\frac{\langle E'_\alpha+V(P_\alpha)_{ii}\rangle}{m_\alpha N_\alpha}\,. \tag{2.16}$$

This quantity is not equal to the specific partial enthalpy h_α. The difference lies in the fact that in defining $\tilde{h}_\alpha$ we have attributed to each species 50% of the energy contribution. This corresponds to the approximation of ideal mixtures. The approximation is exact in the case of isotopic mixtures, when the components only differ in masses, the potentials being the same. In our case—LJ Ar-Kr equimolar mixture—the difference $\Delta_\alpha=h_\alpha-\tilde{h}_\alpha$ is likely to be negligible. A rough estimate of Δ_α in the case of equimolar Ar-Kr mixture has been made[11] on the basis of McDonald's results.[12] Though the computations of Refs. 11 and 12 correspond to slightly different state points, a small percent difference of about 4% for $\alpha=1$ and of 9% for $\alpha=2$ has been found, indicating that for such simple systems the microscopic approximation for the partial enthalpy is good. This result, i.e., the fact that the Ar-Kr mixture may be regarded as quasiideal, can be simply understood given the similarity between the Ar-Kr interactions and the Ar-Ar and Kr-Kr ones.

Taking (2.13) as the microscopic definition of the heat current—from now on we will drop the superscript and refer to the quantity in (2.13) as $\mathbf{J}_Q$—the four phenomenological transport coefficients L_{ij} are connected to the microscopic currents given (2.7) and (2.13) by the following Green-Kubo relations:[13]

$$\frac{L_{11}}{T}=\frac{V}{k_BT}\int_0^{+\infty}\langle J_{1z}(t)J_{1z}(0)\rangle dt\,, \tag{2.17a}$$

$$\frac{L_{Q1}}{T}=\frac{V}{k_BT}\int_0^{+\infty}\langle J_{Qz}(t)J_{1z}(0)\rangle dt=\frac{L_{1Q}}{T}\,, \tag{2.17b}$$

$$\frac{L_{QQ}}{T}=\frac{V}{k_BT}\int_0^{+\infty}\langle J_{Qz}(t)J_{Qz}(0)\rangle dt\,. \tag{2.17c}$$

These coefficients are related to the four effects which can be observed in a binary mixture when applying a concentration or a temperature gradient. L_{11} is connected to the matter transport due to a concentration gradient, i.e., ordinary diffusion; L_{1Q} expresses the transport of matter caused by a temperature gradient, thermal diffusion or Soret effect; L_{Q1} is related to heat transport induced by a concentration gradient, Dufour effect, and L_{QQ} to the heat transport due to a temperature gradient.[7,8]

C. Equations of motion

The system of N particles $\mathbf{q}_{i\alpha},\mathbf{p}_{i\alpha}$ is described, in the absence of an external perturbation, by the Hamiltonian

$$H_0=\sum_{i\alpha}\frac{p_{i\alpha}^2}{2m_\alpha}+\tfrac{1}{2}\sum_{i\alpha,j\beta}\phi_{i\alpha,j\beta}$$

generating the equations of motion

$$\dot{\mathbf{q}}_{i\alpha}=\frac{\partial H_0}{\partial \mathbf{p}_{i\alpha}}=\frac{\mathbf{p}_{i\alpha}}{m_\alpha}\,,$$

$$\dot{\mathbf{p}}_{i\alpha}=\frac{-\partial H_0}{\partial \mathbf{q}_{i\alpha}}=\mathbf{F}_{i\alpha}\,, \tag{2.18}$$

where $\mathbf{F}_{i\alpha}=\sum_\beta\sum_j^\beta\mathbf{F}_{i\alpha,j\beta}$.

When an external perturbation $\boldsymbol{F}(t)$, not necessarily Hamiltonian, is applied to the system, the equations of motion will modify as follows[2,5,14]

$$\dot{\mathbf{q}}_{i\alpha}=\frac{\mathbf{p}_{i\alpha}}{m_\alpha}+\overleftrightarrow{\mathbf{C}}_{i\alpha}\cdot\boldsymbol{F}(t)\,,$$

$$\dot{\mathbf{p}}_{i\alpha}=\mathbf{F}_{i\alpha}+\overleftrightarrow{\mathbf{D}}_{i\alpha}\cdot\boldsymbol{F}(t)\,, \tag{2.19}$$

where $\overleftrightarrow{\mathbf{C}}_{i\alpha}=\overleftrightarrow{\mathbf{C}}_{i\alpha}(\Gamma)$ and $\overleftrightarrow{\mathbf{D}}_{i\alpha}=\overleftrightarrow{\mathbf{D}}_{i\alpha}(\Gamma)$ are suitable tensors which are phase-space functions and which describe the coupling of the perturbation to the system. If Eqs. (2.19) are such that they preserve the phase-space incompressibility we can apply linear-response theory in its standard form[15] and get the linear response of a phase-space function $\mathbf{B}$ as

$$\langle \mathbf{B}\rangle_t=\beta\int_0^t\langle \mathbf{B}(t-s)\mathbf{O}(0)\rangle_{\text{eq}}\cdot\boldsymbol{F}(s)ds\,, \tag{2.20}$$

with the hypothesis that $\langle \mathbf{B}\rangle_{\text{eq}}=0$, $\mathbf{O}$ being the variable that couples with the imposed perturbation, defined as

$$\mathbf{O}=\sum_{\alpha}\sum_{i}{}^{\alpha}\left[\frac{\mathbf{p}_{i\alpha}}{m_\alpha}\cdot\overleftrightarrow{\mathbf{D}}_{i\alpha}-\mathbf{F}_{i\alpha}\cdot\overleftrightarrow{\mathbf{C}}_{i\alpha}\right] . \tag{2.21}$$

We employed two sets of perturbed equations of motion, obtained by applying a diffusive and a thermal perturbation to the system. We applied a diffusive perturbation by changing the equations of motion in the following way:

$$\begin{aligned}\dot{\mathbf{q}}_{i\alpha}&=\frac{\mathbf{p}_{i\alpha}}{m_\alpha} ,\\ \dot{\mathbf{p}}_{i\alpha}&=\mathbf{F}_{i\alpha}+A_\alpha \boldsymbol{F}_D(t) ,\end{aligned} \tag{2.22}$$

with $A_1=x_2$, $A_2=-x_1$,$x_\alpha=N_\alpha/N$ being the number concentration of species α. The dynamical variable which couples to the external force $\boldsymbol{F}_D(t)$ is then, within this formalism,

$$\mathbf{O}_D=\sum_{\alpha}\sum_{i}{}^{\alpha}\frac{\mathbf{p}_{i\alpha}}{m_\alpha}\cdot A_\alpha\overleftrightarrow{1}=V\mathbf{J}_D . \tag{2.23}$$

