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# The Ludwig–Soret effect and stochastic processes $\stackrel{\star}{\sim}$

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#### ARTICLE INFO

ABSTRACT

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#### New general stochastic models of thermodiffusion are proposed, which include velocity-dependent friction coefficient and noise tensor. These coefficients are computed exactly from the Boltzmann equation for the particular case of thermodiffusion in dilute gas mixtures. The Soret coefficients predicted by the new thermodiffusion models are computed via a Chapman–Enskog expansion and compared favorably to predictions of earlier models. In particular, the new models can accommodate for Soret coefficients of both signs, as observed experimentally.

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#### 1. Introduction

Thermodiffusion is diffusion generated by temperature gradients and is presently the object of active research, with applications ranging from chemistry to biology and petroleum extraction [1–5].

The first, purely macroscopic description of thermodiffusion [6] dates back to the 19th century, and assumes that diffusion currents are generally made up of two contributions, one proportional to density gradients (Fick law) and the other proportional to temperature gradients (Ludwig–Soret effect).

Such purely macroscopic descriptions are certainly very simple, but they only model close to equilibrium situations; for strongly out of equilibrium situations, as for example the short time regime in a diffusion problem, a statistical description is needed. The statistical description of the Soret effect first proposed in the literature was developed in the context of standard kinetic theory [7,8] and, thus, only applies to dilute gas mixtures. More general statistical descriptions are based on stochastic processes; these model the effective motion of a diffusing particle through a Langevin-like Markov process [9-11]. In these models, the effective force acting on the diffusing particle is made up of three distinctive contributions. Two are the standard Langevin friction and stochastic forces, with coefficients depending only on the temperature and not on its gradient, and the third one is the so-called thermophoresis force, proportional to the temperature gradient, with constant coefficient.

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In many cases, however, these stochastic models fail to reproduce the observed values and even orders of magnitude and signs of the Ludwig–Soret coefficient [11]. The aim of this manuscript is to analyze this failure and find a remedy. The main conclusion is that the stochastic processes introduced so far [9–11] do not include all forces acting on the diffusing particle and that one must allow the friction and noise coefficient to depend on the temperature gradient if one wants to obtain theoretical predictions of Soret coefficients which better fit measured values.

Here is a brief outline of the manuscript. Thermodiffusion of dilute gases mixtures is revisited in section 2 as a particularly simple case. An explicit expression of the effective force acting on a gas particle diffusing in a temperature gradient is derived from the Boltzmann equation in the context of the diffusion approximation. The obtained expression of the force is much richer than the expression used in traditional stochastic models. In particular, both friction and noise coefficients contain contributions which depend explicitly on temperature gradients.

The physical relevance of these new contributions is also addressed in section 2. The diffusion approximation is only valid when the mass ratio between the diffusing particle and the solvent particle is small enough. This qualitative statement is made quantitative by using conditional entropies and it is then shown that at least some of the above derived new contributions to the force experienced by the diffusing particle are comparable to the thermophoresis force well inside the validity domain of the diffusion approximation.

The results from section 2 are generalized in section 3 where new stochastic models of thermodiffusion are presented. These new models are not a priori restricted to dilute gas mixtures, but have a form similar to those derived for dilute gas mixtures. The Ludwig–Soret coefficients predicted by these new models are computed in section 3 by a Chapman–Enskog expansion. All results are finally summarized and discussed in section 4.



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#### 2. Dilute gas mixtures

#### 2.1. Kinetics

Consider first a solvent gas *S* made of particles of mass  $m_S$  (conveniently called *S*-particles). For sufficiently high dilutions, all statistical properties of *S* are encoded in the one-particle distribution function *f*. If one neglects the internal structure of *S*-particles, *f* is a time-dependent function of six real degrees of freedom (for example, three position coordinates and three velocity components) and this function obeys the Boltzmann equation [8,12].

