Thermophoretic Properties of Nonspherical Particles and Large Molecules

The $Kn_p \gg 1$ gas-kinetic approach of Waldmann (1959, 1961) is extended to predict the thermophoretic properties of nonspherical aerosol *particles*, and massive nonspherical gas *molecules*. Calculations are presented for sphero-cylindrical particles (molecules) of arbitrary aspect ratio, L/R, predicting that in a local temperature gradient ***grad** T* they will thermophoretically drift: i) more rapidly when their major axis is aligned with $-$***grad** T*; ii) at a velocity different from that of a sphere of radius R equal to the cylinder radius; iii) at an angle with respect to $-$***grad** T* when their major axis is not parallel to, nor perpendicular to, $-$***grad** T*; and iv) *without* a net torque tending to orient the particle with respect to $-$***grad** T*. Important corollaries are that nonspherical particles in a temperature gradient should also experience new thermophoretically-induced coagulation mechanisms. We predict that the orientation-averaged thermal diffusion factor α_T should increase approximately linearly with particle (molecule) length.

Pedro Garcia-Ybarra
Daniel E. Rosner
High Temperature Chemical Reaction
Engineering Laboratory
Department Chemical Engineering
Yale University
New Haven, CT 06520

Introduction

The importance of thermal diffusion *mass* transport in gases (Soret effect for vapors, and "thermophoresis" for submicron aerosol particles) in many technologies has been recently discussed (*e.g.*, Rosner, 1980). In addition, its decisive influence on the appearance of several kinds of combustion wave instabilities has been recently studied (Garcia-Ybarra *et al.*, 1984). But in all areas, accurate predictions require a knowledge of the *thermal diffusion factor* α_T of the transported species in the prevailing gaseous mixture. Although theoretical and experimental values of the other transport coefficients are readily available in the literature (*e.g.*, Galloway and Sage, 1967) little is known about the thermal diffusion coefficient of, say, long-chain paraffin hydrocarbons and other gaseous fuels. Theoretically, the difficulty comes from the great complexity of available kinetic theory when one must take into account the "nonspherical" nature of the intermolecular potential, as well as the effects of internal degrees of freedom. Molecules of the usual fuels and adduct intermediates formed from them are complex enough to make both effects nonnegligible.

A classical kinetic theory for a gas of rigid sphero-cylinders has been elaborated by Curtiss and his coworkers (Curtiss, 1956; Curtiss and Muckenfuss, 1957; Muckenfuss and Curtiss, 1958). Based on the Wang Chang-Uhlenbeck-de Boer semiclassical treatment of polyatomic gases, expressions for the transport coefficients have been obtained (Monchick *et al.*, 1963, 1968) even for the case of slightly nonspherical molecules (Matzen and Hoffman, 1975). Nevertheless, for many practical purposes, such expressions are too complicated and a more tractable approach is needed. For spherical potentials, Fristrom and Monchick (1988) have recently suggested a phenomenological relationship to easily compute the thermal diffusion factor of molecules having internal degrees of freedom, but the case of highly nonspherical polyatomic molecules seems to be out of the realm of practical applicability *via* gas kinetic theory. The alternative pursued here is based on one used by Waldmann (1959, 1968) in problems related to aerosol *particle* diffusion. The method, initially developed to interpret Millikan's oil drop experiment (Epstein, 1924), considers the carrier gas to be in a nonequilibrium state in which the scale Λ of the thermodynamic inhomogeneities (*e.g.*, gradient of temperature) is very large compared with the gas mean-free path l. The corresponding carrier gas Knudsen number $Kn = l/\Lambda$ is a small parameter and the results of the Enskog-Chapman theory apply to the corresponding distribution function for the molecule velocities. Immersed in this carrier gas a very heavy particle is assumed to be in local thermal equilibrium with its neighborhood and to have a size R very small compared to the gas mean-free path, in such a way

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P. Garcia-Ybarra is a visiting scholar, Yale HTCRE Laboratory. His permanent address is U.N.E.D. Dpto. Fisica Fundamental, Apdo.60141, Madrid 28080, Spain.
Correspondence concerning this paper should be addressed to D. E. Rosner.

that the associated particle Knudsen number $Kn_p = l/(2R)$ is a *large* parameter. In these circumstances, the "hydrodynamic" (continuum) limit fails and a "free-molecule" flow approach is adopted to calculate the force on the particle by adding all of the impulses transferred to it by the colliding gas molecules. In addition, an effective spherical shape for the particle was assumed by Epstein and Waldmann and the effects arising from its complex local and internal structure were summarized in a single parameter: the fraction of the colliding molecules diffusely reflected, *a*. Results of this theory have been tested by comparison with the corresponding ones obtained from the kinetic theory of polyatomic gases under suitable assumptions (Mason and Chapman, 1962; Monchick *et al.*, 1963), *i.e.*, in the quasi-Lorentzian or "dusty-gas" model (Mason, 1957; Fernandez de la Mora and Mercer, 1982) and excellent agreement has been found.

A more general criterion for the applicability of Waldmann's approach and one which motivates our extensions from aerosol *particles* to heavy vapor *molecules* can be obtained by imposing the condition that the displacement of the "particle" during a time of the order of the characteristic time τ between gas/particle collisions must be small compared to its own dimensions. For the illustrative case of a large sphere of radius R, this condition is simply $V\tau \ll 2R$, V being the particle velocity. Now the mean momentum transferred to the particle per collision with the gas molecules is of the order $MV \sim (\pi/2)m\bar{c}$, where $\bar{c}$ is the mean gas molecule velocity, and M and m are the particle and molecule masses, respectively. Moreover, the time τ may be roughly estimated as $\tau \sim 4/(\pi R^2 N \bar{c})$, N being the number of molecules per unit volume. Therefore, this criterion can be written:

$$8\pi\sqrt{2}\cdot\frac{m}{M}\cdot\left(\frac{r_g}{R}\right)^2\cdot Kn_p \ll 1 \tag{1}$$

where we used $l = (4\sqrt{2}\pi N r_g^2)^{-1}$ for the gas mean-free path, and r_g is the gas molecule radius.