As for the thermally perturbed equations we applied the MacGowan-Evans[1] extension of the thermal conductivity algorithm for a simple fluid[2]

$$\begin{aligned}\dot{\mathbf{q}}_{i\alpha}&=\frac{\mathbf{p}_{i\alpha}}{m_\alpha} ,\\ \dot{\mathbf{p}}_{i\alpha}&=\mathbf{F}_{i\alpha}+\overleftrightarrow{\mathbf{T}}_{i\alpha}\cdot \boldsymbol{F}_Q(t) ,\end{aligned} \tag{2.24}$$

where we define the tensor $\overleftrightarrow{\mathbf{T}}_{i\alpha}$ as

$$\overleftrightarrow{\mathbf{T}}_{i\alpha}=\overleftrightarrow{\mathbf{S}}_{i\alpha}-\frac{1}{N_\alpha}\sum_{k}{}^{\alpha}\overleftrightarrow{\mathbf{S}}_{k\alpha} , \tag{2.25}$$

and

$$\begin{aligned}\overleftrightarrow{\mathbf{S}}_{i\alpha}&=\widetilde{E}\,'_{i\alpha}\overleftrightarrow{1}+\tfrac{1}{2}\sum_{\beta}\sum_{j}{}^{\beta}\mathbf{F}_{i\alpha,j\beta}\mathbf{q}_{i\alpha,j\beta} ,\\ \widetilde{E}\,'_{i\alpha}&=\frac{m_\alpha}{2}\left[\frac{p_{ix\alpha}^2}{m_\alpha}+\frac{p_{iy\alpha}^2}{m_\alpha}+\left[\frac{p_{iz\alpha}}{m_\alpha}-u_{z\alpha}\right]^2\right]\\ &\quad+\tfrac{1}{2}\sum_{\beta}\sum_{j}{}^{\beta}\phi_{i\alpha,j\beta} .\end{aligned}$$

We note that when the perturbing field is directed along the z axis $\widetilde{E}\,'_{i\alpha}$ will coincide with $E'_{i\alpha}$ as defined in Sec. II B, the average currents induced being directed in the same way as the imposed perturbation. Exploiting this reasoning we obtain

$$\mathbf{O}_Q=\sum_{\alpha}\sum_{i}{}^{\alpha}\frac{\mathbf{p}_{i\alpha}}{m_\alpha}\cdot\overleftrightarrow{\mathbf{T}}_{i\alpha}=V\mathbf{J}_Q . \tag{2.26}$$

The external fields $\boldsymbol{F}_D(t)$ and $\boldsymbol{F}_Q(t)$ imposed to the system are both impulsive forces directed along the z axis, given by

$$\boldsymbol{F}_D(t)=(0,0,\widetilde{F}_D)\delta(t) , \tag{2.27}$$

$$\boldsymbol{F}_Q(t)=(0,0,\widetilde{F}_Q)\delta(t) . \tag{2.28}$$

Substituting such expressions into (2.20) we get for diffusive and thermal response to both kinds of imposed perturbations,

$$\begin{aligned}\langle J_{iz}\rangle_{D,t}&=\beta\widetilde{F}_D\left[\frac{x_2}{m_1}+\frac{x_1}{m_2}\right]V\langle J_{iz}(t)J_{1z}(0)\rangle_{\text{eq}} ,\\ \langle J_{iz}\rangle_{Q,t}&=\beta\widetilde{F}_Q V\langle J_{iz}(t)J_{Qz}(0)\rangle_{\text{eq}},\quad i=1,Q .\end{aligned} \tag{2.29}$$

In the linear region the four transport coefficients (2.17) can be obtained by direct integration of (2.29),

$$\begin{aligned}\frac{L_{i1}}{T}&=\frac{1}{\widetilde{F}_D(x_2/m_1+x_1/m_2)}\int_0^{+\infty}\langle J_{iz}\rangle_{D,t}dt ,\\ \frac{L_{iQ}}{T}&=\frac{1}{\widetilde{F}_Q}\int_0^{+\infty}\langle J_{iz}\rangle_{Q,t}dt,\quad i=1,Q .\end{aligned} \tag{2.30}$$

III. MODEL AND IMPLEMENTATION

We have studied an equimolar ($x_1=x_2=\frac{1}{2}$) mixture of argon-krypton atoms, with masses $m_1=39.944$, $m_2=83.80$ a.u. The system of $N=N_1+N_2=256$ particles is enclosed in a cube of volume $V=L^3$. The model for interactions is basically a Lennard-Jones potential

$$\phi_{\text{LJ}}^{\alpha\beta}(q)=4\epsilon_{\alpha\beta}\left[\left[\frac{\sigma_{\alpha\beta}}{q}\right]^{12}-\left[\frac{\sigma_{\alpha\beta}}{q}\right]^{6}\right],\quad q=q_{i\alpha,j\beta}$$

with parameters $\epsilon_{11}=119.8k_B$, $\epsilon_{22}=167.0k_B$, $\sigma_{11}=3.405$ Å, $\sigma_{22}=3.633$ Å, and with cross parameters defined by Lorentz-Berthelot[16] rules

$$\begin{aligned}\sigma_{12}&=\frac{\sigma_{11}+\sigma_{22}}{2} ,\\ \epsilon_{12}&=\sqrt{\epsilon_{11}\epsilon_{22}} .\end{aligned}$$

Our units are σ for length, ϵ for energy, and $\tau=(m\sigma^2/\epsilon)^{1/2}$ for time, defined with respect to argon. All of the quantities we use will be quoted in such units, unless explicit declaration. The potential model is such that pair forces $|\mathbf{F}_{i\alpha,j\beta}|$ go to zero in a continuous way at the edge of the box. To obtain this, a spline is made with a straight line, such as to satisfy the conditions

$$\begin{aligned}\frac{\partial\phi^{\alpha\beta}(q_1)}{\partial q}&=\frac{\partial\phi_{\text{LJ}}^{\alpha\beta}(q_1)}{\partial q},\quad q_1=3.2\\ \frac{\partial\phi^{\alpha\beta}(q_2)}{\partial q}&=0,\quad q_2=\frac{L}{2} .\end{aligned} \tag{3.1}$$

The potential $\phi^{\alpha\beta}(q)$ is the integral over q of the pair force $\partial\phi^{\alpha\beta}(q)/\partial q$ with the condition that $\phi^{\alpha\beta}(q)\rightarrow 0$ as $q\rightarrow\infty$.

