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Comment on Symmetry Properties of the Linear Enskog Kinetic Operators

Grzegorz Szamel[1]

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The one-particle average consistent with the structure of the revised Enskog theory is introduced. Symmetry properties of the linear kinetic operators reflecting those of the N-particle pseudo-Liouville operators are derived, implying a recently proved symmetry of kinetic expressions for equilibrium time correlation functions.

KEY WORDS: Time correlation functions; kinetic theory; hard spheres; Enskog equation.

In a recent paper by Cohen and de Schepper[1] (hereafter referred to as CS), symmetry properties of approximate kinetic expressions for equilibrium correlation functions of local physical quantities in a hard-sphere fluid were considered. Enskog theory expressions for these correlation functions were proved to be symmetric with respect to the local quantities. In this connection a new symmetric kinetic operator, which manifestly yields the desired relation, was introduced.

The purpose of this paper is to point out a different formulation of the symmetry properties of Enskog theory expressions for correlation functions. The traditional one-particle average used in CS, which traces back to the low-density Boltzmann kinetic theory, is replaced here by a new one. Consistently with the revised Enskog theory, the new average gives exact results for the static correlations. Then the structure analogous to that on the N-particle level is found on the level of the revised Enskog theory. In particular, one can prove that the linear Enskog operators for forward and backward evolution are conjugate with each other with respect to the scalar product corresponding to the one-particle average. The CS result

[1] Institute of Theoretical Physics, Warsaw University, 00-681 Warsaw, Poland.

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appears then in a very natural way without introducing any new symmetric kinetic operator. This result can be also easily generalized to the case of hard-sphere mixtures.

I restrict myself to the autocorrelation function of time-displaced μ space densities in a fluid at thermal equilibrium:

$$\begin{aligned} F(x; t \mid x'; 0) &= \langle \rho(x'; \Gamma^N)\, \rho(x; \Gamma_t^N) \rangle \\ &= \langle \rho(x'; \Gamma^N) \exp(tL)\, \rho(x; \Gamma^N) \rangle \end{aligned} \tag{1}$$

Here $\rho(x; \Gamma_t^N) = \sum_{i=1}^N \delta(x - X_i(t))$ denotes the microscopic μ space density at point $x \equiv (\mathbf{r}, \mathbf{v})$, $\Gamma_t^N \equiv (X_1(t),..., X_N(t))$ represents the microscopic state of the fluid at time t with $X_i(t) \equiv (\mathbf{R}_i(t), \mathbf{V}_i(t))$ the phase of particle i, $i = 1,..., N$, and $\Gamma^N \equiv \Gamma_{t=0}^N$. The brackets in Eq. (1) denote a canonical equilibrium ensemble average at temperature T and number density $n = N/V$, with N the number of particles and V the volume of the fluid:

$$\langle \cdots \rangle = \int d\Gamma^N \rho^{\text{eq}}(\Gamma^N) \cdots \tag{2}$$

$d\Gamma^N = dX_1 \cdots dX_N$. Note that by convention the equilibrium ensemble density ρ^{eq} stands on the left-hand side of the averaged quantity. Finally, L in Eq. (1) is the N-particle Liouville operator of the system.

From the μ space density autocorrelation function one can obtain correlation functions of all local physical quantities which are sums over one-particle contributions, in particular, the functions considered in CS.

For the continuous interparticle interactions the antisymmetry of the Liouville operator

$$\int d\Gamma^N a(\Gamma^N)\, Lb(\Gamma^N) = -\int d\Gamma^N b(\Gamma^N)\, La(\Gamma^N) \tag{3}$$

(a, b are any two phase functions) and commutation of the equilibrium ensemble density ρ^{eq} with the streaming operator $\exp(tL)$ lead to the relation

$$F(x; t \mid x'; 0) = F(x'; -t \mid x; 0) \tag{4}$$

This equation implies that the correlations between the μ space density at point x and time t and the density at x' and $t = 0$ are the same as those between the density at x' and $-t$ and the density at x and $t = 0$. Then the equivalence of the space and time reflection yields

$$F(\mathbf{r}, \mathbf{v}; t \mid \mathbf{r}', \mathbf{v}'; 0) = F(-\mathbf{r}', \mathbf{v}'; t \mid -\mathbf{r}, \mathbf{v}; 0) \tag{5}$$

Equation (5) is equivalent to the symmetry relation considered in CS [see Eq. (2.2) there].