With respect to particle rotations, if I is the particle moment of inertia, ω is its angular velocity and $F \cdot R$ the torque due to a collision, we have $I\omega \sim \int FRdt$ but $I \sim MR^2$ and $\int Fdt \sim m\bar{c}$, then the inverse of the characteristic rotation time of the particle is given by $\omega \sim m\bar{c}/MR$. Thus, we find that criterion 1 is equivalent to $\omega\tau \ll 1$, which indicates that the particle does not appreciably rotate between successive molecular impacts. These conditions can also be satisfied for sufficiently small *nonspherical* aerosol particles and even sufficiently large vapor molecules in a "light" carrier gas. In general, the nonsphericity of a particle should play an important role in determining its transport characteristics, and it will *not* be sufficient to assume an effective spherical shape for a particle, hoping to include "nonsphericity effects" in the diffuse reflection coefficient, *a*. Rather, one must consider the actual overall particle shape and retain this coefficient only to account for the more localized effects of internal degrees of freedom. Fortunately, the Waldmann approach, as described below, provides the means to predict such "shape" effects.

Since we need $Kn_p \gg 1$ to use results valid in the free-molecule flow limit, condition 1 imposes an important restriction to the theory. Its range of validity can be roughly estimated from Figure 1, where we have plotted the dimensionless group appearing in Eq. 1 and the particle Knudsen number as functions of the particle size R (we have, for this illustration only, assumed spherical shapes and equal mass densities, with $r_g = 1.6$ Å for the gas molecule radius). Evidently, for the nominal conditions $p \approx 1$ atm, $T \approx 1{,}000$ K, one can expect the present theory to be valid for small particles or giant molecules in the approximate range: 10–100 Å in size.

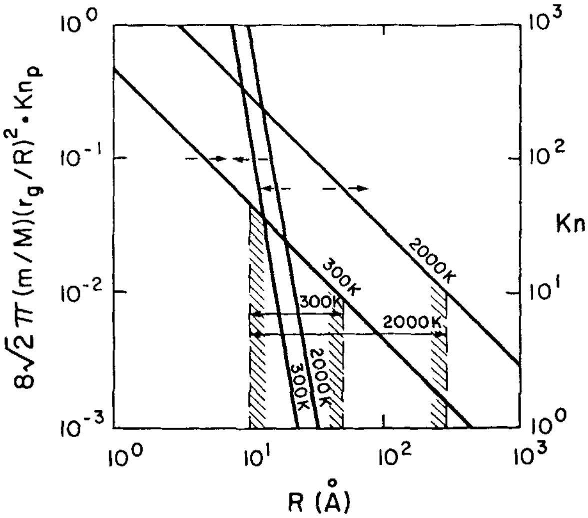

Figure 1. Knudsen number Kn_p and group $8\pi\sqrt{2}(m/M)\cdot(r_g/R)^2\cdot Kn_p$ as functions of the effective aerosol particle radius R.

The shaded regions show the regime of validity of the present approach for $p \approx 1$ atm, $T \approx 300$ and 2,000 K.

Recapitulating, the idea developed in this introductory paper is to apply the Waldmann approach to investigate the thermal diffusion of heavy nonspherical *molecules* (*e.g.*, paraffin hydrocarbons) in low molecular weight atmospheres, although our results also apply, of course, to the very important thermophoretic properties of small nonspherical "aerosol" particles such as "soot" aggregates formed in combustion (Rosner, 1986). In the following sections, we therefore extend Waldmann's theory to nonspherical particles and then particularize our results to spherocylinders as an approximation to the effective shape of paraffin molecules.

Method of Calculation

We proceed here by first evaluating the thermophoretic and resistance forces on a particle of convex (but otherwise arbitrary) shape, using Waldmann's theory.

Let us consider a gas subjected to a temperature gradient in such a way that its linearized distribution function for molecular velocities, as given by the Enskog-Chapman first-order approximation, is (*e.g.*, Chapter 5 of Ferziger and Kaper, 1972):

$$f^- = f_M \cdot (1 + \phi) \tag{2}$$

where f_M is the local Maxwellian distribution function:

$$f_M = N\left(\frac{m}{2\pi k_B T}\right)^{3/2} \cdot \exp\left(-\frac{mC^2}{2\,k_B T}\right) \tag{3}$$

and ϕ is the correction due to each of the prevailing gradients, *i.e.*:

$$\phi = -\frac{3\mu}{2Nk_BT}\cdot\left(\frac{mC^2}{2k_BT}-\frac{5}{2}\right)\boldsymbol{C}\cdot\textbf{grad}\ln T - \frac{m\mu}{Nk_B^2T^2}\cdot\left(\boldsymbol{CC}-\frac{1}{3}C^2\boldsymbol{I}\right):\textbf{grad}\,\boldsymbol{v} \tag{4}$$

Here N is the local molecular number density, m the molecular mass, k_B the Boltzmann constant, T the absolute temperature, $\boldsymbol{C}$ the molecular velocity, μ the dynamic viscosity coefficient, $\boldsymbol{I}$ the unit matrix, and $\boldsymbol{v}$ the macroscopic gas velocity.

The relative importance of the temperature and velocity gradient terms in ϕ is:

$$\frac{\mathbf{C}\cdot\textbf{grad}\ln T}{\boldsymbol{CC}:\textbf{grad}\,\boldsymbol{v}}\sim\frac{1}{Ma}\gg 1 \quad \text{iff} \quad \frac{\delta_h}{\delta_{mom}}\sim O(1) \tag{5}$$

where $Ma \approx v/C \ll 1$, is the local Mach number, and δ_h and δ_{mom} are the thermal and momentum boundary layer thickness, respectively. Since we will restrict our attention to subsonic flows, in what follows we will disregard the contribution of velocity gradients to ϕ.