We studied the diffusive and thermal response of our system to both a diffusive and a temperature gradient, using the perturbations defined in (2.27) and (2.28) with two sets of magnitudes $\widetilde{F}_D=0.144\times10^{-7}$, $\widetilde{F}_Q=0.114\times10^{-8}$, and $\widetilde{F}_D=0.722$, $\widetilde{F}_Q=0.043$. The first set corresponds to very small gradients, changing the temperature of the system of less than 1 over 10^6. The second set was chosen to lie more or less at the end of the linear region, producing changes in the temperatures of less than 3%. Employing the same criterion used in Refs. 17 and 18 to compare the strengths of impulsive and stationary perturbations, we define a quantity τ_D (τ_Q) which represents the decay time of the normalized diffusive (thermal) autocorrelation function. This is such that

$$\frac{\tilde{F}_D}{\tau_D}=\bar{F}_D\,,$$

$$\frac{\tilde{F}_Q}{\tau_Q}=\bar{F}_Q\,.$$

The values utilized for $\tilde{F}_D$ and $\tilde{F}_Q$ in our case—for impulsive external fields—then correspond approximately to stationary perturbations $\bar{F}_D=2.0\times10^{-6}$, $\bar{F}_Q=1.4\times10^{-7}$ for the first set, and $\bar{F}_D=1.0\times10^{2}$, $\bar{F}_Q=4.3\times10^{-1}$ for the second set. The perturbations of the second set are thus comparable in strength to the ones employed in Ref. 1.

The thermodynamical point is $N/V=\rho=0.7138$, $T=0.987$. This point differs from the one studied in Ref. 1 (and in Refs. 19–22 for diffusion) because our temperature is slightly larger ($\sim2\%$), a seemingly irrelevant fact. Our boundary conditions are periodic in all directions.

We employed the subtraction technique[6] and integrated the equations of motion (2.22) and (2.24) using the standard Verlet algorithm, with a slight modification at the beginning of each segment, due to the impulsive perturbation employed.[23] The time step is $h=0.462\times10^{-2}$, corresponding to 10^{-14} sec.

With the use of a δ-like external field we were able to observe the decay of the diffusive current driven by $\tilde{F}_D$, $\langle J_{1z}\rangle_{D,t}$, and of the heat current induced by the thermal perturbation $\tilde{F}_Q$, $\langle J_{Qz}\rangle_{Q,t}$, as well as the behavior of the cross currents, $\langle J_{1z}\rangle_{Q,t}$ and $\langle J_{Qz}\rangle_{D,t}$, as a function of t—the time elapsed since the switching on of the perturbation.

We computed the decay of the thermal autocorrelation function by

$$N_{QQ}(t)=\frac{\langle J_{Qz}\rangle_{Q,t}}{\langle J_{Qz}\rangle_{Q,t=0_+}}\,, \tag{3.2}$$

and that of the diffusive autocorrelation function by

$$N_{11}(t)=\frac{\langle J_{1z}\rangle_{D,t}}{\langle J_{1z}\rangle_{D,t=0_+}}\,, \tag{3.3}$$

while for the cross currents we employed the nonnormalized quantities

$$C_{1Q}(t)=\frac{V\langle J_{1z}\rangle_{Q,t}}{\tilde{F}_Q}\,, \tag{3.4}$$

$$C_{Q1}(t)=\frac{V\langle J_{Qz}\rangle_{D,t}}{\tilde{F}_D\left[\dfrac{x_2}{m_1}+\dfrac{x_1}{m_2}\right]}\,. \tag{3.5}$$

The corresponding phenomenological coefficients are then given by

$$L_{ii}=K_{ii}\int_0^{+\infty}N_{ii}(t)dt=K_{ii}I_{ii}\,,\quad i=1,Q \tag{3.6}$$

$$L_{jk}=\frac{T}{V}\int_0^{+\infty}C_{jk}(t)dt=\frac{T}{V}I_{jk}\,,\quad j,k=1,Q,\quad j\neq k\,; \tag{3.7}$$

where

$$K_{11}=\frac{T\langle J_{1z}\rangle_{D,t=0_+}}{\tilde{F}_D\left[\dfrac{x_2}{m_1}+\dfrac{x_1}{m_2}\right]}\,, \tag{3.8}$$

$$K_{QQ}=\frac{T\langle J_{Qz}\rangle_{Q,t=0_+}}{\tilde{F}_Q}\,, \tag{3.9}$$

and the quantities I_{ij} are the weighted averages of the integrals over times $t_{\min}\leq t\leq t_{\mathrm{MAX}}$, corresponding to the stationary part of the integral response. The averages are weighted with the inverse of the variance of the integrals.

IV. RESULTS

A. Low perturbations

We present in Figs. 1–4 our results for the direct and cross responses at very low perturbations—$\tilde{F}_D=1.443\times10^{-7}$, $\tilde{F}_Q=1.443\times10^{-8}$. Such values correspond approximately to gradients $\bar{F}_D=2.0\times10^{-6}$, $\bar{F}_Q=1.4\times10^{-7}$.

As regards the direct effects—diffusive response to $\tilde{F}_D$ and thermal response to $\tilde{F}_Q$—we see in Figs. 1 and 2 that a well-defined asymptotic value is reached in both cases before 1 ps. From appropriately weighted averages of such values we get, via Eqs. (3.5) and (3.6), the direct coefficients $L_{11}=0.0174\pm0.0004$ and $L_{QQ}=4.375\pm0.086$. We computed such coefficients by equilibrium Green-Kubo technique too, obtaining $L_{11}=0.0173\pm0.0001$ and $L_{QQ}=4.280\pm0.001$, in very good agreement with our NEMD values.