The singularity of the hard-sphere interaction makes the problem a little more difficult: in Eq. (1) one should use different pseudo-Liouville operators[2,3] L_+ and L_- for forward and backward evolution, respectively ($t=0$ is always taken as an initial moment):

$$F(x; t \mid x'; 0) = \begin{cases} \langle \rho(x'; \Gamma^N) \exp(tL_+) \rho(x; \Gamma^N) \rangle, & t>0 \\ \langle \rho(x'; \Gamma^N) \exp(tL_-) \rho(x; \Gamma^N) \rangle, & t<0 \end{cases} \tag{6}$$

The pseudo-Liouville operators $L_\pm$ are given by

$$L_\pm = \sum_{i=1}^{N} \mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{R}_i} \pm \sum_{i>j=1}^{N} T_\pm(ij) \tag{7}$$

with binary collision operators[2,3]

$$T_\pm(ij) = \sigma^2 \int d\hat{\boldsymbol{\sigma}} \, |\mathbf{V}_{ij} \cdot \hat{\boldsymbol{\sigma}}| \, \theta(\mp \mathbf{V}_{ij} \cdot \hat{\boldsymbol{\sigma}}) \, \delta(\mathbf{R}_{ij} - \sigma\hat{\boldsymbol{\sigma}})[b_{\hat{\boldsymbol{\sigma}}}(ij) - 1] \tag{8}$$

Here $\hat{\boldsymbol{\sigma}}$ is a unit vector defining the geometry of the binary collision between the hard spheres i and j with diameter σ, $\theta(x)$ is the Heaviside step function, $\mathbf{V}_{ij} = \mathbf{V}_i - \mathbf{V}_j$, and $\mathbf{R}_{ij} = \mathbf{R}_i - \mathbf{R}_j$. The operator $b_{\hat{\boldsymbol{\sigma}}}(ij)$ replaces the velocities $\mathbf{V}_i$ and $\mathbf{V}_j$ by the velocities $\mathbf{V}_i'$ and $\mathbf{V}_j'$ resulting from the binary collision.

The operators $L_\pm$ are not related by a transposition [compare Eq. (3)] and the pseudo-streaming operators do not commute with the hard-sphere equilibrium ensemble density.[2,3] However, one can obtain the following relation[2]:

$$\langle a(\Gamma^N) \, L_+ b(\Gamma^N) \rangle = -\langle b(\Gamma^N) \, L_- a(\Gamma^N) \rangle \tag{9}$$

With the use of this equation one finds for $t>0$

$$\begin{aligned} F(x; t \mid x'; 0) &= \langle \rho(x'; \Gamma^N) \exp(tL_+) \, \rho(x; \Gamma^N) \rangle \\ &= \langle \rho(x; \Gamma^N) \exp(-tL_-) \, \rho(x'; \Gamma^N) \rangle = F(x'; -t \mid x; 0) \end{aligned} \tag{10}$$

The space reflection changes $-L_-$ into L_+ and the desired relation (5) follows.

[2] Usually in intermediate stages one introduces so-called barred psuedo-Liouville operators $\bar{L}_\mp$ which are related to $L_\pm$ by a transposition.[2,3]

Now consider approximate expressions for the autocorrelation function on the revised Enskog kinetic theory level. Here it is convenient to take the thermodynamic limit and to pass to the autocorrelation function of μ space density fluctuations. Usually one starts from the nonlinear revised Enskog equation[4] for the one-particle distribution function f,

$$\left(\frac{\partial}{\partial t}+\mathbf{v}_1\cdot\frac{\partial}{\partial \mathbf{r}_1}\right) f(x_1;t)$$
$$=\int dx_2\, \bar{T}_-(12)\, f(x_1;t)\, f(x_2;t)\, g(\mathbf{r}_1,\mathbf{r}_2\,|\,n(t)) \tag{11}$$

In Eq. (11), g is the pair distribution function calculated as if the fluid was in a nonuniform equilibrium state corresponding to the momentary density field $n(\mathbf{r};t)=\int d\mathbf{v}\, f(\mathbf{r},\mathbf{v};t)$ and $\bar{T}_-$ is one of two barred collision operators.[2,3] They are given by

$$\bar{T}_{\mp}(ij)=\sigma^2\int d\hat{\boldsymbol{\sigma}}\;|\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}}|\;\theta(\pm\mathbf{v}_{ij}\cdot\hat{\boldsymbol{\sigma}})\{\delta(\mathbf{r}_{ij}-\sigma\hat{\boldsymbol{\sigma}})\,b_{\hat{\boldsymbol{\sigma}}}(ij)-\delta(\mathbf{r}_{ij}+\sigma\hat{\boldsymbol{\sigma}})\} \tag{12}$$

