Comment on a Paper of Mori on Time-Correlation Expressions for Transport Properties

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An auto-correlation expression given by Mori for the thermal conductivity of a fluid is shown to be only apparently different from an expression previously derived by the author.

RECENTLY, Mori,[1] using a method due to Kubo,[2] has derived time-correlation expressions for the transport properties of fluids which are similar to expressions derived earlier by the author,[3] by a somewhat different method. In their classical version, Mori's formulas differ from the author's in two respects. Averages are taken in the grand canonical ensemble rather than the microcanonical ensemble with fixed total number, momentum, and energy, and in the case of the thermal conductivity, the flux whose time-correlation is relevant is different from the corresponding flux in the author's expression. Mori suggests that, in view of the fact that the microcanonical and grand canonical averages usually give the same result, while the quantity to be averaged is different in the two cases, there is a contradiction between the two expressions. The purpose of this comment is to show that in their classical version the two expressions differ only by quantities which are completely negligible for large systems, and that Mori's expressions are in complete agreement with the earlier expressions of the author.

In general terms, the reason why the two expressions agree even though the fluxes are different, is that time-correlations are average fluctuation products which, as is well known, may be different in different ensembles. The effect of averaging in a grand ensemble is thus just compensated by the changed flux. Before following this compensation in detail, we remark that the fluctuations of total number, momentum, and energy which are present in the grand canonical ensemble, and which have their source in the interaction of the system with surrounding reservoirs, have a much longer time scale than the fluctuations of the fluxes relevant to transport processes. Indeed, the former time-scale is the time to reach macroscopic equilibrium while the latter is the time-scale of the microscopic processes in the fluid. The fluxes are therefore ergodic in a particular microcanonical ensemble with fixed number, momentum, and energy, long before enough molecules, momentum, and energy have flowed in from the reservoirs to move the system to a significantly different microcanonical ensemble. Thus a microcanonical average is theoretically more relevant though, perhaps, practically less convenient than a grand canonical average.

The formula for the thermal conductivity given in reference 2 [Eqs. (38B), (46B)] is

$$kT^2K\mathbf{1}=\int_0^\infty d\sigma \lim_{a\to\infty} a^{-3}\langle \mathbf{B}\mathbf{B}'(\sigma)\rangle, \tag{1}$$

where K is the thermal conductivity, k, Boltzmann's constant, T, temperature, $\mathbf{1}$ the unit dyadic, and a is the side of a cubical volume to which the system is confined. $\mathbf{B}$ is the energy flux, corresponding to Mori's $\mathfrak{J}_H$, considered as a function of the positions and momenta of all the particles of the system at some particular time, t; $\mathbf{B}'(\sigma)$ is the same function of the positions and momenta at $t+\sigma$.[4] In the case of point molecules of a single species mutually exerting pairwise forces

$$\mathbf{B}=\sum_{i=1}^{N}\frac{\mathbf{p}_i}{m}\left(\frac{\mathbf{p}_i^2}{2m}+\tfrac{1}{2}\sum_{j\neq i}V(\mathbf{x}_i-\mathbf{x}_j)\right)+\sum_{i\neq j}^{N}\sum^{N}(\mathbf{x}_i-\mathbf{x}_j)\mathbf{F}_{ij}(\mathbf{p}_i+\mathbf{p}_j)/2m. \tag{2}$$

[Eq. (38c) of reference 2.] The significance of symbols is the same as in reference 2. The angular brackets signify averaging over positions and momenta at time t in a microcanonical ensemble in which the number N is fixed to be $a^3\rho$, the energy E_0 to be $a^3\epsilon$, and the total momenta $\mathbf{P}$ to be 0. K is then a function of ρ and ϵ. In the case of a single species, Mori's expression differs from Eq. (1) in the replacement of $\mathbf{B}$ by $\mathbf{B}-(H\mathbf{P}/Nm)$, where H is the enthalpy of the system, and by the replacement of the microcanonical average by a grand canonical average.

In reference 2, in order that the total number, energy, and momentum should be strictly conserved, it is assumed that the system is isolated, and the boundary conditions are periodic. Actually, this is not essential and the system may be in contact with reservoirs of these three quantities since, as we remarked above, correlation between $\mathbf{B}$ and $\mathbf{B}'$ is lost long before significant transfer from the reservoirs occurs.