Our results for the cross currents—thermal response to $\tilde{F}_D$ and diffusive response to $\tilde{F}_Q$—are affected by a larger statistical noise, as we can see in Figs. 3 and 4. This is not unexpected, since both the cross responses are rather weak with respect to the direct ones. Their negative minimum is 10% lower when compared to the initial values of direct currents. In both cases, however, a plateau value is attained. Comparison between the two NEMD responses

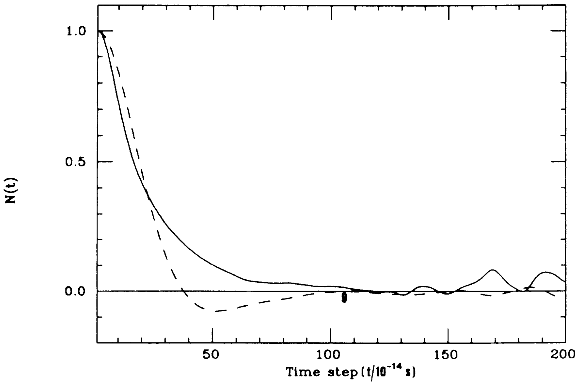

FIG. 1. Normalized average relaxation of the heat current $N_{QQ}(t)$ (solid curve) and of the particle current $N_{11}(t)$ (dashed curve). Average over 400 segments. $\tilde{F}_D=1.443\times10^{-7}$; $\tilde{F}_Q=1.443\times10^{-8}$.

and with Green-Kubo results—Figs. 3(a) and 3(b)—shows that the three methods are in very good agreement and give identical values for the cross coefficients, within the statistical errors. We get $L_{Q1} = -(0.0249 \pm 0.0040)$, $L_{1Q} = -(0.0267 \pm 0.0032)$ and, from GK, L_{Q1} $(=L_{1Q}) = -(0.0268 \pm 0.0013)$.

From Fig. 3(a) we see that the two NEMD responses both start from zero, reach a negative minimum after about 0.25 ps and a smaller positive maximum after 0.7 ps. At longer times the larger statistical noise affects the responses, but comparing the NEMD currents to the GK function—Fig. 3(a)—we conclude that the correlation is negligible at times larger than 1 ps. We note that the GK cross correlation does not start from zero. On the other

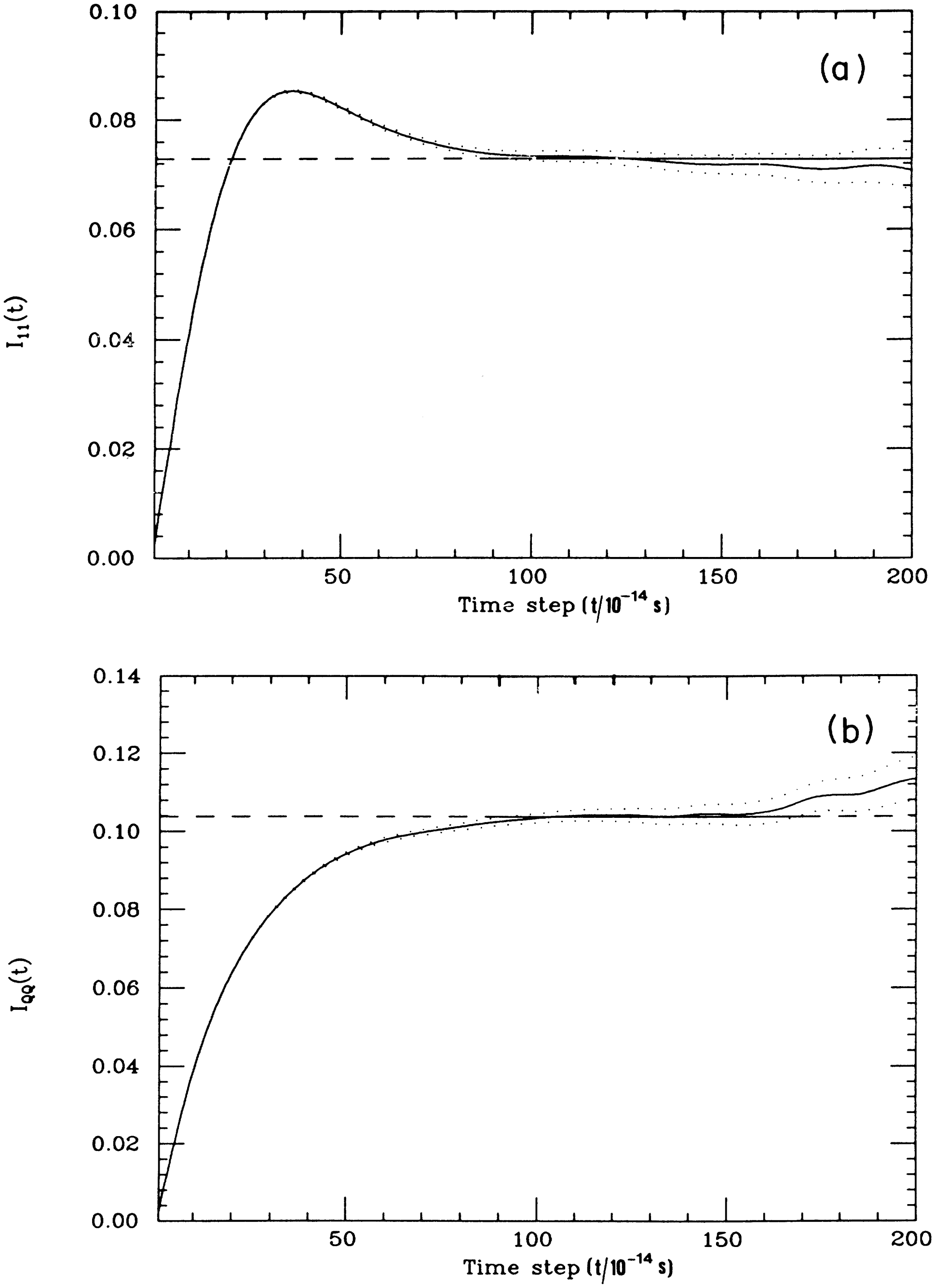

FIG. 2. (a) Integral of the normalized average relaxation of the particle current $N_{11}(t)$: $\tilde{F}_D = 1.443 \times 10^{-7}$. (b) Integral of the normalized average relaxation of the heat current $N_{QQ}(t)$; $\tilde{F}_Q = 1.443 \times 10^{-8}$. Straight lines represent the values of the weighted averages (a) I_{11}; (b) I_{QQ} (see text). The solid part delimits the set of points employed in the average. The outer (dotted) curves delimit the errors.

hand, from the very definition of $\mathbf{J}_1$ and $\mathbf{J}_Q$—Eqs. (2.7) and (2.13)—, we see that the initial value of the cross correlation should be zero for symmetry. The behavior of the GK correlation is not astonishing, since at small times the NEMD results are more reliable than the GK ones.

