Journal of Statistical Physics, Vol. 11, No. 5, 1974

On a Modified Thorne Kinetic Equation for a Binary Mixture of Rigid Spheres

E. Piña[1,2]

Received December 28, 1973

Thorne's kinetic equation for a binary mixture of hard spheres has been corrected to be consistent with irreversible thermodynamics. It has been found necessary to change the functions that take into account the shielding and excluded volume in the collision of molecules. On the other hand, irreversible thermodynamics does not give any prescription to fix the location where the modified functions are to be evaluated.

KEY WORDS: Transport coefficients; rigid spheres; binary mixture; modified Thorne theory; comparison between kinetic theory and irreversible thermodynamics; first order in the density.

In a previous paper,(1) Barajas, García-Colín, and Piña have pointed out the failure of the Thorne's extension,(2) for binary mixtures, of the Enskog kinetic equation for dense gases of rigid spheres. It was shown that there is an inconsistency of Thorne's kinetic equations with irreversible thermodynamics, at least for those diffusional effects which are of second order in the density.

Thorne's kinetic equations are reviewed here, in an attempt to find consistency with irreversible thermodynamics, but keeping the Enskog ideas as far as possible.

---

[1] Instituto Mexicano del Petróleo, Mexico City, Mexico.

[2] Also at Escuela Superior de Física y Matemáticas, Instituto Politécnico Nacional, Zacatenco, Mexico City, Mexico.

A Thorne type system of kinetic equations is considered which written in standard notation is⁽¹⁾

$$\begin{aligned}\frac{\partial f_1}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}} = \iint & [\chi_{11}(\mathbf{r} + \tfrac{1}{2}\sigma_{11}\hat{\mathbf{k}}) f'_{1'}(\mathbf{r} + \sigma_{11}\hat{\mathbf{k}}) f_1'(\mathbf{r}) \\ & - \chi_{11}(\mathbf{r} - \tfrac{1}{2}\sigma_{11}\hat{\mathbf{k}}) f_{1'}(\mathbf{r} - \sigma_{11}\hat{\mathbf{k}}) f_1(\mathbf{r})] \sigma_{11}^2 \mathbf{g}_{11} \cdot \hat{\mathbf{k}}\, d\hat{\mathbf{k}}\, d\mathbf{v}_{1'} \\ & + \iint [\chi_{12}(\mathbf{r} + \tfrac{1}{2}\alpha_1\hat{\mathbf{k}}) f_2'(\mathbf{r} + \sigma_{12}\hat{\mathbf{k}}) f_1'(\mathbf{r}) \\ & - \chi_{12}(\mathbf{r} - \tfrac{1}{2}\alpha_1\hat{\mathbf{k}}) f_2(\mathbf{r} - \sigma_{12}\hat{\mathbf{k}}) f_1(\mathbf{r})] \sigma_{12}^2 \mathbf{g}_{21} \cdot \hat{\mathbf{k}}\, d\hat{\mathbf{k}}\, d\mathbf{v}_2 \qquad (1)\end{aligned}$$

with a corresponding equation obtained by interchanging 1 and 2. In these equations α_i $(i = 1, 2)$ is a parameter introduced to indicate the point of evaluation of the χ_{12} function.

Two modifications (the second a new one) to Thorne's kinetic equations are considered here. Both affect the χ_{ij} functions, which are the ones that account for the "shielding" and the excluded volume in a collision between molecules of species i and j:

1. The function χ_{11} is evaluated at an arbitrary point located between the centers of the colliding molecules⁽¹⁾ and determined by the α_i parameters.
2. The "virial" coefficients for the χ_{ij} functions (zeroth order and first order in density) are also put undetermined at the beginning and are fixed at the end by the compatibility requirements.

The phenomenological information that the Enskog solution for these modified Thorne equations has to satisfy is the following:

1. The pressure, appearing twice in the Euler balance equations, is assumed to be given by the usual virial expansion, up to third order in density, with constant coefficients (hard spheres), namely

$$p = kT\left\{n_1 + n_2 + \sum_{ij} B_{ij} n_i n_j + \sum_{ijk} B_{ijk} n_i n_j n_k\right\} \qquad (2)$$

where the B coefficients are symmetric with respect to any subindex interchange.