Let us assume that the particle is moving with respect to the gas with a constant velocity $\boldsymbol{V}$ small in magnitude compared with the average gas molecular velocity. Then, written in a frame attached to the particle and neglecting second order terms, the distribution function is:

$$f^- \simeq N\left(\frac{h}{\pi}\right)^{3/2}\cdot e^{-hc^2}\cdot\left[1-2h\boldsymbol{c}\cdot\boldsymbol{V}-3\nu h\left(hc^2-\frac{5}{2}\right)\boldsymbol{c}\cdot\textbf{grad}\ln T\right] \tag{6}$$

where $\boldsymbol{c} \equiv \boldsymbol{C} - \boldsymbol{V}$ is the molecule velocity relative to the moving particle,

$$h \equiv \frac{m}{2\,k_BT} \tag{7}$$

and

$$\nu \equiv \frac{\mu}{Nm} \tag{8}$$

is the momentum diffusivity ("kinematic viscosity" coefficient).

Let $d^2\Sigma$ be an element of the particle surface and $\boldsymbol{n}$ the exterior normal unit vector that forms with the tangential vectors $\boldsymbol{t}_1$ and $\boldsymbol{t}_2$ a local orthogonal system. The number of molecules striking per unit time on $d^2\Sigma$ with velocities between $\boldsymbol{c}$ and $\boldsymbol{c} + d^3\boldsymbol{c}$ is $-f^-(\boldsymbol{c}\cdot\boldsymbol{n})d^3\boldsymbol{c}d^2\Sigma$, where attention must be restricted to $(\boldsymbol{c}\cdot\boldsymbol{n}) < 0$. Then the force $d\boldsymbol{F}_I$ exerted on $d^2\Sigma$ by the impinging molecules is:

$$d\boldsymbol{F}_I = -d^2\Sigma\, m\int_{\boldsymbol{c}\cdot\boldsymbol{n}<0}\boldsymbol{c}(\boldsymbol{c}\cdot\boldsymbol{n})f^-\,d^3\boldsymbol{c} \tag{9}$$

Projecting in the normal and tangential directions and performing the indicated integral, we find:

$$\boldsymbol{n}\cdot d\boldsymbol{F}_I = -\frac{mN}{\sqrt{\pi h}}\cdot\left(\frac{1}{4}\sqrt{\frac{\pi}{h}}+\boldsymbol{n}\cdot\boldsymbol{V}+\frac{3\nu}{4}\boldsymbol{n}\cdot\textbf{grad}\ln T\right)d^2\Sigma \tag{10}$$

$$\boldsymbol{t}_i\cdot d\boldsymbol{F}_I = -\frac{mN}{2\sqrt{\pi h}}\cdot\left(\boldsymbol{t}_i\cdot\boldsymbol{V}+\frac{3\nu}{4}\boldsymbol{t}_i\cdot\textbf{grad}\ln T\right)d^2\Sigma \quad (i=1,2) \tag{11}$$

To take into account inelastic collisions, it is assumed that a fraction a of the total number of molecules impinging per unit time undergoes diffuse (nonspecular) reflection and is therefore scattered with a Maxwellian distribution function f^+, that is:

$$f^+ = N_D\left(\frac{h}{\pi}\right)^{3/2}\cdot\exp\left(-hc^2\right) \tag{12}$$

where the coefficient N_D must be chosen such that the total number per unit time of molecules diffusively reflected equalizes the fraction a of the impinging molecules. This condition leads to:

$$N_D = a\,N\cdot\left(1+\sqrt{\pi h}\,\boldsymbol{V}\cdot\boldsymbol{n}\right) \tag{13}$$

Once f^+ is known we can evaluate the corresponding force $d\boldsymbol{F}_{DR}$ on the surface element $d^2\Sigma$, which is given by:

$$d\boldsymbol{F}_{DR} = -d^2\Sigma m\int_{\boldsymbol{c}\cdot\boldsymbol{n}>0}\boldsymbol{c}(\boldsymbol{c}\cdot\boldsymbol{n})f^+\,d^3\boldsymbol{c} \tag{14}$$

After projecting in the normal and tangential directions, and evaluating the indicated integrals, we find:

$$\boldsymbol{n}\cdot d\boldsymbol{F}_{DR} = -d^2\Sigma\frac{amN}{4}\sqrt{\frac{\pi}{h}}\cdot\left(\frac{1}{\sqrt{\pi h}}+\boldsymbol{V}\cdot\boldsymbol{n}\right) \tag{15}$$

$$\boldsymbol{t}_i\cdot d\boldsymbol{F}_{DR} = 0 \qquad (i=1,2) \tag{16}$$

The remaining fraction $1 - a$ of the colliding molecules is assumed to be specularly reflected (without tangential momentum transfer) in such a way that if the velocity of a molecule was c then its velocity after reflection must be $\boldsymbol{c} - 2(\boldsymbol{c}\cdot\boldsymbol{n})\boldsymbol{n}$. So the force produced will be:

$$d\boldsymbol{F}_{SR} = d^2\Sigma\, m(1-a)\cdot\int_{\boldsymbol{c}\cdot\boldsymbol{n}<0}\left[\boldsymbol{c}-2(\boldsymbol{c}\cdot\boldsymbol{n})\,\boldsymbol{n}\right](\boldsymbol{c}\cdot\boldsymbol{n})f^-\,d^3\boldsymbol{c} \tag{17}$$

which leads to the projections:

$$\boldsymbol{n}\cdot d\boldsymbol{F}_{SR} = (1-a)\boldsymbol{n}\cdot d\boldsymbol{F}_I \tag{18}$$

$$\boldsymbol{t}_i\cdot d\boldsymbol{F}_{SR} = -(1-a)\boldsymbol{t}_i\cdot d\boldsymbol{F}_I \tag{19}$$