Now a grand canonical ensemble permits fluctuations of all three of the quantities N, E, and $\mathbf{P}$, and can, in a certain sense, be considered to be made up of micro-

[1] H. Mori, Phys. Rev. **112**, 1829 (1958).
[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[3] M. S. Green, J. Chem. Phys. **22**, 398 (1954).

[4] We note that $\langle \mathbf{B}\rangle$ is zero in an ensemble with total momentum fixed to be zero.

canonical ensembles with various fixed values of N, E, and $\mathbf{P}$. The average, in the grand ensemble, of any phase function F can be written

$$\langle F\rangle_{GC}=\sum_N \int \exp\beta(pV-E-\mu N) \times\langle F\rangle_{NPE}\Omega(N,\mathbf{P},E)d\mathbf{P}dE, \quad (3)$$

where $\langle F\rangle_{GC}$ and $\langle F\rangle_{NPE}$ are the grand canonical and microcanonical averages, respectively. $\beta=1/kT$, p is the pressure, V the volume, μ the chemical potential, and $\Omega(N,\mathbf{P},E)$ the phase volume per unit energy and momentum interval of the microcanonical ensemble. If $\langle F\rangle_{N,P,E}$ is of the order of magnitude of N, it is well known that

$$\langle F\rangle_{GC}=\langle F\rangle_{\bar{N}0\bar{E}}, \quad (4)$$

where $\bar{N}$, 0, $\bar{E}$ are the grand canonical averages of N, $\mathbf{P}$, E at the given temperature and chemical potential. If, on the other hand, $\langle F\rangle_{NPE}$ is of the order N^2 (or larger) for some values of N, $\mathbf{P}$ or E the two sides of Eq. (4) may differ by a quantity of order N, due to the fluctuations. This may be the case even if $\langle F\rangle_{\bar{N}0\bar{E}}$ is itself of order N. If we take F to be $\mathbf{BB}'$, it is just the latter circumstance which obtains since

$$\langle \mathbf{BB}'\rangle_{NPE}\approx\langle \mathbf{B}\rangle_{NPE}\langle \mathbf{B}'\rangle_{NPE}. \quad (5)$$

Each of the factors on the right-hand side is of order N unless $\mathbf{P}=0$. Thus

$$\langle \mathbf{BB}'\rangle_{GC}\neq\langle \mathbf{BB}'\rangle_{\bar{N}0\bar{E}}. \quad (6)$$

Consider now the function $\mathbf{B}^*$ obtained by the substitution of $\mathbf{p}_i-m\mathbf{v}$ for $\mathbf{p}_i$ in $\mathbf{B}$, where $\mathbf{v}$ is the velocity of the center of gravity of all the particles,[5]

$$\mathbf{v}=\frac{1}{Nm}\sum_{i=1}^{N}\mathbf{p}_i=\frac{1}{Nm}\mathbf{P}. \quad (7)$$

$\mathbf{B}^*$ is, then, the energy flux with respect to the center of gravity of all the particles. By the principle of Galilean relativity, we have

$$\langle \mathbf{B}^*\mathbf{B}^{*\prime}\rangle_{NPE}=\langle \mathbf{BB}'\rangle_{N0E-\frac{1}{2}Nmv^2}, \quad (8)$$

i.e., the autocorrelation of $\mathbf{B}^*$ in the microcanonical ensemble N, $\mathbf{P}$, E is the same as the autocorrelation of $\mathbf{B}$ in the microcanonical ensemble $N,0,E-\frac{1}{2}Nmv^2$, where $E-\frac{1}{2}Nmv^2$ is the intrinsic energy or the energy with respect to a coordinate frame moving with the center of gravity. Since the right-hand side of Eq. (8) is of order N so is the left-hand side. Thus

$$\langle \mathbf{B}^*\mathbf{B}^{*\prime}\rangle_{GC}=\langle \mathbf{BB}'\rangle_{\bar{N}0\bar{E}}, \quad (9)$$

and the thermal conductivity can be computed by taking the autocorrelation of $\mathbf{B}^*$ in a grand ensemble.