Then, proceeding in the standard way,[1,5] one obtains the following result: time dependence of the autocorrelation function is determined by the linearized Enskog equation and, as the static correlations are properly included in the theory, for $t=0$ the exact expression is taken:

$$F^{\mathrm{E}}(x;t\,|\,x';0)=\exp[-t\bar{L}_-^{\mathrm{E}}(x)]\,F^{\mathrm{E}}(x\,|\,x') \tag{13}$$

$$F^{\mathrm{E}}(x\,|\,x')\equiv F^{\mathrm{E}}(x;0\,|\,x'0)$$
$$=n\phi^{\mathrm{eq}}(v)\,\delta(x-x')+n^2\phi^{\mathrm{eq}}(v)\,\phi^{\mathrm{eq}}(v')\,h^{\mathrm{eq}}(|\mathbf{r}-\mathbf{r}'|) \tag{14}$$

Here ϕ^{eq} and $h^{\mathrm{eq}}=g^{\mathrm{eq}}-1$ denote the equilibrium Maxwell velocity distribution and the equilibrium pair correlation function, respectively, and the inhomogeneous linear Enskog operator[1,4] $\bar{L}_-^{\mathrm{E}}$ is given by

$$\bar{L}_-^{\mathrm{E}}(x_1)=\mathbf{v}_1\cdot\frac{\partial}{\partial\mathbf{r}_1}-n\phi^{\mathrm{eq}}(v_1)\mathbf{v}_1\cdot\frac{\partial}{\partial\mathbf{r}_1}\int d\mathbf{r}_2[c^{\mathrm{eq}}(r_{12})-\chi\theta(r_{12}-1)]$$
$$\times\int d\mathbf{v}_2\,P_{12}-n\chi\int dx_2\,\bar{T}_-(12)(1+P_{12})\,\phi^{\mathrm{eq}}(v_2) \tag{15}$$

where $\chi=g^{\mathrm{eq}}(\sigma^+)$, c^{eq} is the Ornstein–Zernicke direct correlation function, and the permutation operator P_{12} interchanges x_1 and x_2.

However, in this way one obtains time dependence of the autocorrelation function for $t>0$ only. For $t<0$ one should start from the backward Enskog equation, i.e., from Eq. (11) with $\bar{T}_-$ replaced by $-\bar{T}_+$. In this case the standard procedure gives

$$F^{\mathrm{E}}(x; t \mid x'; 0) = \exp[-t\bar{L}_+^{\mathrm{E}}(x)]\, F^{\mathrm{E}}(x \mid x') \tag{16}$$

where the linear Enskog operator $\bar{L}_+^{\mathrm{E}}$ is given by Eq. (15) with $\bar{T}_-$ replaced by $-\bar{T}_+$.

I now show how to cast relations (13) and (16) in a scheme corresponding to that on the N-particle level. First, one should introduce a one-particle (kinetic) average, which, consistently with the revised Enskog theory, gives exact results for the static correlations of the local physical quantities:

$$\langle a(X_1)\, b(X_2)\rangle_1 = \int dX_1\, dX_2\, F^{\mathrm{E}}(X_1 \mid X_2)\, a(X_1)\, b(X_2) \tag{17}$$

Here a and b are any functions on the μ space. Having the one-particle average, one can define the corresponding scalar product:

$$\langle a \mid b\rangle_1 = \langle a(X_1)\, b(X_2)\rangle_1 \tag{18}$$

The physical interpretation of the scalar product is clear. In particular, the space of functions with finite norm corresponds to the class of local physical quantities with finite static correlations. It should be noted here that the scalar product (18) is equivalent to a scalar product generated by a physically motivated norm in the linear vector space of solutions of the linearized Enskog equation.[6]

With the help of the one-particle average Enskog theory, expressions for the autocorrelation function can be rewritten in the following way (for $t > 0$ see CS; a calculation for $t < 0$ is almost the same):

$$F^{\mathrm{E}}(x; t \mid x'; 0) = \begin{cases} \langle \rho_1(x'; X_1) \exp[tL_+^{\mathrm{E}}(X_2)]\, \rho_1(x; X_2)\rangle_1, & t > 0 \\ \langle \rho_1(x'; X_1) \exp[tL_-^{\mathrm{E}}(X_2)]\, \rho_1(x; X_2)\rangle_1, & t < 0 \end{cases} \tag{19}$$

Here $\rho_1(x; X) = \delta(x - X)$ and the inhomogeneous linear Enskog operators $L_\pm^{\mathrm{E}}$ are given by

$$\begin{aligned} L_\pm^{\mathrm{E}}(X_1) = {} & \mathbf{V}_1 \cdot \frac{\partial}{\partial \mathbf{R}_1} - n \int d\mathbf{R}_3\, [c^{\mathrm{eq}}(R_{13}) - \chi\theta(R_{13} - 1)] \\ & \times \int d\mathbf{V}_3\, \phi^{\mathrm{eq}}(V_3) \mathbf{V}_3 \cdot \frac{\partial}{\partial \mathbf{R}_3} P_{13} \pm n\chi \int dX_3\, \phi^{\mathrm{eq}}(V_3)\, T_\pm(13)(1 + P_{13}) \end{aligned} \tag{20}$$