Then, by addition, we find the total force in the normal and tangential directions:

$$\boldsymbol{n} \cdot d\boldsymbol{F} = -d^2\Sigma \frac{mN}{\sqrt{\pi h}} \cdot \Big\{\frac{1}{2}\sqrt{\frac{\pi}{h}} + \Big[2 - a\Big(1 - \frac{\pi}{4}\Big)(\boldsymbol{n} \cdot \boldsymbol{V}) + (2 - a)\frac{3\nu}{4}(\boldsymbol{n} \cdot \boldsymbol{grad} \ln T)\Big\} \qquad (20)$$

$$\boldsymbol{t}_i \cdot d\boldsymbol{F} = d^2\Sigma \frac{amN}{2\sqrt{\pi h}} \cdot \Big(\boldsymbol{t}_i \cdot \boldsymbol{V} + \frac{3\nu}{4}\boldsymbol{t}_i \cdot \boldsymbol{grad} \ln T\Big), (i = 1, 2) \qquad (21)$$

Finally, the total force $\boldsymbol{F}$ on the particle would be the integral of the elementary forces $d\boldsymbol{F}$ over the total particle surface Σ,

$$\boldsymbol{F} = \int_{\Sigma} d\boldsymbol{F} \qquad (22)$$

where $d\boldsymbol{F}$ is obtained from the projections (Eqs. 20 and 21) as:

$$d\boldsymbol{F} = (\boldsymbol{n} \cdot d\boldsymbol{F})\boldsymbol{n} + (\boldsymbol{t}_1 \cdot d\boldsymbol{F})\boldsymbol{t}_1 + (\boldsymbol{t}_2 \cdot d\boldsymbol{F})\boldsymbol{t}_2 \qquad (23)$$

A similar result, but for the diffusiophoresis phenomenon, has been obtained by Yalamov et al. (1979).

We will now apply these results to a "sphero-cylindrical" particle: i.e., a cylinder of length L and radius R with hemispherical caps at both ends, Figure 2.

Due to the linearity of the calculation, the force on a sphero-cylinder can be obtained by addition of the forces on its spherical and cylindrical parts. A straightforward computation leads to:

$$\begin{aligned}\boldsymbol{F} = -\frac{mN}{\sqrt{h}} \cdot \pi R^2 \cdot \Big\langle \Big\{\Big[\frac{8}{3}\Big(1 + a\frac{\pi}{8}\Big) &+ \frac{2L}{R}\Big(1 + a\frac{\pi - 2}{8}\Big)\Big] V_y \\ &+ \frac{3\nu}{4}\Big[\frac{8}{3} + \frac{2L}{R}\Big(1 - \frac{a}{4}\Big)\Big]\frac{\partial \ln T}{\partial y}\Big\} \boldsymbol{e}_y \\ &+ \Big\{\Big[\frac{8}{3}\Big(1 + a\frac{\pi}{8}\Big) + \frac{L}{R}a\Big] V_z \\ &+ \frac{3\nu}{4}\Big(\frac{8}{3} + \frac{L}{R}a\Big)\frac{\partial \ln T}{\partial z}\Big\} \boldsymbol{e}_z \Big\rangle \qquad (24)\end{aligned}$$

where $\boldsymbol{e}_y$ and $\boldsymbol{e}_z$ are unit vectors along the y and z axis. Taking advantage of the axial symmetry of the sphero-cylinder without loss of generality, it has been assumed that it was aligned in the e_z direction and that both $\boldsymbol{V}$ and *-**grad** T* lie in the yz plane, as shown in Figure 2.

When we pass to the limit $L/R \rightarrow 0$ (*i.e.*, the spherical case), Eq. 24 reduces to Waldmann's result. In the opposite limit $L/R \rightarrow \infty$ (*i.e.*, the cylindrical case) a partial check can be obtained by noting that Eq. 24 specializes to a previous result of Dahneke (1973) for the drag force, $\boldsymbol{F} \cdot \boldsymbol{V}/V$, in a constant temperature environment: *i.e.*, $-\boldsymbol{grad}\ T = 0$.

As shown by Eq. 24, when $a = 0$ (pure specular reflection) the cylindrical surfaces themselves experience thermophoretic and resistance forces along a direction normal to its axis of revolution, these forces being proportional to the corresponding components of *-**grad** T* and $\boldsymbol{V}$ along the same direction, in such a way that if these two vectors are directed along the cylinder axis of revolution no thermophoresis nor resistance force exist. When we "close" both ends of the cylinder with hemispherical caps, we must add to the previous forces new ones directed along *-**grad** T* and $\boldsymbol{V}$ (just the thermophoretic drift and the resistance force corresponding to a sphere). If $a \neq 0$ (diffuse reflection also occurs, implying tangential momentum transfer), the situation is somewhat more complex but, in any case, the resulting thermophoretic (*cf.* resistance) force does not coincide with the direction of *-**grad** T* and, as a consequence, the nonspherical shape leads to a "lift" in the resistance force as well as to a force normal to *-**grad** T* in the thermophoretic force. So, in general, when a stationary motion is attained (and $\boldsymbol{F} = 0$) the vectors $\boldsymbol{V}$ and *-**grad** T* will have different directions: *i.e.*, the giant elongated molecule does not drift "down" the temperature gradient. Equating both components of $\boldsymbol{F}$ to zero, we obtain two equations that allow us to calculate both components of $\boldsymbol{V}$. If the sphero-cylinder is aligned in the $\boldsymbol{e}_z$ direction and β is the angle between $\boldsymbol{e}_z$ and $\boldsymbol{grad}\ T$, then the magnitude V and the angle α between $\boldsymbol{e}_z$ and $\boldsymbol{V}$ (see Figure 2) are given, respectively, by:

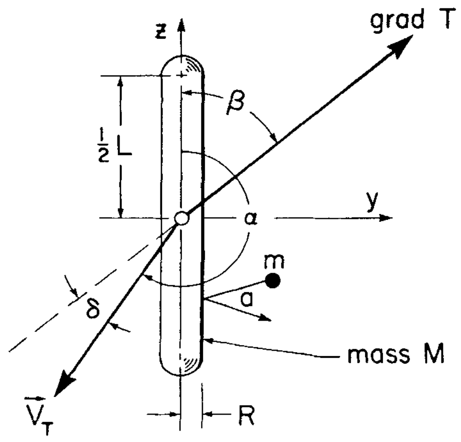

Figure 2. Sphero-cylindrical particle in a nonuniform temperature gas showing the choice of coordinates and notation.