The mean free path  $\lambda_s$  of the *S*-particles is defined in terms of the total cross-section  $\sigma_s$  by  $\lambda_s = \frac{1}{2^{\frac{1}{2}n_s}\sigma_s}$ , where  $n_s$  is the density of *S*-particles (*i.e.* the number of *S*-particles per unit volume). Approximating the interaction of *S*-particles by elastic collisions between hard spheres of radius  $R_s$ , one obtains:

$$\lambda_{S} = \frac{1}{2^{\frac{1}{2}} n_{S} \pi (2R_{S})^{2}}.$$
 (1)

Suppose that the gas *S* is at rest in a reference frame  $\mathcal{R}$  but that a non-uniform temperature field  $\theta(\mathbf{r})$  is maintained in *S*; the distribution  $f_{\theta}$  describing this situation is a time-independent solution of the Boltzmann equation which reduces to the standard Maxwell distribution for vanishing temperature gradients. This distribution can be expanded in terms of the dimensionless quantity  $\lambda_S \nabla \theta/\theta$  and reads, at first order:

$$f_{\theta}(\mathbf{v}_{S}) = \left(\frac{2\pi k_{B}\theta}{m_{S}}\right)^{-\frac{3}{2}} \exp\left(-\frac{m_{S}v_{S}^{2}}{2k_{B}\theta}\right) \cdot \left\{1 - \frac{16}{5(2\pi)^{\frac{1}{2}}} \left(\frac{m_{S}v_{S}^{2}}{2k_{B}\theta} - \frac{5}{2}\right) \left(\frac{m_{S}}{k_{B}\theta}\right)^{\frac{1}{2}} \mathbf{v}_{S} \cdot \frac{\lambda_{S}\frac{d\theta}{dt}}{\theta}\right\},\tag{2}$$

where  $k_B$  is the Boltzmann constant and  $\mathbf{v}_S$  is the random velocity of a solvent particle. Note that the kinematic shear viscosity  $v_S(\theta)$  is proportional to  $\lambda_S$  and to the thermal velocity of an *S*-particle [8]:  $v_S(\theta) = \frac{5(2\pi)^2}{16} \lambda_S \left(\frac{k_B \theta}{m_S}\right)^{\frac{1}{2}}$ , and that (2) is thus sometimes expressed in

terms of  $v_s(\theta)$  [11]. We will suppose that (2) correctly describes the state of the sol-

vent *S*; this amounts to supposing that the temperature field  $\theta$  varies on scales much larger than the mean free path  $\lambda_S$ , *i.e.* on macroscopic scales only.

Consider now particles of mass  $m_B$ , conveniently called Brownian or *B*-particles, diffusing in the above solvent through shortrange interactions. We suppose that there are sufficiently few Brownian particles in *S* to neglect interactions between *B*-particles and between more than one *B*- and one *S*-particle at a time. All properties of diffusion can then be recovered by studying the motion of a single, arbitrary *B*-particle and the statistical properties of this motion are entirely characterized by expression (2) for the solvent distribution  $f_{\theta}$  and by a law characterizing the short-range interaction between a *B*- and an *S*-particle. We neglect the internal structure of *B*-particles and assume, in coherence with (1), that the short-range interaction between a *B*- and an *S*-particle can be modelled as an elastic collision between hard spheres and that the associated sphere radius for *B*-particles is  $R_B$ .

#### 2.2. Stochastics

In the above model, the trajectory of a *B*-particle is a succession of line segments started and ended by collisions with *S*-particles. At a fixed initial momentum  $\mathbf{p}_B$  of the *B*-particle before such a collision, the momentum loss  $\mathbf{q}_B = \mathbf{p}_B - \mathbf{p}'_B$  of the *B*-particle during the collision is a random variable whose distribution depends on the collision cross-section and on the distribution of *S*-particles.

Langevin-like equations (Ito processes [13]) are driven by Gaussian noises. Approximating the motion of a *B*-particle by a Langevin-like equation thus comes down to approximating, for each  $\mathbf{p}_B$ , the distribution of the momentum loss  $\mathbf{q}_B$  by a Gaussian. The law of a stochastic process defined by such a Langevin equation is described by a distribution function  $\phi$  of the time *t* and of the position  $\mathbf{r}_B$  and momentum  $\mathbf{p}_B$  of a *B*-particle; this function obeys the Fokker–Planck equation [13]:

$$\frac{\partial \phi}{\partial t} + \frac{p_B^i}{m} \frac{\partial \phi}{\partial r_B^i} = \frac{\partial}{\partial p_B^i} \left( -F^i \phi + \frac{\partial}{\partial p_B^j} (D^{ij} \phi) \right), \tag{3}$$

where **F** is the deterministic part of the force experienced by the *B*-particle and *D* is the noise tensor. This force **F** and the noise tensor *D* can be computed from the expectation (mean value) of  $\mathbf{q}_B$  and  $\mathbf{q}_B \otimes \mathbf{q}_B$ , respectively.

