

Equilibrium Distribution of Hard-Sphere Systems and Revised Enskog Theory

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(Received 20 June 1983)

It is shown that for hard-sphere systems in a constant external potential revised Enskog theory yields the correct single-particle equilibrium distribution function, whereas standard Enskog theory does not.

PACS numbers: 05.20.Dd

About ten years ago it was pointed out by Barajas, García-Colín, and Piña¹ that Thorne's generalization to mixtures² of Enskog's kinetic equation for a hard-sphere system³ is not consistent with the laws of irreversible thermodynamics; specifically Onsager's reciprocal relations were violated. The same could be shown to be true for several obvious modifications of Thorne's equations.^{1,4} In a paper by van Beijeren and Ernst⁵ a revised Enskog equation was proposed, which under certain approximations can be derived from the Liouville equation for hard spheres, and which is completely consistent with irreversible thermodynamics. For these reasons we believed revised Enskog theory (RET) to be an improvement over standard Enskog theory (SET). Yet, there remained doubts whether indeed RET is preferable over SET (see e.g. Ref. 6), as well as doubts whether RET is indeed the only straight-

forward modification of SET resolving the problems mentioned above.

Therefore I have proposed another argument, which even more compellingly singles out RET as preferable among all simple modifications of SET. In a recent paper⁶ López de Haro, Cohen, and Kincaid quote this argument, but only so briefly that its content does not become clear. In this paper I want to clarify the point in some detail.

The gist of my argument is that for hard-sphere systems in a stationary external potential RET leads to the correct equilibrium distribution whereas SET does not. This applies to one-component systems equally well as to mixtures. The starting point is the Enskog equation for an s -component hard-sphere mixture with constant external potential $\Phi_i(\vec{r})$ acting on particles of species i ,

$$\left[\frac{\partial}{\partial t} + \vec{v}_i \cdot \frac{\partial}{\partial \vec{r}} - \frac{1}{m_i} \frac{\partial \Phi_i(\vec{r})}{\partial \vec{r}} \cdot \frac{\partial}{\partial \vec{v}_i} \right] f_i(\vec{r}, \vec{v}_i, t) = \sum_{j=1}^s \mathcal{G}_{ij}(f_i, f_j), \quad (1a)$$

with

$$\begin{aligned} \mathcal{G}_{ij}(f_i, f_j) = & \iiint \Theta(\hat{k} \cdot \vec{v}_{ji}) (\hat{k} \cdot \vec{v}_{ji}) [\delta(\vec{r}_j - \vec{r} - \sigma_{ij} \hat{k}) \chi_{ij}(\vec{r}, \vec{r}_j | \{n_i\}) f_i(\vec{r}, \vec{v}_i', t) f_j(\vec{r}_j, \vec{v}_j', t) \\ & - \delta(\vec{r}_j - \vec{r} + \sigma_{ij} \hat{k}) \chi_{ij}(\vec{r}, \vec{r}_j | \{n_i\}) f_i(\vec{r}, \vec{v}_i, t) f_j(\vec{r}_j, \vec{v}_j, t)] d^3k d^3v_j d^3r_j. \end{aligned} \quad (1b)$$

Here $f_i(\vec{r}, \vec{v}_i, t)$ is the usual one-particle distribution function describing the probability density to find a particle of species i with velocity \vec{v}_i and position \vec{r} at time t ; Θ is the Heaviside step function; $\vec{v}_{ji} = \vec{v}_j - \vec{v}_i$; \hat{k} is the impact parameter of a binary collision, and runs over the three-dimensional unit sphere. Finally, σ_{ij} is the distance at contact between two particles of species i and j , respectively, and \vec{v}_i' and \vec{v}_j' are the restituting velocities for a collision with final velocities \vec{v}_i and \vec{v}_j and collision parameter \hat{k} . The difference between RET and SET resides in the definition of the pair correlation function at contact, χ_{ij} . In SET χ_{ij} is defined as the pair correlation function in a uniform equilibrium state evaluated as a function of the local densities at some point intermediate between \vec{r} and \vec{r}_j . Usually² this point is chosen halfway between \vec{r} and \vec{r}_j but the point of contact and the center of mass of the two particles have also been proposed.⁴ In RET χ_{ij} is defined as a functional of the local densities $n_i(\vec{r})$, which is of the same form as in a nonuniform equilibrium state.⁷

The equilibrium solution of (1) has to be a stationary solution of the form

$$f_i(\vec{r}, \vec{v}_i) = n_i(\vec{r}) (\beta m_i / 2\pi)^{3/2} \exp(-\beta m v_i^2 / 2). \quad (2)$$

Substituting this into (1), setting $\partial f_i / \partial t = 0$, and using the fact that (2) satisfies $f_i(\vec{r}, \vec{v}_i') f_j(\vec{r}_j, \vec{v}_j')$