$$V = -\frac{\cos\beta}{\cos\alpha} \cdot A\nu \cdot |\boldsymbol{grad} \ln T| \qquad (25)$$

with

$$A = \frac{3}{4\left[1 + \dfrac{a\pi/3}{(8/3) + (aL/R)}\right]} \qquad (26)$$

and

$$\tan\alpha = B\tan\beta \qquad (27)$$

with

$$B = \frac{3}{4A \cdot \left[1 + \dfrac{a\pi/8}{1 - \dfrac{aL/2R}{(8/3) + (2L/R)}}\right]} \qquad (28)$$

The behavior predicted by Eq. 25 and the deviation angle $\delta = \pi + \beta - \alpha$ for a very long particle ($L/R \rightarrow \infty$) are depicted in Figures 3 and 4, respectively, which summarize the "shape effects" of greatest interest. Figure 3 shows that, provided the impinging gas molecules can transport tangential momentum (*i.e.* are not fully specularly reflected, we have chosen $a = 0.8$), a long sphero-cylindrical particle with a major axis aligned with the direction of ***-grad*** T will thermophoretically drift approximately 31% *faster* down the temperature gradient than a sphere of radius R (equal to the cylindrical radius), whereas a long spherocylindrical particle with its major axis perpendicular to ***-grad*** T will thermphoretically drift approximately 6% *slower* than a sphere of radius R in the same local environment. An important corollary of this orientation dependence of the thermophoretic velocity is a "new" mechanism of coagulation for nonspherical particles in a temperature gradient (*i.e.*, particles of one orientation are able to "overtake" particles of another orientation). Since, when $Kn_p \gg 1$, the thermophoretic velocity of a sphere is size-*independent*, this result also implies that a noncoalescing liquid (or solid) aerosol in a temperature gradient will coagulate faster than a coalescing one. A somewhat subtler mechanism of coagulation, also new and associated with thermophoresis, is implied in Figure 4. It shows that the direction of thermophoretic drift of "nonaligned" (neither parallel nor perpendicular) particles departs (by as much as 12°) from the direction of ***-grad*** T. The stochastic effect of such "lateral" displacements for particles which are experiencing Brownian rotation will be to introduce a "thermo-Brownian" contribution to the coagulation rate for nonspherical particles in a temperature gradient. These particle coagulation implications of the results displayed in Figures 3 and 4 will be pursued elsewhere.

Due to Brownian rotatory motion, after a very long time compared to the rotation time, the giant molecule will go through all possible orientations. Then, if all orientations were equiprobable, the orientation-averaged thermophoretic velocity $\langle V_T \rangle$, in the direction of ***-grad*** T, would be:

$$\langle V_T \rangle = \frac{1}{2}\int_0^{\pi} V \cos\delta \sin\beta \, d\beta$$

$$= \frac{1}{3} A(1 + 2B)\,\nu \cdot |\boldsymbol{grad} \ln T| \quad (29)$$

In the equivalent result of kinetic theory, the proportionality factor between the thermophoretic velocity and the gradient ***grad***$\ln T$ is usually written as the product $\alpha_T D$ of the binary thermal diffusion factor α_T and the binary diffusion coefficient D. For a quasi-Lorentzian gas of hard spheres, the kinetic theory gives the result (Mason, 1957):

$$[\alpha_T D]_{QL} = (3/4)\nu \quad (30)$$

which reduces to the following result of Waldmann (1961) when only "specular" collisions occur ($a = 0$):

$$[\alpha_T D]_W = \frac{[\alpha_T D]_{QL}}{1 + (a\pi/8)} \quad (31)$$

This result predicts a decrease in the thermophoretic drift velocity when inelastic collisions occur ($a > 0$) but contains no information about shape effects. In the quasi-Lorentzian and Waldmann model, the shape dependence of the thermal diffusion factor is contained in the ratio $Sc = \nu/D$, known as the Schmidt number (see, *e.g.*, Israel, 1983). Then our results (Eq. 29) can be written as:

$$\langle \alpha_T D \rangle = 4/9\, A(1 + 2B)[\alpha_T D]_{QL} \quad (32)$$

where the brackets indicate the orientation-averaged value.

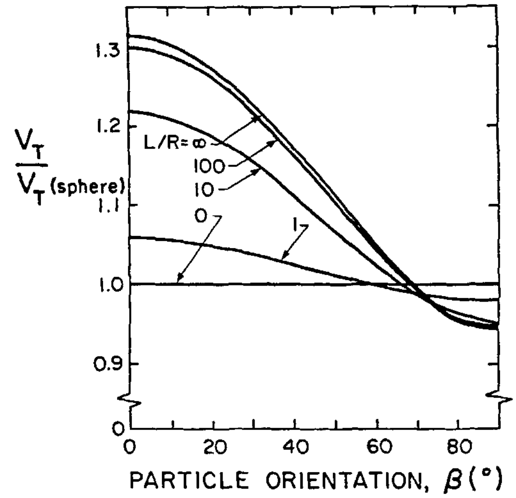

Figure 3. Normalized magnitude of the thermophoretic velocity for a sphero-cylindrical particle as a function of particle orientation β (diffuse fraction $a = 0.8$).