One finds expressions of the form:

$$\mathbf{F} = \kappa(\theta, \mathbf{v}_B^2) \frac{d\theta}{d\mathbf{r}} - \left(\alpha_0(\theta, \mathbf{v}_B^2) + \alpha_1(\theta, \mathbf{v}_B^2) \mathbf{v}_B \cdot \frac{d\theta}{d\mathbf{r}}\right) \mathbf{v}_B, \tag{4}$$

and

$$D = \left(\sigma_0(\theta, \mathbf{v}_B^2) + \sigma_1(\theta, \mathbf{v}_B^2)\mathbf{v}_B \cdot \frac{d\theta}{d\mathbf{r}}\right) \mathcal{E} + \left(\sigma_2(\theta, \mathbf{v}_B^2) + \sigma_3(\theta, \mathbf{v}_B^2)\mathbf{v}_B \cdot \frac{d\theta}{d\mathbf{r}}\right) \mathbf{v}_B \otimes \mathbf{v}_B + \sigma_4(\theta, \mathbf{v}_B^2) \frac{\mathbf{v}_B \otimes \frac{d\theta}{d\mathbf{r}} + \frac{d\theta}{d\mathbf{r}} \otimes \mathbf{v}_B}{2},$$
(5)

where  $\mathcal{E}$  is the (inverse) Euclidean metric tensor ( $\mathcal{E}^{ij} = 1$  if i = j and 0 otherwise) and  $\mathbf{v}_B = \mathbf{p}_B/m_B$  is the velocity of the Brownian particle. The tensor D depends on  $\nabla \theta$  if at least one of the coefficients  $\sigma_1$ ,  $\sigma_3$  or  $\sigma_4$  does not vanish. Naturally, all coefficients introduced above also depend on the masses  $m_B$  and  $m_S$ , and on the characteristic radii  $R_B$  and  $R_S$ . The expressions of the coefficients in (4) and (5) are more readable if the following conventions are done:

- $\mathbf{u}_B$  denotes the dimensionless velocity of the *B*-particles:  $\mathbf{u}_B = \mathbf{v}_B m_S / k_B \theta^2$ . Note that the velocity scale  $k_B \theta / m_S$  chosen to make  $\mathbf{u}_B$  dimensionless is the thermal velocity of *S*-particles. Thus, when the *B*-particles have a much larger mass than the *S*-particles,  $|\mathbf{u}_B|$  is much smaller than unity.
- $u_B$  and  $v_B$  denote the moduli of  $\mathbf{u}_B$  and  $\mathbf{v}_B$ .
- $\mu$  denotes  $(m_{\rm S}^{-1} + m_{\rm B}^{-1})^{-1}$ .
- $\zeta(x)$  stands for exp  $(-x^2/2)$ , and  $\zeta(x)$  for  $(\frac{\pi}{2})^{\frac{1}{2}} \frac{\operatorname{erf}(x/\sqrt{2})}{x}$ , where analytical continuation is implied for x = 0.

With this notation, the exact expressions for the coefficients in (4) and (5) are:

• Thermophoresis coefficient:

$$\kappa(\theta, v_B^2) = 3n_S \frac{v_S(\theta)}{\theta} \left(\frac{2\pi k_B \theta}{m_S}\right)^{\frac{1}{2}} \mu (R_B + R_S)^2 \cdot \left(\frac{1 - u_B^2}{u_B^2} \zeta(u_B) - \frac{1}{u_B^2} \zeta(u_B)\right).$$
(6)

• Friction coefficient:

$$\alpha_{0}(\theta, v_{B}^{2}) = n_{S} \left(\frac{2\pi k_{B}\theta}{m_{S}}\right)^{\frac{1}{2}} \mu (R_{B} + R_{S})^{2} \cdot \left(\frac{-1 + 2u_{B}^{2} + u_{B}^{4}}{u_{B}^{2}} \zeta(u_{B}) + \frac{1 + u_{B}^{2}}{u_{B}^{2}} \zeta(u_{B})\right).$$
(7)