By a straightforward calculation one can prove that the relation (9) is retained on the Enskog theory level,

$$\langle a(X_1)\, L_+^{\mathrm{E}}(X_2)\, b(X_2)\rangle_1 = -\langle b(X_1)\, L_-^{\mathrm{E}}(X_2)\, a(X_2)\rangle_1 \tag{21}$$

So, the operators L_+^{E} and $-L_-^{\mathrm{E}}$ are conjugate to each other with respect to the scalar product (18). Equation (21) makes it possible to relate Enskog theory expressions for the autocorrelation function for $t>0$ and $t<0$. In fact, one recovers the analogue of relation (10),

$$\begin{aligned} F^{\mathrm{E}}(x; t \mid x'; 0) &= \langle \rho_1(x'; X_1) \exp[tL_+^{\mathrm{E}}(X_2)]\, \rho_1(x; X_2)\rangle_1 \\ &= \langle \rho_1(x; X_1) \exp[-tL_-^{\mathrm{E}}(X_2)]\, \rho_1(x'; X_2)\rangle_1 \\ &= F^{\mathrm{E}}(x'; -t \mid x; 0) \end{aligned} \tag{22}$$

(note that here $t>0$). Now one can easily obtain the CS result. It is sufficient to note that also on the Enskog theory level the space reflection changes operators for backward evolution into operators for forward evolution: $-L_-^{\mathrm{E}}$ is changed into L_+^{E}. So, with the use of Eq. (22) one gets

$$F^{\mathrm{E}}(\mathbf{r}, \mathbf{v}; t \mid \mathbf{r}', \mathbf{v}'; 0) = F^{\mathrm{E}}(-\mathbf{r}', \mathbf{v}'; t \mid -\mathbf{r}, \mathbf{v}; 0) \tag{23}$$

The generalization of the outlined structure to hard-sphere mixtures is straightforward. For lack of space I give only the final result: the Enskog theory expression $F_{\alpha\beta}^{\mathrm{E}}$ for the autocorrelation function of fluctuations of the μ space densities of species α and β is symmetric in the following sense:

$$F_{\alpha\beta}^{\mathrm{E}}(\mathbf{r}, \mathbf{v}; t \mid \mathbf{r}', \mathbf{v}'; 0) = F_{\beta\alpha}^{\mathrm{E}}(-\mathbf{r}', \mathbf{v}'; t \mid -\mathbf{r}, \mathbf{v}; 0) \tag{24}$$

I end with three remarks.

1. The one-particle average and the corresponding scalar product advantageously replace the traditional ones, which proved very useful in the low-density Boltzmann kinetic theory considerations (ref. 1; ref. 5, Chapter V). The linear Enskog operators appear in a very natural way. Their mutual relations correspond to those between the N-particle pseudo-Liouville operators.

2. The "replacement rule" which makes it possible to obtain Enskog theory expressions for the time correlation functions now takes a very simple form. Following CS, I consider here correlations between local quantities $\sum_{i=1}^{N} a(\mathbf{V}_1)\, \delta(\mathbf{r} - \mathbf{R}_i)$ and $\sum_{j=1}^{N} b(\mathbf{V}_j)\, \delta(\mathbf{r}' - \mathbf{R}_j)$. With the use of

the representation (19) of the autocorrelation function one obtains the following rule (for a comparison see Table I in CS):

$$\left\langle \sum_{j=1}^{N} b(\mathbf{V}_j)\,\delta(\mathbf{r}'-\mathbf{R}_j)\exp(tL_\pm)\sum_{i=1}^{N} a(\mathbf{V}_i)\,\delta(\mathbf{r}-\mathbf{R}_i)\right\rangle \to \langle b(\mathbf{V}_1)\,\delta(\mathbf{r}'-\mathbf{R}_1)\exp[tL^{\mathrm{E}}_\pm(X_2)]\,a(\mathbf{V}_2)\,\delta(\mathbf{r}-\mathbf{R}_2)\rangle_1 \qquad (25)$$

Note that in relation (25) I pass from correlations of the local quantities on the N-particle level to the correlations of their fluctuations on the kinetic theory level.

3. Finally, I indicate consequences of the outlined structure for the Fourier representation of the autocorrelation function. The Fourier transform can be written with the help of a **k**-dependent average (or a corresponding scalar product in the space of velocity functions) and **k**-dependent Enskog operators $L^{\mathrm{E}}_\pm(\mathbf{k}, \mathbf{V})$. A straightforward calculation shows that the operators $L^{\mathrm{E}}_\pm(\mathbf{k}, \mathbf{V})$ are symmetric (self-adjoint) with respect to the scalar product. It is possible that this fact will facilitate the analysis of the low-**k** and long-time (hydrodynamic) behavior of the correlation functions.

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