$= f_i(\vec{r}, \vec{v}_i) f_j(\vec{r}_j, \vec{v}_j)$ one obtains, after integrating over \vec{v}_j , the result

$$\vec{v}_i \cdot \{ \nabla n_i(\vec{r}) + \beta n_i(\vec{r}) \nabla \Phi_i(\vec{r}) \} = n_i(\vec{r}) \sum_j \iint (1/|\vec{r} - \vec{r}_j|) (\vec{r} - \vec{r}_j) \cdot \vec{v}_i \delta(\vec{r}_j - \vec{r} - \sigma_{ij} \hat{k}) \chi_{ij}(\vec{r}, \vec{r}_j | \{n_i\}) n_j(\vec{r}_j) d^3k d^3r_j. \quad (3)$$

Next one can use the fact that for a hard-sphere mixture the Mayer functions are of the form

$$f_{ij}(r) = \Theta(r - \sigma_{ij}) - 1 \quad (4)$$

to rewrite (3) in the form

$$\vec{v}_i \cdot \{ \nabla \ln n_i(\vec{r}) + \beta \nabla \Phi_i(\vec{r}) \} = \vec{v}_i \cdot \sum_j [\partial f_{ij}(|\vec{r} - \vec{r}_j|) / \partial \vec{r}] \chi_{ij}(\vec{r}, \vec{r}_j | \{n_i\}) n_j(\vec{r}_j) d^3r_j. \quad (5)$$

This equation must be valid for arbitrary \vec{v}_i . Hence follow the relations

$$\nabla \ln n_i(\vec{r}) + \beta \nabla \Phi_i(\vec{r}) = \int [\partial f_{ij}(|\vec{r} - \vec{r}_j|) / \partial \vec{r}] \chi_{ij}(\vec{r}, \vec{r}_j | \{n_i\}) n_j(\vec{r}_j) d^3r_j. \quad (6)$$

These are nothing but the Born-Green equations⁸ for the hard-sphere mixture under consideration, provided the pair correlation functions χ_{ij} in the presence of the external potentials $\{\Phi_i\}$ depend functionally on $\{n_i\}$ in the way prescribed by equilibrium statistical mechanics.⁷ This follows as well from the fact that in equilibrium the revised Enskog equation (1) becomes identical to the first Bogoliubov-Born-Green-Kirkwood-Yvon-hierarchy equation for a hard-sphere mixture,⁹ again provided the functionals χ_{ij} are of the form prescribed by equilibrium statistical mechanics. As is well known (6) defines a set of integral equations for the density fields $\{n_i\}$. It is obvious that the solutions of these equations depend on the functional form of the pair correlation functions χ_{ij} . Only if the latter is chosen as described above will the resulting density fields be of the form required by equilibrium statistical mechanics. Equation (6) may be interpreted in still another way by using the identity

$$\nabla \beta \mu_i(\vec{r} | \{n_i\}) = \nabla \ln n_i(\vec{r}) - \sum_j \int [\partial f_{ij}(|\vec{r} - \vec{r}_j|) / \partial \vec{r}] \chi_{ij}(\vec{r}, \vec{r}_j | \{n_i\}) n_j(\vec{r}_j) d^3r_j. \quad (7)$$

Here $\mu_i(\vec{r} | \{n_i\})$ is the so-called intrinsic chemical potential of species 1, which can be defined as a functional of $\{n_i\}$ through a Mayer expansion. The explicit form of this expansion is given, e.g., in equation (4.5) of Ref. 7. Applying a gradient with respect to \vec{r} to the latter equation immediately yields (7). Insertion of (7) into (6) leads to the result

$$\nabla \beta [\Phi_i(\vec{r}) + \mu_i(\vec{r} | \{n_i\})] = 0, \quad (8)$$

whence follow the well-known equilibrium conditions

$$\Phi_i(\vec{r}) + \mu_i(\vec{r} | \{n_i\}) = \mu_i = \text{const.} \quad (9)$$

Just as (6), these equations determine the equilibrium density fields as functionals of the external potentials $\{\Phi_i\}$. Again, a different choice for the dependence of χ_{ij} on the density fields would lead to a set of equilibrium conditions similar to (9), but the functional dependence of the intrinsic chemical potentials on the densities would differ from that prescribed by equilibrium statistical mechanics.

Hence we may conclude that among all variants of the Enskog theory obtained by choosing different options for the functional form of the χ_{ij} , only revised Enskog theory is consistent with standard equilibrium statistical mechanics if arbitrary ex-

ternal potentials $\Phi_i(\vec{r})$ are allowed for.

Karkheck and Stell⁹ have shown that for SET a monotonically increasing entropy functional can be defined, just as can be done for RET.¹⁰ However, as they pointed out, for mixtures the thermodynamic driving forces resulting from this entropy functional do not coincide with the phenomenological ones, and again, the argument given above shows that in the presence of external potentials the state of maximal entropy for this equation does not coincide with the correct nonuniform equilibrium state.

To avoid misunderstandings I want to stress the well-known fact that for one-component systems RET and SET yield identical hydrodynamic equations through the Navier-Stokes level of description, whether or not an external potential is present. Beyond the Navier-Stokes level there are differences and for hard-sphere mixtures differences show up already at the Navier-Stokes level. Finally, I want to remind the reader that RET, just as SET, is not an exact kinetic theory, since velocity correlations due to memory effects (recollisions) are not included.

The author acknowledges partial support for the work discussed here by a NATO grant for International Collaboration in Research.

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