• Thermally induced correction to the friction term:

$$\alpha_1(\theta, \nu_B^2) = 6\pi n_S \frac{\nu_S(\theta)}{T} \left(\frac{m_S}{2\pi k_B \theta}\right)^{\frac{1}{2}} \mu (R_B + R_S)^2 \cdot \left(\frac{3 - u_B^2}{u_B^4} \zeta(u_B) - \frac{3}{u_B^4} \zeta(u_B)\right).$$

$$\tag{8}$$

• Noise coefficient:

$$\sigma_{0}(\theta, v_{B}^{2}) = \frac{1}{12\pi} n_{S} \left(\frac{2\pi k_{B}\theta}{m_{S}}\right)^{2} \mu^{2} (R_{B} + R_{S})^{2} \cdot \left(\frac{-3 + 9u_{B}^{2} + 9u_{B}^{4} + u_{B}^{6}}{u_{B}^{2}} \zeta(u_{B}) + \frac{3 + 8u_{B}^{2} + u_{B}^{4}}{u_{B}^{2}} \zeta(u_{B})\right).$$
(9)

• Thermally induced correction to the noise term:

$$\sigma_{1}(\theta, v_{B}^{2}) = \frac{9}{4} n_{S} \frac{v_{S}(\theta)}{T} \left(\frac{2\pi k_{B}\theta}{m_{S}}\right)^{\frac{1}{2}} \mu^{2} (R_{B} + R_{S})^{2} \cdot \left(\frac{3 - 2u_{B}^{2} + u_{B}^{4}}{u_{B}^{4}} \zeta(u_{B}) + \frac{-3 + u_{B}^{2}}{u_{B}^{4}} \zeta(u_{B})\right).$$
(10)

• Second order noise coefficient:

$$\sigma_{2}(\theta, v_{B}^{2}) = \frac{1}{2} n_{S} \left(\frac{2\pi k_{B}\theta}{m_{S}}\right)^{\frac{1}{2}} \mu^{2} (R_{B} + R_{S})^{2} \cdot \left(\frac{3 - 3u_{B}^{2} + 3u_{B}^{4} + u_{B}^{6}}{u_{B}^{4}} \zeta(u_{B}) + \frac{-3 + 2u_{B}^{2} + u_{B}^{4}}{u_{B}^{4}} \zeta(u_{B})\right).$$

$$(11)$$

• Thermally induced correction to the second order noise term:

$$\sigma_{3}(\theta, \nu_{B}^{2}) = \frac{9\pi}{2} n_{S} \frac{\nu_{S}(\theta)}{\theta} \left(\frac{m_{S}}{2\pi k_{B}\theta}\right)^{2} \mu^{2} (R_{B} + R_{S})^{2} \cdot \left(\frac{15 - 6u_{B}^{2} + u_{B}^{4}}{u_{B}^{6}} \zeta(u_{B}) + \frac{-15 + u_{B}^{2}}{u_{B}^{6}} \zeta(u_{B})\right).$$
(12)

• Thermally induced noise term:

$$\sigma_{4}(\theta, v_{B}^{2}) = \frac{3}{2} n_{S} \frac{v_{S}(\theta)}{\theta} \left(\frac{2\pi k_{B}\theta}{m_{S}}\right)^{\frac{1}{2}} \mu^{2} (R_{B} + R_{S})^{2} \cdot \left(\frac{9 + 9u_{B}^{2} - 45u_{B}^{4} - 36u_{B}^{6} + 4u_{B}^{8} + u_{B}^{10}}{u_{B}^{4}} \zeta(u_{B}) + \frac{-9 - 12u_{B}^{2} - 37u_{B}^{4} + 3u_{B}^{6} + u_{B}^{8}}{u_{B}^{4}} \zeta(u_{B})\right).$$
(13)

#### 2.3. Physical relevance of the new terms

To properly assess the physical relevance of the new, gradientdependent contributions derived in the previous section, one first needs to assess the validity of the stochastic approach in the absence of temperature gradients. This is done in section 2.3.1. The newly derived contributions to the force acting on a Brownian particle diffusing in the presence of a temperature gradient are then examined in section 2.3.2.