Figure 5 shows the dependence of $\langle \alpha_T D \rangle$ on shape for a sphero-cylinder compared with a sphere at the same a (diffuse fraction) value. It is interesting to note that $\langle \alpha_T D \rangle$ would be rel-

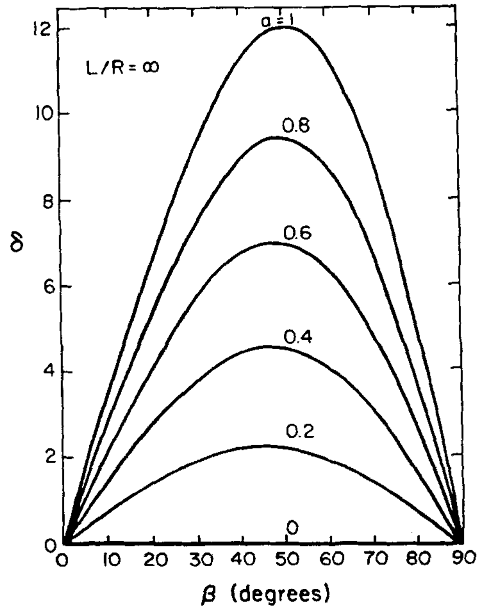

Figure 4. Deviation angle δ (drift direction with respect to *-grad T*) for an infinite cylinder ($L/R \rightarrow \infty$) as function of cylinder orientation β with respect to *-grad T*.

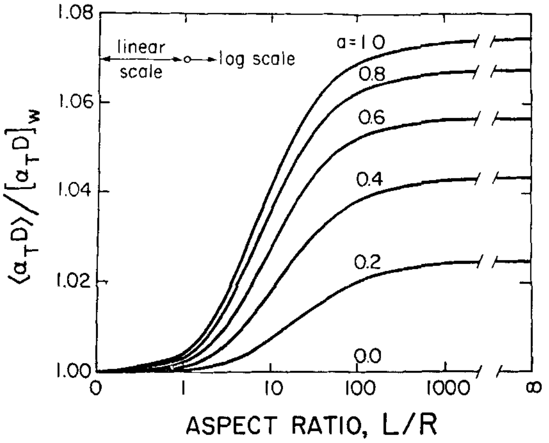

Figure 5. Values of $\langle \alpha_T D \rangle$ for a sphero-cylinder normalized with the corresponding Waldmann result for a *sphere* at the same diffuse-fraction *a* value.

Dependence on aspect ratio L/R and diffuse-fraction coefficient a.

evant for high Schmidt number, thermophoretically-dominated particle transport across continuum thermal boundary layers because Brownian rotation would not be "frozen" on the (transit-) time scale $\delta_h / \langle V_T \rangle$. Further implications of this shape dependence are discussed in the next section.

Using Eq. 24 the thermophoretic torque τ on the "particle" may be evaluated by integration of the torque $d\tau$ on each elemental surface $d^2\Sigma$, over the whole particle surface. That is:

$$\tau = \int_\Sigma d\tau = \int_\Sigma r \times dF \tag{33}$$

where r is the position vector of the surface points. Calculation shows that, for the chosen spherocylindrical model, there is no net torque on the particle. This is a consequence of the particular shape symmetry. In fact, *any* particle (molecule) having three mutually perpendicular planes of symmetry would experience zero net torque. Moreover, it can be shown that translation and rotation are uncoupled. This is a well known result for the low Reynolds number continuum regime (Happel and Brenner, 1965) that can be "verbatim" translated to the free molecule regime whenever a convex body is considered, due to the formal analogy between both theories (Rohatschek and Zulehner, 1987).

Discussion

If all collisions were specular ($a = 0$), our result corresponds to the quasi-Lorentzian gas in the hard-sphere limit (Eq. 30). On the other hand, in the limit of a very long particle, $L/R \longrightarrow \infty$, the result (Eq. 32) is:

$$\langle \alpha_T D \rangle_\infty = \frac{1 + [(\pi/3) - 2]a/8}{1 + (\pi - 2)a/8} \cdot [\alpha_T D]_{QL} \tag{34}$$

so the ratio $\langle \alpha_T D \rangle / [\alpha_T D]_{QL}$ is always smaller than unity, taking its minimum value when all collisions are "diffuse" ($a = 1$). In other words, as shown by Waldmann's sphere result, Eq. 31, *inelastic* collisions ($a > 0$) *decrease* thermophoretic drift velocity, despite the fact that an elongated shape reduces this tendency (cf. Figure 5).

Evaluation of the thermal diffusion factor α_T from Eq. 32 requires computation of the binary diffusion coefficient D. This can be done by using Einstein's relation:

$$D = k_B T b \tag{35}$$

where the "mobility" b is obtained from the principal values c_1, c_2, c_3, of the resistance coefficient matrix as (see, *e.g.*, the book of Landau and Lifshitz, 1975, p. 228):

$$b = \frac{1}{3}\left(\frac{1}{c_1} + \frac{1}{c_2} + \frac{1}{c_3}\right) \tag{36}$$

In our case, due to the special choice of coordinate frame along the symmetry axis of the sphero-cylinder, the resistance matrix obtained from Eq. 24 is diagonal and $c_1 = c_2 = c_y$, $c_3 = c_z$, where:

$$c_y = \frac{mN}{\sqrt{\pi h}} \cdot \pi R^2 \cdot \left[\frac{8}{3}\left(1 + a\frac{\pi}{8}\right) + 2\frac{L}{R}\left(1 + a\frac{\pi - 2}{8}\right)\right] \tag{37}$$

$$c_z = \frac{mN}{\sqrt{\pi h}} \cdot \pi R^2 \cdot \left[\frac{8}{3}\left(1 + a\frac{\pi}{8}\right) + \frac{L}{R}a\right] \tag{38}$$

By denoting

$$b_W \equiv \frac{3\sqrt{\pi h}}{8mN\pi R^2(1 + a\pi/8)} \tag{39}$$

the corresponding Waldmann mobility for a sphere of radius R and using Eq. 37 and 38 in Eq. 36 the mobility of a sphero-cylinder can be written:

$$b = E b_W \tag{40}$$

where

$$E = \cfrac{1}{1 + \cfrac{L}{2R} \cdot \cfrac{1 + \cfrac{L}{R}\cfrac{a}{1 + a\pi/8}\left(\cfrac{3}{2} - \cfrac{a}{1 + a\pi/8}\right)}{1 + \cfrac{L}{2R}\left(\cfrac{1}{2} + \cfrac{a}{1 + a\pi/8}\right)}} \tag{41}$$