In Tables I—IV we report our results for the L_{ij}, together with the values previously obtained by other authors from equilibrium simulations for L_{11}, and with the MacGowan-Evans results for all L_{ij}. As regards the diffusive coefficient L_{11}, for which other data are available, we are in better agreement with the results of other authors than with those of Ref. 1. As for the other coefficients there is, broadly speaking, consistency, though a weak numerical discrepancy. However, it seems to us not

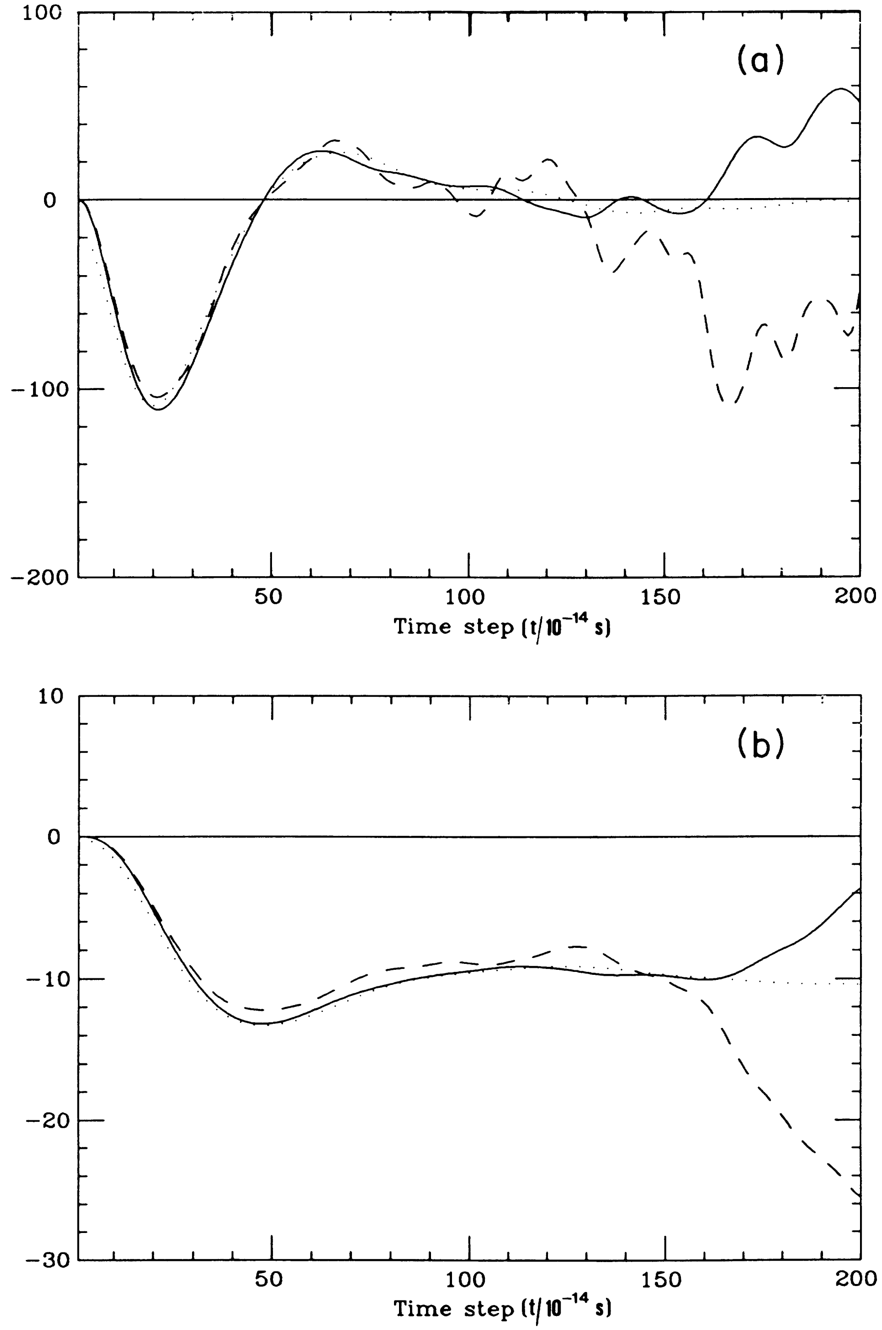

FIG. 3. Comparison among different cross correlations (a) and their integrals (b). Solid curve: diffusive response to $\tilde{F}_Q = 1.443 \times 10^{-8}$. Dashed curve: thermal response to $\tilde{F}_D = 1.443 \times 10^{-7}$. Dotted curve: Green-Kubo results. The perturbed responses are averaged over 400 segments. For the Green-Kubo correlation 330 000 averaging steps are employed.

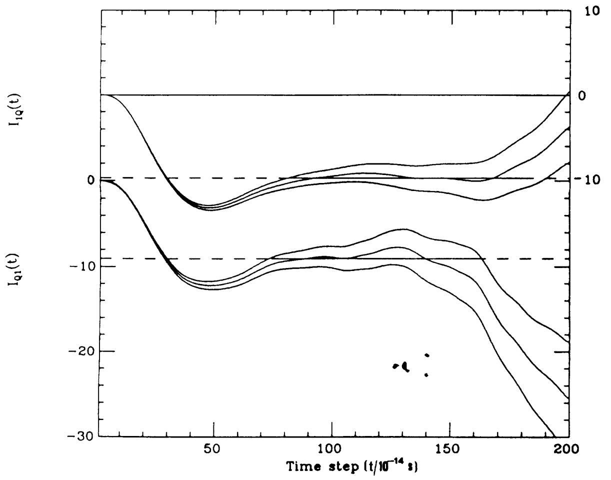

FIG. 4. Upper plot: integral of $C_{1Q}(t)$, diffusive response to $\tilde{F}_Q = 1.443 \times 10^{-8}$. Lower plot: integral of $C_{Q1}(t)$, thermal response to $\tilde{F}_D = 1.443 \times 10^{-7}$. The outer curves delimit the errors.

a serious one, especially for what concerns the cross-coupling coefficients, for which the statistical error is quite large since we are dealing with very weak responses.