#### 2.3.1. Homogeneous temperature case

Consider thus the homogeneous temperature case and focus on the simplest regime, *i.e.* equilibrium. The real, physically correct equilibrium density is then the Maxwell–Boltzmann distribution  $\Phi_M$  defined by:

$$\Phi_M(\mathbf{v}_B) = \left(\frac{2\pi k_B \theta}{m_B}\right)^{-\frac{3}{2}} \exp\left(-\frac{m_B v_B^2}{2k_B \theta}\right). \tag{14}$$

On the other hand, the transport equation (3) also admits a timeindependent or 'equilibrium' solution  $\Phi_{E}$ . This function obeys:

$$\frac{\partial}{\partial v_B^i} \left( -F^i \Phi_E + \frac{1}{m_B} \frac{\partial}{\partial v_B^j} (D^{ij} \Phi_E) \right) = 0.$$
(15)

By isotropy, the solution of (15) can be expressed as a function the modulus  $v_B$  of the velocity:  $\Phi_E(\mathbf{v}_B) = \phi(v_B)$ . Inserting this form into the above equation leads to:

$$A(\nu_B)\phi'(\nu_B) + B(\nu_B)\phi(\nu_B) = 0, \tag{16}$$

where  $\phi'$  stands for the derivative of  $\phi$ . In (16), the coefficients  $A(v_B)$  and  $B(v_B)$  are:

$$A(\nu_B) = \alpha_0(\nu_B) + \frac{1}{m_B} \left( \frac{\sigma'_0(\nu_B)}{\nu_B} + \nu_B \sigma'_2(\nu_B) + 4\sigma_2(\nu_B) \right), \tag{17}$$

and

$$B(\nu_B) = \frac{1}{m_B} \left( \frac{\sigma_0(\nu_B)}{\nu_B} + \nu_B \sigma_2(\nu_B) \right). \tag{18}$$

The solution of (16) is:

$$\phi(v_B) = \phi_0 \exp\left[-\int_0^{v_B} \frac{B(v)}{A(v)} dv\right],\tag{19}$$

the constant  $\phi_0$  being determined by the normalization condition  $\int_0^\infty \phi(v_B) 4\pi v_B^2 dv_B = 1$ . The function  $\phi(v_B)$  can be determined numerically for all values of the mass ratio r; it is plotted in figure 1 for r = 0.01 (Brownian particle 100 times heavier than solvent particles), together with the corresponding Maxwellian distribution.

The function  $\Phi_E$  coincides with the physically correct Maxwellian distribution  $\Phi_M$  only in the limit of vanishingly small mass ratio  $m_B/m_S$ . For finite values of this ratio,  $\Phi_E$  does *not* coincide  $\Phi_M$ and the above determined stochastic diffusion model is not realistic. This echoes the well-known fact that the diffusion approximation is, strictly speaking, valid only in the limit of vanishing mass ratio between Brownian and solvent particles.

Suppose now that one wants, *e.g.* for simplicity reasons, to use anyway the above determined stochastic process as diffusion model, but in a cautious manner, *i.e.* in knowing the error made in assimilating the real diffusion to this simple Markov process. The simplest and most natural way to do so is to quantify this error by a numerical measure of the discrepancy between  $\Phi_E$  and  $\Phi_M$ . A natural measure for this discrepancy is the conditional or Kullback entropy  $S_c[\Phi_M/\Phi_E]$  of  $\Phi_M$  with respect to  $\Phi_E$ , defined by the following relation [14,15]:



**FIGURE 1.** Invariant measure of the diffusion process for a mass ratio r = 0.01, as a function of the dimensionless velocity  $v/v_0$  with  $v_0 = (k_B \theta/m_B)^{\frac{1}{2}}$  (solid curve). The corresponding Maxwellian distribution is plotted in dashed line. The scale of the vertical axis is arbitrary.

$$S_{c}[\Phi_{M}/\Phi_{E}] \equiv \int_{\mathbb{R}^{3}} \Phi_{M}(\mathbf{v}) \ln\left(\frac{\Phi_{M}(\mathbf{v})}{\Phi_{E}(\mathbf{v})}\right) d^{3} \nu.$$
(20)

