TRANSPORT COEFFICIENTS FROM THORNE'S MODIFIED EQUATION FOR BINARY MIXTURES

E. Piña, L. Barajas and L. S. García-Colín*

Instituto Mexicano del Petróleo,

México 14, D. F., México.

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ABSTRACT: The transport coefficients for a binary mixture of hard spheres which originate from Thorne's kinetic equation corrected for inconsistencies that appear when evaluating collision dependent quantities, are obtained explicitly. The experimentally measurable quantities related to diffusional processes and their compatibility with Non-equilibrium thermodynamics is discussed.

In a previous communication,[1] we have pointed out some inconsistencies that arise from the specific way in which collisional dependent quantities which appear in Thorne's method to obtain transport coefficients, are evaluated. In particular, the correct expression for the diffusion force is,

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*Also at the Facultad de Ciencias, Universidad Nacional de México. México.

$$d_{12}^{(T)} = \frac{\rho_1 \rho_2}{\rho n k_B T} \left\{ \frac{1}{\rho_1} \nabla p_1 - \frac{1}{\rho_2} \nabla p_2 \right\} + \frac{n_2}{n} b_{11}^{11} \rho_1 \chi_{12} \left\{ \nabla \ln \frac{n_2}{n_1} + \right. \tag{1}$$

$$\left. + (M_1 - M_2) \nabla \ln T + \frac{\sigma_1 - \sigma_2}{\sigma_1 + \sigma_2} \nabla \ln \chi_{12} \right\}$$

the notation being the standard one[2]. If this force is used in the kinetic equations for the mixture and care is also taken when the potential contribution to the fluxes of molecular properties during collisions is calculated, namely, by choosing a plane passing through the point of contact between the molecules, the following results are obtained

a): The coefficient of diffusion as well as the shear viscosity for the gas are identical to Thorne's results. The thermal diffusion ratio is χ_{12} times the value quoted by Thorne. This could be a misprint or an error in his calculations but it is independent of d_{12}. A similar comment applies to the thermal conductivity which is k_B^{-1} times Thorne's value, k_B being Boltzmann's constant.

b): The bulk viscosity of the mixture is given by

$$\zeta = 4/9\, (\pi k_B T)^{\frac{1}{2}} \{ m_1^{\frac{1}{2}} n_1^2 \chi_1 \sigma_1^4 + 2 (2 m_0 M_1 M_2)^{\frac{1}{2}} n_1 n_2 \sigma_{12}^4 \chi_{12} + m_2^{\frac{1}{2}} n_2^2 \chi_2 \sigma_2^4 \} \tag{2}$$

showing that it is an effect at least of order n^2. This result is identical to the one obtained by Tham and Gubbins[3].

c): The corrected form of d_{12} shows itself when the expression for the diffusion flux is compared with those based on irreversible thermodynamics and the resulting transport coefficients are given in terms of those used by experimentalists.

The expression used by Thorne for the diffusion flux is the standard one[2] in kinetic theory, namely,

$$\mathbf{C}_1 - \mathbf{C}_2 = - \frac{n_2}{n_1 n_2} D_{12} \left(d_{12} + \frac{k_T}{T} \frac{\partial T}{\partial r} \right) \tag{3}$$

This equation is almost identical to the one used in irreversible thermodynamics[4] where d_{12} is a known expression given in terms of thermodynamic quantities. If one now uses eq. (1), the corrected form of Thorne's diffusion force and compares it with the corresponding thermodynamic force computed from the equation of state for the binary mixture of hard spheres[5] one finds, in powers of density, the following results:

i): To zero order (corresponding to the dilute mixture) both vectors are identical.

ii): To first order in the density $\boldsymbol{d}_{12}^{(T)}$, eq. (1), does not correspond to $\boldsymbol{d}_{12}^{(H)}$ (Hirschfelder's expression, cf. ref. (4)) but the difference is proportional to a term containing the temperature gradient. Henceforth it is possible to re-arrange the terms in the right hand side of eq. (3) and cast it in $\boldsymbol{d}_{12}^{(H)}$ form. When this is done the diffusion flux is consistent with irreversible thermodynamics but the thermal diffusion ratios are different. In fact, one can show that

$$K_T^{(H)} - K_T^{(Th)} = \frac{n_1 n_2}{n^2} \frac{2\pi}{3} \left\{ n_1 \sigma_1^3 - n_2 \sigma_2^3 + 2\sigma_{12}^3 \frac{m_2 n_2 - m_1 n_1}{m_1 + m_2} \right\} \tag{4}$$

To this order in the density the diffusion coefficients D_{12} are the same in both cases, (although care must be taken for different notations)

iii): To second order in the density the difference between the two $\boldsymbol{d}_{12}$ vectors is much more complicated, namely,

$$\boldsymbol{d}_{12}^{(H)} - \boldsymbol{d}_{12}^{(T)} = \frac{\pi^2}{18} \sigma_1 \sigma_2 \frac{\sigma_1 - \sigma_2}{2} \frac{n_1 - n_2}{n_1 + n_2} \left\{ \sigma_1^3 \frac{\partial n_1}{\partial r} + \sigma_2^3 \frac{\partial n_2}{\partial r} \right\} \tag{5}$$

plus a term proportional to a temperature gradient which may be included in K_T. Thus, eq. (5) shows that to this order in the density, Thorne's corrected force is inconsistent with irreversible thermodynamics.

Finally we have related the diffusion coefficient and the thermal diffusion ratio obtained from kinetic theory with the forms for diffusional transport coefficients which are more closely adapted to experimental measurements[6,7]. In refs. (6) and (7), the diffusion coefficient D is related to D_{12} appearing in eq. (3) through the expression

$$D = D_{12} \frac{n\rho_1 \rho_2 m_1 m_2}{\rho^3 k_B T} \left(\frac{\partial \mu}{\partial c_1}\right)_{P,T} \qquad (6)$$

where c_1 is the mass concentration of species 1 and μ is the chemical potential of the mixture, $\mu = m_1^{-1}\mu_1 - m_2^{-1}\mu_2$. Also, the thermal diffusion ratio used is not identical to $K_T^{(H)}$ but are related through the expression

$$\frac{n^2}{n_1 n_2} D_{12} K_T^{(H)} = \frac{\rho^2}{\rho_1 \rho_2} D K_T \qquad (7)$$

which thus relates $K_T^{(H)}$ with K_T. This quantity is also related to the Soret and Dufour coefficients, the relationships among all of them being well known[7]. The details of all the calculations bearing the results quoted in this letter will be published elsewhere.

REFERENCES

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RESUMEN

Se obtienen explícitamente los coeficientes de transporte para una mezcla binaria de esferas duras, calculadas a partir de la ecuación cinética de Thorne, una vez que se han corregido algunas inconsistencias que aparecen al calcular cantidades dependientes de la colisión. Se discuten también cantidades medibles experimentalmente relacionadas a procesos de difusión, así como su compatibilidad con la termodinámica fuera de equilibrio.