Let

$$D_W = k_B T b_W \tag{42}$$

be the diffusion coefficient of a sphere of radius R, and

$$D_{QL} = k_B T \cdot \frac{3\sqrt{\pi h}}{8mN\pi R^2} \tag{43}$$

be the diffusion coefficient of the analogous "quasi-Lorentzian" gas of hard spheres. Then our result can be written:

$$D = E D_W = \frac{E}{1 + a\pi/8} \cdot D_{QL} \tag{44}$$

This expression gives the diffusion coefficient of a sphero-cylinder as a function of three parameters: L, R and a. These parameters must be adjusted to fit experimental values of D. It is noteworthy that in the case of paraffin hydrocarbons diffusing in nitrogen, such agreement is attained with reasonable values of these three parameters. The special choices $R = 2$ Å, and $L = (n - 1)R$, n being the number of carbons in the paraffin, are compared with the experimental measurements in Figure 6 (Galloway and Sage, 1967), which reveals gradually better agreement upon increasing the number of carbons of the paraffin (as the criterion 1 is more accurately fulfilled).

Now we can use Eq. 32 to compute the values of the thermal diffusion factor:

$$\alpha_T = \frac{4A(1 + 2B)}{9E} \cdot \left(1 + a\frac{\pi}{8}\right) \cdot \alpha_{T_{QL}} \tag{45}$$

where we have used Eq. 44 and $\alpha_{T,QL} = 3\nu/(4D_{QL})$ is the thermal diffusion factor of the associated quasi-Lorentzian gas. This factor is intimately related to the relative size of the "particle," R, and the surrounding gas r_g, (Eisner and Rosner, 1985) because using Eq. 43 and the hard-sphere kinetic theory to determine ν, we find $\alpha_{T,QL} = [5/(4\sqrt{2})](R/r_g)^2$. Note that we have defined $\alpha_T = \langle \alpha_T D \rangle / D$ because this is the parameter obtained from steady-state experiments in which concentration-(Brownian or Fick) diffusion counterbalances Soret diffusion. In Figure 7 we have plotted the values obtained from Eq. 45 corresponding to our computed values of D plotted in Figure 6.

Incidentally, we have also displayed the values given by the kinetic theory for a binary mixture of hard spheres where one of the species is highly diluted. This last approach then assumes spherical shape and variable mass for the diluted species (the praffin) and should be a good approximation for the light paraffins. The present theory assumes a very large mass for the paraffin but variable nonspherical shape, thereby giving a better description of the heavy paraffin behavior. Figure 7 shows a rather encouraging matching of both descriptions in the intermediate region. This figure also shows the limit of expression 45 for large values of n, whose analytical form is:

$$\alpha_{T\infty} = [\alpha_T D]_{QL} \cdot \frac{2(a/a_0)(3/8 - a/4a_0)}{k_B T b_W (1/4 + a/2a_0)} \cdot \frac{1 + (\pi/6 - 1)a/4}{1 + (\pi/2 - 1)a/4}\, n \cdot \left\{1 + \frac{(\pi a^2/4) - \pi[1 + (\pi/2 - 1)a/4]^2}{3n[1 + (\pi/2 - 1)a/4][3 + (\pi/2 - 3)a/4]} - \frac{1 - (a_0/a) + [1/(1/4 + a/2a_0)]}{n} + 0(n^{-2})\right\} \tag{46}$$

where $a_0 = (8 + a\pi)/3$ and we have assumed that $L/R = n - 1$. Then we predict a straight line for the dependence of α_T on n when $n \rightarrow \infty$. Figure 7 reveals that this limit is in fact reached quickly, even for moderate values of n.

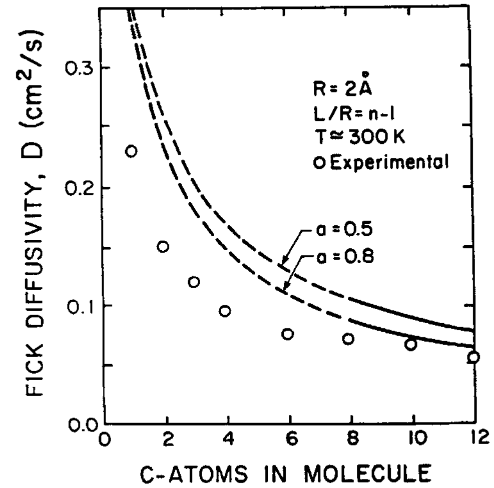

Figure 6. Experimental and predicted diffusion coefficients D for paraffin hydrocarbons as function of the number of C atoms in the molecule.

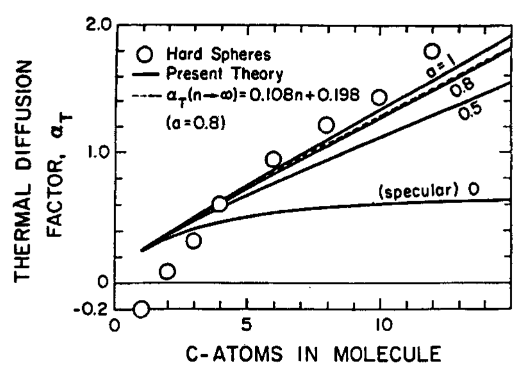

Figure 7. Predicted values for the dimensionless thermal diffusion factor α_T for paraffin hydrocarbons as function of the number of C atoms in the molecule.

Conclusions

The formalism used by Epstein (1924) and Waldmann (1959, 1968) to study the dynamics of small spherical particles in a nonisothermal gas is here shown to be useful to investigate not only the behavior of small *nonspherical* particles, but also the behavior of "giant" nonspherical molecules.