Roughly speaking, this entropy measures the difference of information content between  $\Phi_M$  and  $\Phi_E$  and it can serve as a quantitative estimate of the error made in approximating the real transport by a diffusion process. Indeed, if both distributions are close to each other, say symbolically  $\Phi_E(\mathbf{v}) = \Phi_M(\mathbf{v})(1 + \epsilon(\mathbf{v}))$  with  $\epsilon \ll 1$ , then

$$S_{c}[\Phi_{M}/\Phi_{E}] \simeq \int_{\mathbb{R}^{3}} \Phi_{M}(\mathbf{v})(\epsilon(\mathbf{v}))^{2} d^{3} \nu$$
(21)

and the conditional entropy then measures the mean value or average of the squared discrepancy between the  $\Phi_E$  and  $\Phi_M$ . Thus, the smaller the conditional entropy, the better the diffusion approximation. Note that the definition of  $S_c[\Phi_M/\Phi_E]$  is asymmetrical between  $\Phi_E$  and  $\Phi_M$  and that  $S_c[\Phi_M/\Phi_E]$  makes more physical sense than  $S_c[\Phi_M/\Phi_E]$  because it makes more sense to compute the above average by using the true equilibrium measure  $\Phi_M d^3 v$  rather than the approximation  $\Phi_E d^3 v$ .

The conditional entropy  $S_c[\Phi_M/\Phi_E]$  is plotted in figure 2 against the mass ratio r. This plot shows that the diffusion approximation is actually quite robust. For example, with a mass ratio as high as r = 0.01 (Brownian particles only 100 times heavier than solvent particles), the conditional entropy  $S_c[\Phi_M/\Phi_E]$  is as low as 2.2 ·  $10^{-4}$ . But figure 2 also displays the breakdown of the diffusion approximation. Indeed, a mass ratio of r = 1 leads to a conditional entropy of order 0.3, which means that, for this mass ratio,  $\Phi_M/\Phi_E$  is of order 1.3 when v stays inside the central peak of the Gaussian  $\Phi_M$ ; the corresponding mean relative difference between  $\Phi_M$ and  $\Phi_E$  is thus around 30%.

#### 2.3.2. Relative importance of the new gradient-dependent terms

Let us now compare the magnitudes of the new, gradientdependent contributions to the force with the magnitude the usual thermophoresis force. The correction  $(\alpha_1 \mathbf{v}_B \cdot \frac{d\nu}{d\mathbf{r}}) \mathbf{v}_B$  to the friction term is linear in the thermal gradient and can be compared naturally with the thermophoresis force. Let us define the ratio  $\rho_a(T, \mathbf{v}_B)$ of the two by:

$$\rho_{a}(T, \mathbf{v}_{B}) = \frac{\left|\alpha_{1}\left(\theta, \mathbf{v}_{B}^{2}\right)\left(\mathbf{v}_{B} \cdot \frac{d\theta}{d\mathbf{r}}\right)\mathbf{v}_{B}\right|}{\left|\kappa\left(\theta, \mathbf{v}_{B}^{2}\right)\frac{d\theta}{d\mathbf{r}}\right|}.$$
(22)

In the most 'favorable' case ( $\mathbf{v}_B$  parallel to  $\frac{d\theta}{dt}$ ), this ratio can be expressed as a function of the dimensionless variable  $u_B^2 = \mathbf{v}_B^2 m_S / k_B \theta$  only. *A priori*, *B*-particles can have velocities with arbitrary moduli. However, if we assume that the *B*-particles are in statistical equilibrium with the surrounding gas, their most probable velocity scales



**FIGURE 2.** Conditional entropy  $S_c[\Phi_M/\Phi_E]$  of  $\Phi_M$  with respect to  $\Phi_E$ , as a function of the mass ratio  $r = m_s/m_B$ .



**FIGURE 3.** Relative importance of the thermally induced correction to the friction term and of the thermophoresis term, as a function of the mass ratio.

like  $(k_B\theta/m_B)^{\frac{1}{2}}$ , and the dimensionless variable  $u_B^2$  scales like the mass ratio  $m_s/m_B$ . This yields a way to estimate the ratio  $\rho_a$  as a function of the mass ratio only. Figure 3 shows how this estimate of the ratio  $\rho_a$  varies as a function of the mass ratio  $m_s/m_B$ . This shows that the correction to the friction force induced by the temperature gradient cannot be neglected if the mass of *B*-particles is not very large when compared with the mass of the *S*-particles.