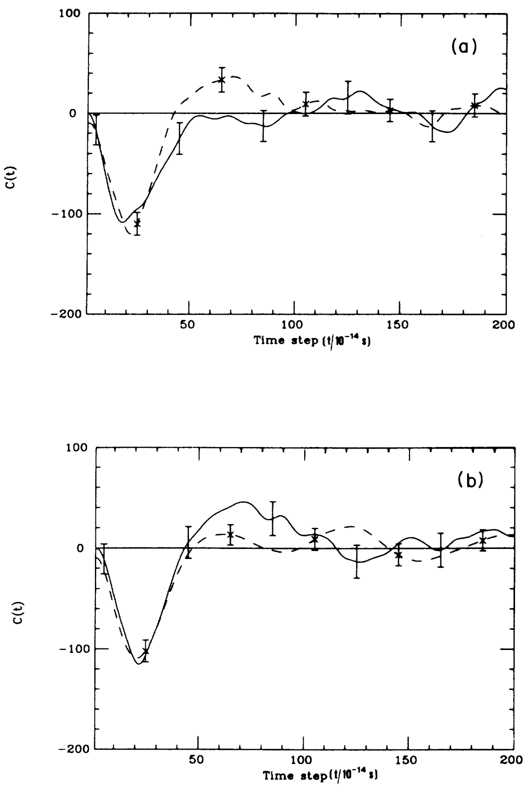

FIG. 5. Comparison between different analysis of the cross responses at high perturbations. (a) $C_{Q1}(t)$, $\tilde{F}_D = 0.722$. (b) $C_{1Q}(t)$, $\tilde{F}_Q = 4.33 \times 10^{-2}$. Solid curve: subtraction technique. Dashed curve: no subtraction (see text). The errors on the curves are plotted just on some representative points.

B. High perturbations

In Figs. 5(a) and 5(b) our results for the cross currents obtained using high perturbations—$\tilde{F}_D = 0.722$, $\tilde{F}_Q = 0.0433$—are shown. With such values of $\tilde{F}_D$ and $\tilde{F}_Q$—corresponding approximately to $F_D = 1.0 \times 10^2$, $F_Q = 4.3 \times 10^{-1}$—we detect a change in the temperatures of the perturbed systems of about 2%. With this choice for the perturbation strengths we lie more or less at the end of the linear region, since we expect[18] that a change in the temperature of a few percent will correspond to the onset of nonlinearity.

As the external fields are rather high, the responses will be somewhat larger than the typical fluctuations of the corresponding equilibrium currents. In fact the direct responses are about five times larger than the equilibrium fluxes. In this region the subtraction technique loses efficacy at large times, since the difference only introduces another source of noise without improving the response.[18] Thus we analyzed our high-field runs both by subtraction and by taking only the perturbed response. In both cases we can see from Figs. 5(a) and 5(b) and Tables III and IV that the results are very noisy—though still consistent within the large errors with the GK values—with a slight gain in statistical accuracy in the nonsubtraction case—as we see in Tables III and IV. From Tables I–IV it is apparent that the error bars on the direct coefficients L_{11} and L_{QQ} are less affected by the increase in the perturbation strengths than the ones on L_{1Q} and L_{Q1}. Approximating the generic perturbed response J_+^P at $t = 0_+$ with the expansion

$$J_+^P \simeq J_+^0 + \tilde{F} g(\Gamma)\delta t(\nabla_+ J) + \tilde{F}^2 h(\Gamma)(\delta t)^2(\nabla_+^2 J) \, , \qquad (4.1)$$

—where $g(\Gamma)$ and $h(\Gamma)$ are phase functions—and substituting (4.1) into the formula giving the variance of the response with the subtraction technique[18] we get

$$v\left[\frac{J_+^P - J_+^0}{\tilde{F}}\right] \simeq g^2(\delta t)^2 v(\nabla_+ J) + \tilde{F}^2 h^2 (\delta t)^4 v(\nabla_+^2 J) + 2\tilde{F} g h \,\mathrm{cov}(\nabla_+ J, \nabla_+^2 J) \, . \qquad (4.2)$$

In the direct case only the first term in the right-hand side is important at not very high perturbations, so the error is nearly independent on the field strength. In the cross case, however, it seems reasonable to think that this term plays a minor role with respect to higher-order terms—$\nabla_+ J$ being zero almost mechanically—thus producing a statistical indetermination that grows with $\tilde{F}$. This reasoning might explain the apparent instability in the cross-correlation results at high perturbations quoted by other authors.[24]

TABLE I. Results for the diffusive direct coefficient L_{11}. $N_P=256$; $x_1=x_2=\frac{1}{2}$; $\rho=0.7138$; $\sigma=\sigma_{11}$; $\epsilon=\epsilon_{11}$; $m=m_1$. T, temperature; $\tilde{F}_D$, diffusive perturbation; K_{11} and L_{11} are defined in Sec. III. ST: our results via subtraction technique; NST: our results without subtraction; GK: our equilibrium results. The length of each NE run is $N=80\,000$ (400×200). For GK 165 000 averaging events are employed. ME: data from Ref. 1, zero field extrapolation; JM, JB, SH, data from Refs. 22, 19, 21, respectively.

T (ϵ/k_B)	$\tilde{F}_D$ $[(m\epsilon)^{1/2}]$	$t_{\min}$:$t_{\max}$	$k_{11}\pm\Delta k_{11}$ $[(m\epsilon)/(\sigma^3k_B)]$	$L_{11}\pm\Delta L_{11}$ $[(m^3\epsilon)^{1/2}/(\sigma^2k_B)]$	Source
0.987	1.443×10^{-7}	90:200	0.239 ± 0.000	0.0174 ± 0.0004	ST
0.987	0.722	90:200	0.237 ± 0.000	0.0172 ± 0.0007	NST
0.987	0.722	90:200	0.239 ± 0.000	0.0178 ± 0.0003	ST
0.987		90:200		0.0173 ± 0.0001	GK
0.965	extrapolated			0.0145 ± 0.0010	ME
0.965				0.0170	JM
0.965				0.0165	JB
0.965				0.0174	SH

TABLE II. Results for the thermal direct coefficient L_{QQ}, $N_P=256$; $x_1=x_2=\frac{1}{2}$; $\rho=0.7138$; $\sigma=\sigma_{11}$; $\epsilon=\epsilon_{11}$; $m=m_1$. T, temperature; $\tilde{F}_Q$, thermal perturbation; K_{QQ} and L_{QQ} defined in Sec. III. ST: our results via subtraction technique; NST: our results without subtraction; GK: our equilibrium results. The length of each NE run is $N=80\,000$ (400×200). For GK 165 000 averaging events are employed. ME: data from Ref. 1, zero field extrapolation.