Interesting results of this analysis include the predictions that, provided gas molecule reflection is not completely specular, sphero-cylindrical particles in a local temperature gradient ***grad*** T will thermophoretically drift: (i) more rapidly when their major axis is aligned with -***grad*** T than when perpendicular to -***grad*** T (by about 48% for the limiting case $L/R \rightarrow \infty$, $a = 1$); (ii) at a different velocity (depending upon particle orientation and L/R) than that of a sphere of radius R equal to the cylinder radius, (iii) at an angle (up to 12°) with respect to -***grad*** T when their major axis is not parallel to, or perpendicular to, ***grad*** T, (iv) *without* a net torque tending to orient the particle with respect to -***grad*** T. Important corollaries of these findings, now under quantitative investigation, are that nonspherical particles in a temperature gradient should also experience new thermophoretically-induced coagulation mechanisms, and that thermophoretically augmented coagulation rates in the presence of rapid coalescence should be slower than those in the absence of rapid coalescence (*i.e.*, when nonspherical aggregates form).

In the case of sphero-cylindrical "particles" studied here, we find that there is no net thermophoretically oriented *torque* so that the only particle rotation would be the rotational Brownian motion. This would be also the case for other differently shaped particles which possess the same symmetry: all axisymmetric nonspherical bodies with a plane of symmetry normal to the axis of revolution, like cylinders and discs. In fact, this result can be generalized further to bodies possessing three mutually perpendicular planes of symmetry (see, *e.g.*, Davies, 1979, for particle dynamics in the continuum limit). However, in general, the thermophoretic torque on the particle will be nonzero, leading either to nonspherical particle alignment or continuous rotation, depending on the particle symmetry. These implications of our present work, when applied to unsymmetrical nonspherical particles or heavy molecules, are currently under investigation. However, as a particular result for sphero-cylindrical "particles" we have estimated the thermophoretic velocity of the paraffin hydrocarbons, modelled as sphero-cylinders. Our formulae depend on three parameters associated with the molecular geometry and structure, but additional experimental information will be required before assigning precise values to them.

This asymptotic kinetic theory approach is now also being used to predict the behavior of molecules with flat nonaxisymmetric structures, such as benzene and anthracene, of great current importance in hydrocarbon fuel and coal processes.

It should be noted that particle shape effects on thermophoretic behavior have recently been investigated in the opposite limit of *small* particle Knudsen number by several authors (Leong, 1984; Reed, 1971). Although an exhaustive study of particle orientation implications is still lacking in this "near-continuum" limit, it has been shown that in this case also the particle thermophoretic drift is strongly dependent of both shape and relative orientation. Results, however, depend on the ratio of the *thermal conductivity* of the particle to the gas, whereas in the present ($Kn_p \gg 1$) case they depend on the momentum accommodation coefficient a. But, despite the fact that in both limiting cases ($Kn_p \ll 1$, $Kn_p \gg 1$) thermophoretic drift is "caused" by different phenomena (thermal "slip," and momentum transfer, respectively), we can state in general that an elongated particle will thermophoretically drift faster than a sphere when it is oriented parallel to -***grad*** T. Also, flattened particles behave qualitatively in a similar manner: they drift faster when they have either major axis parallel to -***grad*** T, although, while the lowest drift velocity in the limit of vanishing thickness vanishes for a 'large' particle, it remains nonzero for a small particle. Our present interest in the $Kn_p \gg 1$ limit is, of course, motivated by the realization that results in this limit will often be applicable to 'heavy molecules', rather than just "true particles." This important hypothesis will be tested further for both long (paraffin-like) or platelet (polycycle aromatic) molecules in our follow-on studies.

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Notation

A = parameter
a = diffusively reflected gas molecule fraction
B = parameter
b = particle mobility
C = sound velocity
c_y, c_z = principal values of the resistance matrix
$\mathbf{C}$ = molecular velocity
$\mathbf{c}$ = relative molecular velocity
$\bar{c}$ = mean gas molecule velocity
D = particle diffusion coefficient
E = parameter
$\mathbf{e}_y, \mathbf{e}_z$ = unit vectors along y and z axis
$\mathbf{F}$ = total force on the particle
f^+ = diffusively reflected gas velocity distribution function
f^- = gas velocity distribution function
$\mathbf{F}_{DR}$ = force due to the diffusively reflected molecules
$\mathbf{F}_I$ = force due to the impinging molecules
$\mathbf{F}_{SR}$ = force due to the specularly reflected molecules
f_M = Maxwellian distribution function
h = $m/2k_BT$
I = particle moment of inertia
$\mathbf{I}$ = unit matrix
k_B = Boltzmann constant
Kn = gas Knudsen number
Kn_p = particle Knudsen number
L = cylinder length
l = gas mean-free path
M = particle mass
m = gas molecule mass
N = gas molecule number per unit volume
N_D = coefficient in f^+
n = number of C atoms
$\mathbf{n}$ = normal unit vector
R = particle radius
$\mathbf{r}$ = position vector
r_g = gas molecule radius
T = absolute temperature
$\mathbf{t}_1, \mathbf{t}_2$ = tangential unit vectors
$\mathbf{V}$ = particle velocity
$\mathbf{v}$ = macroscopic gas velocity
V_T = thermophoresis velocity

Greek letters

α = angle between $\mathbf{e}_z$ and $\mathbf{V}$
α_T = thermal diffusion factor
β = angle between $\mathbf{e}_z$ and ***grad*** T
δ = $\pi + \beta - \alpha$
δ_h = thermal boundary layer thickness
δ_{mom} = momentum boundary layer thickness
ϕ = gradient correction to the distribution function
Λ = macroscopic gradient scale
μ = dynamic viscosity coefficient
ν = momentum diffusivity
Σ = particle surface
$\boldsymbol{\tau}$ = torque on particle
τ = gas-particle collision time
$\boldsymbol{\omega}$ = particle angular velocity

Subscripts

QL = quasi-Lorentzian
W = Waldmann
∞ = infinitely long particle

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