The comparison of the thermally induced noise terms to the thermophoresis force is not as straightforward as for the deterministic terms. A glance at equation (3) suggests that the deterministic force terms are to be compared with the *derivative* of the noise terms, with respect to the momentum  $\mathbf{p}_B$  of the Brownian particle. Consequently, to compare the new thermally induced corrections  $\sigma_1(\mathbf{v}_B \cdot \frac{d\theta}{dr})\mathcal{E}, \ \sigma_3(\mathbf{v}_B \cdot \frac{d\theta}{dr})\mathbf{v}_B \otimes \mathbf{v}_B$ , and  $\sigma_4(\mathbf{v}_B \otimes \frac{d\theta}{dr} + \frac{d\theta}{dr} \otimes \mathbf{v}_B)/2$  to the usual thermophoresis term  $\kappa(T, \mathbf{v}_B^2) \frac{d\theta}{dr}$ , we introduce the following dimensionless ratios:

$$\rho_{b}(\theta, \mathbf{v}_{B}) = \frac{\left|\frac{1}{|m_{B}} \nabla_{\mathbf{v}_{B}} \cdot \left(\sigma_{1}\left(\theta, \mathbf{v}_{B}^{2}\right)\left(\mathbf{v}_{B} \cdot \frac{d\theta}{d\mathbf{r}}\right)\mathcal{E}\right)\right|}{|\kappa(\theta, \mathbf{v}_{B}^{2})\frac{d\theta}{d\mathbf{r}}|},\tag{23}$$

$$\rho_{c}(\theta, \mathbf{v}_{B}) = \frac{\left|\frac{1}{m_{B}} \nabla_{\mathbf{v}_{B}} \cdot \left(\sigma_{3}(\theta, \mathbf{v}_{B}^{2}) \left(\mathbf{v}_{B} \cdot \frac{d\theta}{dt}) \mathbf{v}_{B} \otimes \mathbf{v}_{B}\right)\right|}{\left|\kappa(\theta, \mathbf{v}_{B}^{2}) \frac{d\theta}{dt}\right|},$$
(24)

and

$$o_{d}(\theta, \mathbf{v}_{B}) = \frac{\left|\frac{1}{m_{B}} \nabla_{\mathbf{v}_{B}} \cdot \left(\sigma_{4}(\theta, \mathbf{v}_{B}^{2}) \left(\mathbf{v}_{B} \otimes \frac{d\theta}{d\mathbf{r}} + \frac{d\theta}{d\mathbf{r}} \otimes \mathbf{v}_{B}\right)/2\right)\right|}{\left|\kappa(\theta, \mathbf{v}_{B}^{2}) \frac{d\theta}{d\mathbf{r}}\right|}.$$
(25)

Proceeding as before, one can estimate these ratios by functions of the mass ratio *r* only and these are plotted in figures 4 to 6.

From the plot of figure 2, the conditional entropy of  $\Phi_E$  with respect to  $\Phi_M$  is only  $10^{-2}$  for  $r = 10^{-1}$ , which seems to suggest that, at least for  $0 \le r \le 0.1$ , the whole stochastic approach is certainly a reasonably good approximation to the real dynamics. In this range of mass ratios, at least three of the four new, gradient-dependent terms are non-negligible with respect to the thermophoresis force, the most important new contribution coming from the  $\mathbf{u}_B \otimes \nabla \theta$  noise term (approx. 30% of the thermophoresis force for a mass ratio r = 0.01 and approx. 30% for r = 0.1). This proves that the new, gradient-dependent contributions to the force experienced by the Brownian particle are not an artefact of the computation and are thus physically relevant.



**FIGURE 4.** Relative importance of the thermally induced correction to the diagonal noise term, and of the thermophoresis term, as a function of the mass ratio.



**FIGURE 5.** Relative importance of the thermally induced correction to the  $\mathbf{u}_B \otimes \mathbf{u}_B$  noise term, and of the thermophoresis term, as a function of the mass ratio.

#### 3. New stochastic approach to the Ludwig-Soret effect

#### 3.1. General stochastic models

We now want to construct general models inspired by those derived in the previous section to describe thermodiffusion in dilute gases. The key lesson from section 2 is to allow the friction coefficient and the noise tensor to depend, not only on the position of the Brownian particle (through the temperature field  $\theta$ ), but also on its velocity  $\mathbf{v}_B$  through both  $\mathbf{v}_B \otimes \mathbf{v}_B$  and  $\mathbf{v}_B \otimes \nabla \theta$  (note that the scalars  $\mathbf{v}_B^2$  and  $\mathbf{v}_B \cdot \nabla \theta$  are the traces of these tensors).