T (ϵ/k_B)	$\tilde{F}_Q$ $[(m/\epsilon)^{1/2}]$	$t_{\min}$:$t_{\max}$	$k_{QQ}\pm\Delta k_{QQ}$ $[\epsilon^3/(m\sigma^3k_B)]$	$L_{QQ}\pm\Delta L_{QQ}$ $(\epsilon^3/[(m\epsilon)^{1/2}\sigma^2k_B])$	Source
0.987	1.443×10^{-8}	90:170	$(4.215\pm0.003)\times10^{1}$	4.375 ± 0.086	ST
0.987	0.433×10^{-1}	70:200	$(4.196\pm0.005)\times10^{1}$	4.450 ± 0.148	NST
0.987	0.433×10^{-1}	70:200	$(4.230\pm0.003)\times10^{1}$	4.309 ± 0.082	ST
0.987		90:200		4.280 ± 0.001	GK
0.965	extrapolated			3.95 ± 0.05	ME

TABLE III. Results for the cross coefficient L_{Q1}. $N_P=256$; $x_1=x_2=\frac{1}{2}$; $\rho=0.7138$; $\sigma=\sigma_{11}$; $\epsilon=\epsilon_{11}$; $m=m_1$. T, temperature; $\tilde{F}_D$, diffusive perturbation; I_{Q1} and L_{Q1} are defined in Sec. III. ST: our results via subtraction technique; NST: our results without subtraction; GK: our equilibrium results (the same for the two cross coefficients). The length of each NE run is $N=80\,000$ (400×200). For GK 330 000 averaging events are employed. ME: data from Ref. 1, weighted average at low fields.

T (ϵ/k_B)	$\tilde{F}_D$ $[(m\epsilon)^{1/2}]$	$t_{\min}$:$t_{\max}$	$I_{Q1}\pm\Delta I_{Q1}$ $[(m\epsilon\sigma^2)^{1/2}]$	$L_{Q1}\pm\Delta L_{Q1}$ $[(m\epsilon^3)^{1/2}/(\sigma^2k_B)]$	Source
0.987	1.443×10^{-7}	74:160	$-(9.054\pm1.470)$	$-(0.0249\pm0.0040)$	ST
0.987	0.722	70:200	$-(6.333\pm3.855)$	$-(0.0174\pm0.0106)$	NST
0.987	0.722	70:200	$-(14.218\pm5.098)$	$-(0.0392\pm0.0140)$	ST
0.987		80:200	$-(9.743\pm0.485)$	$-(0.0268\pm0.0013)$	GK
0.965				$-(0.0168\pm0.0013)$	ME[a]
0.965				$-(0.0164\pm0.0013)$	ME

[a] Run with $N_P=108$.

TABLE IV. Results for the cross coefficient L_{1Q}. $N_P=256$; $x_1=x_2=\frac{1}{2}$; $\rho=0.7138$; $\sigma=\sigma_{11}$; $\epsilon=\epsilon_{11}$; $m=m_1$. T, temperature; $\tilde{F}_Q$, thermal perturbation; I_{1Q} and L_{1Q} are defined in Sec. III. ST: our results via subtraction technique; NST: our results without subtraction; GK: our equilibrium results (the same for the two cross-coupling coefficients). The length of each NE run is $N=80\,000$ (400×200). For GK 330 000 averaging events are employed. ME: data from Ref. 1, weighted average at low fields.

T (ϵ/k_B)	$\tilde{F}_Q$ $[(m/\epsilon)^{1/2}]$	$t_{\min}$;$t_{\max}$	$I_{1Q}\pm\Delta I_{1Q}$ $[(m\epsilon\sigma^2)^{1/2}]$	$L_{1Q}\pm\Delta L_{1Q}$ $[(m\epsilon^3)^{1/2}/(\sigma^2k_B)]$	Source
0.987	1.443×10^{-8}	78:180	$-(9.700\pm1.166)$	$-(0.0267\pm0.0032)$	ST
0.987	0.433×10^{-1}	70:200	$-(10.418\pm3.050)$	$-(0.0287\pm0.0084)$	NST
0.987	0.433×10^{-1}	70:200	$-(4.215\pm5.172)$	$-(0.0116\pm0.0142)$	ST
0.987		80:200	$-(9.743\pm0.485)$	$-(0.0268\pm0.0013)$	GK
0.965				$-(0.0155\pm0.0005)$	ME[a]
0.965				$-(0.0168\pm0.0005)$	ME

[a] Run with $N_P=108$.

V. CONCLUDING REMARKS

We have carried out some NEMD and equilibrium GK calculations of thermal and diffusive transport coefficients in a Lennard-Jones mixture of liquid argon and krypton near the krypton's triple point. The main result of this work is that cross-coupling effects in mixtures can be obtained with satisfactory statistics by NEMD. Moreover, we show that NEMD and GK techniques have comparable efficiency and yield results which are in very good agreement with each other and in reasonable agreement with previous MD results.

As regards thermotransport, there still remains the question of the equivalence between the microscopic heat current $\tilde{\mathbf{J}}_Q$ and the phenomenological one $\mathbf{J}_Q$. As we mentioned before, this is not a problem for what concerns equimolar and isotopic mixtures.

However, since direct and cross effects are obtainable by MD, either by a straightforward simulation or by reconstructing the different contributions to the thermal coefficients, the study of transport in mixtures is in the realm of molecular dynamics simulation.

We believe, however, that the question of a suitable microscopic definition of $\mathbf{J}_Q$ is not settled and deserves further investigation.

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APPENDIX

In this appendix we derive the linear relation between the transport coefficients L_{ij} given by Eqs. (2.5) and the results of our calculations, in the hypothesis that $\tilde{h}_\alpha \neq h_\alpha$.