A direct computation shows that

$$\mathbf{B}^*=\mathbf{B}-E\mathbf{v}-\mathbf{A}\cdot\mathbf{v}-Nm\mathbf{v}^2\mathbf{v}, \quad (10)$$

where $\mathbf{A}$ is the momentum flux corresponding to Mori's $\mathfrak{J}_v$. The average of $\mathbf{A}$ is $pV\mathbf{1}$ where p is the pressure and $\mathbf{1}$ the unit dyadic.

$$\mathbf{A}=\sum_{i=1}^{N}\frac{\mathbf{p}_i\mathbf{p}_i}{m}+\tfrac{1}{2}\sum_{i\neq j}^{N}\sum^{N}(\mathbf{x}_i-\mathbf{x}_j)\mathbf{F}_{ij}, \quad (11)$$

[reference 2, Eq. (27A)], and E is the total energy. We note that in Eq. (10) the last term on the right is very small since the typical magnitude of the fluctuation in $\mathbf{v}$ is $N^{-\frac{1}{2}}$ and the typical magnitude of the term is $N\times(N^{-\frac{1}{2}})^2\times N^{-\frac{1}{2}}=N^{-\frac{1}{2}}$. Similarly the typical magnitude of the quantity $\mathbf{A}-\langle\mathbf{A}\rangle$ is $N^{\frac{1}{2}}$ so that neglecting $(\mathbf{A}-\langle\mathbf{A}\rangle)\cdot\mathbf{v}$ which is of order of magnitude $N^{\frac{1}{2}}\times N^{-\frac{1}{2}}=1$, we may replace $\mathbf{A}\cdot\mathbf{v}$ by $\langle\mathbf{A}\rangle\cdot\mathbf{v}=pV\mathbf{v}$. The typical magnitude of $E-\langle E\rangle$ is also $N^{\frac{1}{2}}$ and $Ev\sim\langle E\rangle v$. The typical magnitude of quantities retained is $N^{\frac{1}{2}}$. We have, therefore, up to terms of order less than $N^{\frac{1}{2}}$

$$\mathbf{B}^*=\mathbf{B}-(\langle E\rangle+pV)\mathbf{v} =\mathbf{B}-H\mathbf{v}, \quad (12)$$

where H is the enthalpy of the system. Thus, in the case of a single component system, the thermal conductivity may be determined from the autocorrelation of $\mathbf{B}$ computed in the microcanonical ensemble N, 0, E or from the autocorrelation of $\mathbf{B}^*$ computed in a grand canonical ensemble. $\mathbf{B}^*$ corresponds up to terms of negligible order to Mori's $\mathfrak{J}_T$.

The case of several species requires no modification of our argument and the thermal conductivity as defined in reference 2 for a system of several species may be computed from the autocorrelation of $\mathbf{B}^*$ in a grand ensemble. $\mathbf{B}^*$ does not correspond to Mori's $\mathfrak{J}_T$ in this case. This difference is, however, simply due to a difference in the definition of thermal conductivity. In reference 2, the author has used a definition of thermal conductivity appropriate to the choice of fluxes corresponding to Mori's $\mathfrak{J}_H$ and $\mathfrak{J}_i$ and forces $\nabla(1/T)$ and $\nabla(-\mu_i/T)$, while Mori uses a definition appropriate to the choice of fluxes $\mathfrak{J}_T$ and $\mathfrak{J}_i$ and forces $\nabla(1/T)$ and $-(1/T)(\nabla\mu^k+s^k\nabla T)$. It has been pointed out[6] that for a number of reasons the latter is more advantageous than the former.

[5] It may avoid some confusion to remark that the symbol $\mathbf{v}$ as used in this paper has a different meaning than the same symbol in Mori's. Here $\mathbf{v}$ is a phase function, the actual velocity of the center of gravity. In Mori's paper $\mathbf{v}$ is an intensive parameter analogous to the temperature and chemical potential, which fixes the grand canonical average of the velocity of the center of gravity.

[6] J. Meixner and H. G. Reik, *Handbuch der Physik*, edited by S. Flügge (Verlag Julius Springer, Berlin, 1959), Vol. 3, Part 2, p. 438.