2. The diffusional force is constrained to be compatible up to second order in density with the phenomenological one, and determined by the virial equation of state (2) and the energy expression given by the Euler balance equations. As was pointed out previously,⁽¹⁾ this diffusional force is only fixed up to a term proportional to a temperature gradient.

As a result of these requirements, the coefficients in the new χ functions are determined according to

$$\begin{aligned}
\chi_{11} &= \left(B_{11} + n_1 B_{111} + n_2 B_{112} \frac{3\alpha_2}{\alpha_1 + 2\alpha_2}\right) \Big/ \frac{2}{3}\pi\sigma_{11}^3 \\
\chi_{12} = \chi_{21} &= \left(B_{12} + n_1 B_{112} \frac{3\sigma_{12}}{\alpha_1 + 2\alpha_2} + n_2 B_{221} \frac{3\sigma_{12}}{\alpha_2 + 2\alpha_1}\right) \Big/ \frac{2}{3}\pi\sigma_{12}^3 \\
\chi_{22} &= \left(B_{22} + n_2 B_{222} + n_1 B_{221} \frac{3\alpha_1}{\alpha_2 + 2\alpha_1}\right) \Big/ \frac{2}{3}\pi\sigma_{22}^3
\end{aligned} \tag{3}$$

with an additional condition

$$\alpha_1 + \alpha_2 = 2\sigma_{12} \tag{4}$$

This is also a symmetry requirement.

In the low-density limit one expects that $\chi_{ij} \to 1$ and therefore

$$B_{ij} = \pi\sigma^{\frac{2}{3}3}_{ij} \tag{5}$$

in agreement with the well-known second virial coefficients for hard spheres.

In order to compare our results with Thorne's previous results, we note that both in Thorne's case and in this new case one has

$$p = kT\left(n_1 + n_2 + \sum_{ij} \tfrac{2}{3}\pi\sigma_{ij}^3 n_i n_j \chi_{ij}\right) \tag{6}$$

Also, the Thorne χ_{ij} functions give correctly the first three virial coefficients in (6). This is so because the χ_{ij} functions are related to the pair correlation function of the exact solution of the generalized Percus–Yevick equation for a mixture of hard spheres.(3)

Our B_{ijk} coefficients were determined therefore from Thorne's original equation of state, after symmetrization. By comparison one finds that the coefficients of n_i in our χ_{ii}, namely $B_{iii}/\frac{2}{3}\pi\sigma_{ii}^3$ ($i = 1, 2$), are the same as in Thorne's or in the pure component case.

However, the other first-order density coefficients in Thorne's χ_{ij} functions cannot be expressed as in Eq. (3), for any selection of the evaluation point. The χ_{ij} functions in Thorne's kinetic equations are then in conflict with irreversible thermodynamics.

Our χ_{ij} functions have a simple form in the case where the evaluation point for the χ_{12} function is located at the point in the middle of the line joining the centers of the colliding molecules; one has in this case

$$\chi_{ij} = (1/B_{ij})\left(B_{ij} + \sum_k n_k B_{ijk}\right) \tag{7}$$

In the other hand, the Thorne computations of the transport coefficients are not formally affected by the modified χ functions if the explicit dependence (3) is not used. However, the numerical value changes with the new form of those functions.

This theory still has serious difficulties because no physical argument is available to fix the point of evaluation of the χ_{12} functions and hence the numerical value of the transport coefficients cannot be calculated. In particular, the Onsager relationships are satisfied as in the low-density limit$^{(4)}$ and do not give a new prescription to fix such point.

ACKNOWLEDGMENTS

I would like to thank L. S. García-Colín, J. A. Robles-Domínguez, and R. Alexander for several helpful discussions of this work.

REFERENCES

1. L. Barajas, L. S. García-Colín, and E. Piña, *J. Stat. Phys.* **7**:161 (1973).
2. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 2nd ed., Chapter 16, Cambridge Univ. Press, England (1952); M. K. Tham and K. E. Gubbins, *J. Chem. Phys.* **55**:268 (1971).
3. J. L. Lebowitz, *Phys. Rev.* **133**A:895 (1964); J. A. Robles-Domínguez, private communication.
4. E. Piña, to be published.