Equations (2.1) express the phenomenological relations which describe transport in a binary mixture. Within the local equilibrium assumption—expressed in the variables P,T—we have

$$\nabla\mu_\beta = \left[\frac{\partial\mu_\beta}{\partial P}\right]_T \nabla P + \left[\frac{\partial\mu_\beta}{\partial T}\right]_P \nabla T \ . \tag{A1}$$

We define $\nabla_T\mu_\beta = (\partial\mu_\beta/\partial P)_T \nabla P$ as the gradient of μ_β obtained by subtracting from (A1) the temperature dependence. Then the following relation holds:[1]

$$T\nabla\left[\frac{\mu_\beta}{T}\right] = \nabla_T\mu_\beta - \frac{h_\beta}{T}\nabla T \ , \tag{A2}$$

where h_β is the thermodynamic specific enthalpy of species β. Substituting Eq. (A2) into Eqs. (2.1) and taking into account the fact that $\mathbf{J}_1 = -\mathbf{J}_2$, we get

$$\begin{aligned} \mathbf{J}_1 &= -[\tilde{L}_{1Q} - \tilde{L}_{11}(h_1 - h_2)]\frac{\nabla T}{T^2} - \frac{1}{T}\tilde{L}_{11}(\nabla_T\mu_1 - \nabla_T\mu_2) \ , \\ \mathbf{J}'_Q &= -[\tilde{L}_{QQ} - \tilde{L}_{Q1}(h_1 - h_2)]\frac{\nabla T}{T^2} - \frac{1}{T}\tilde{L}_{Q1}(\nabla_T\mu_1 - \nabla_T\mu_2) \ . \end{aligned} \tag{A3}$$

Inserting Eqs. (2.3)—(2.5) into (A3) we find the relations which tie the $\tilde{L}_{ij}$ to the L_{ij},

$$\begin{aligned} L_{11} &= \tilde{L}_{11} \ , \\ L_{1Q} &= \tilde{L}_{1Q} - \tilde{L}_{11}(h_1 - h_2) \ , \\ L_{Q1} &= \tilde{L}_{Q1} - \tilde{L}_{11}(h_1 - h_2) \ , \\ L_{QQ} &= \tilde{L}_{QQ} - 2\tilde{L}_{1Q}(h_1 - h_2) + \tilde{L}_{11}(h_1 - h_2)^2 \ . \end{aligned} \tag{A4}$$

We notice from Eqs. (A4) that the Onsager reciprocal relations still hold for the L_{ij}. Moreover, if we express the $\tilde{L}_{ij}$ in terms of time-correlation functions involving $\mathbf{J}_1$ and $\mathbf{J}'_Q$,

$$\begin{aligned} \tilde{L}_{11} &= I(\mathbf{J}_1, \mathbf{J}_1) \ , \\ \tilde{L}_{1Q} &= \tilde{L}_{Q1} = I(\mathbf{J}_1, \mathbf{J}'_Q) \ , \\ \tilde{L}_{QQ} &= I(\mathbf{J}'_Q, \mathbf{J}'_Q) \ , \end{aligned} \tag{A5}$$

where $I(\mathbf{J}_\alpha, \mathbf{J}_\beta) = V/k_B \int_0^\infty \langle \mathbf{J}_\alpha(t)\mathbf{J}_\beta(0)\rangle_{\text{eq}} dt$, the same description holds true for the L_{ij},

$$\begin{aligned} L_{11} &= I(\mathbf{J}_1, \mathbf{J}_1) \ , \\ L_{1Q} &= L_{Q1} = I(\mathbf{J}_1, \mathbf{J}_Q) \ , \\ L_{QQ} &= I(\mathbf{J}_Q, \mathbf{J}_Q) \ . \end{aligned} \tag{A6}$$

Let us now introduce the variable $\tilde{\mathbf{J}}_Q$ defined as

$$\tilde{\mathbf{J}}_Q = \mathbf{J}'_Q - \sum_\alpha \tilde{h}_\alpha \mathbf{J}_\alpha \ , \tag{A7}$$

where $\tilde{h}_\alpha$ is given by Eq. (2.16).

This is the current that we excite via our equations of motion (see Sec. II B). According to (2.3) we can rewrite expression (A7) as

$$\tilde{\mathbf{J}}_Q = \mathbf{J}_Q + [(h_1 - \tilde{h}_1) - (h_2 - \tilde{h}_2)]\mathbf{J}_1 \ . \tag{A8}$$

Then (A6) gives

$$\begin{aligned} L_{11} &= I(\mathbf{J}_1, \mathbf{J}_1) \ , \\ L_{1Q} &= I(\mathbf{J}_1, \tilde{\mathbf{J}}_Q) - [(h_1 - \tilde{h}_1) - (h_2 - \tilde{h}_2)]I(\mathbf{J}_1, \mathbf{J}_1) \ , \\ L_{Q1} &= I(\tilde{\mathbf{J}}_q, \mathbf{J}_1) - [(h_1 - \tilde{h}_1) - (h_2 - \tilde{h}_2)]\mathbf{I}(\mathbf{J}_1, \mathbf{J}_1) \ , \\ L_{QQ} &= I(\tilde{\mathbf{J}}_Q, \tilde{\mathbf{J}}_Q) - 2[(h_1 - \tilde{h}_1) - (h_2 - \tilde{h}_2)]I(\tilde{\mathbf{J}}_Q, \mathbf{J}_1) \\ &\quad + [(h_1 - \tilde{h}_1) - (h_2 - \tilde{h}_2)]^2 I(\mathbf{J}_1, \mathbf{J}_1) \ . \end{aligned} \tag{A9}$$

Thus the difference between the physical cross coefficients and the $I(\mathbf{J}_1, \tilde{\mathbf{J}}_Q)$—which are the results of our MD calculations—depends linearly on the difference between the "microscopic" $\tilde{h}_\alpha$ and the thermodynamic h_α.

It is apparent from Eq. (A9) that the second term on the right-hand side is a correction to the cross response we measure. This quantity has a sensible statistical uncertainty, therefore either we measure with great accuracy both $[(h_1 - \tilde{h}_1) - (h_2 - \tilde{h}_2)]$ and the cross response $I(\mathbf{J}_1, \tilde{\mathbf{J}}_Q)$ or the final result is likely to have little significance. Thus we limit ourselves to the evaluation of the order of magnitude of the cross effect.

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