The computations of the next section simplify greatly in the 1D case. Let us therefore consider a Brownian particle of mass m undergoing 1D motion with position x(t) and momentum p(t) and diffusing through its interactions with a surrounding medium. We suppose that the medium is "isotropic" and globally at rest in the chosen reference frame. Let  $\theta(x)$  be its inhomogeneous temperature field. We focus on generalized Ornstein–Uhlenbeck models of the form:

$$\begin{cases} dx = \frac{p}{m} dt, \\ dp = -\kappa(x, p) \frac{d\theta}{d\mathbf{r}} dt - \alpha^{(S)}(x, p) p dt + (2D(x, p))^{\frac{1}{2}} dB_t, \end{cases}$$
(26)

where  $B_t$  is a standard Brownian motion. The functions  $\kappa$ ,  $\alpha$ , and D may depend on p through both  $p^2$  and  $p(d\theta/dx)$  and they depend on



**FIGURE 6.** Relative importance of the  $u_B \otimes \frac{d\theta}{dr}$  noise term, and the thermophoresis term, as a function of the mass ratio.

*x* at least through the temperature field  $\theta$ . Previous models [9,10] allowed these functions to depend on *x* only. A convention is needed to interpret the multiplicative noise and we adopt the Klimontovitch one. This choice is non-restrictive because any Klimontovitch process of the form (26) can be transcribed into a Stratonovich or into an Itô one of the same form (but with different friction coefficient  $\alpha$ ). The density f(t,x,p) of the process with respect to the phase-space measure dx dp obeys the forward Kolmogorov equation:

$$\partial_t f + \partial_x \left(\frac{p}{m}f\right) = \partial_p \left(\kappa(x, p)\frac{d\theta}{d\mathbf{r}}f\right) + Lf, \qquad (27)$$

where

$$Lf = \partial_p \left( \alpha(x, p) p f + D(x, p) \partial_p f \right).$$
(28)

The spatial density n(t,x) of the diffusing particle is defined by:

$$n(t,x) = \int_{\mathbb{R}} f(t,x,p)dp.$$
<sup>(29)</sup>

#### 3.2. Ludwig-Soret coefficient

#### 3.2.1. Scaling laws

Loosely speaking, the hydrodynamical limit corresponds to near equilibrium situations where all considered fields vary slowly in space and time. This definition can be made precise in the following way. The near equilibrium character of the hydrodynamical regimes is taken into account by assuming that the distribution f of the diffusing particle in phase space can be expanded around a Maxwellian local equilibrium distribution of density n(t,x), temperature  $\theta(x)$  and vanishing mean velocity:

$$f_0(t,x,p) = n(t,x) \frac{\exp\left(-\frac{p^2}{2mk_B\theta(x)}\right)}{(2\pi mk_B\theta(x))^{\frac{1}{2}}}.$$
(30)

We thus introduce an infinitesimal parameter  $\epsilon$  and a collection of functions  $f_k(t,x,p)$  for k > 0 such that the solution of the Kolmogorov equation (27) reads:

$$f(t, \mathbf{x}, \mathbf{p}) = \sum_{k=0}^{\infty} \epsilon^k f_k(t, \mathbf{x}, \mathbf{p}).$$
(31)

We treat (31) as a Chapman–Enskog expansion, and therefore, impose that the  $f_k$ 's for k > 0 do not contribute to the particle density in physical space:

$$\int_{\mathbb{R}} f_k(t, x, p) dp = 0, \quad \text{for } k > 0.$$
(32)

The functions  $f_k$  will be obtained by solving the transport equation (27) and condition (32) implies that all  $f_k$ 's depend on n and  $\theta$  only.

We now assume that the temperature field  $\theta(x)$  of the surrounding fluid fluctuates only weakly around its mean value. In other words, we suppose there exists a typical temperature  $\theta_{\star}$ , such that for all x,  $|\theta(x) - \theta_{\star}| \ll \theta_{\star}$ . It is thus natural to restrict the choice of the model's parameters  $\alpha(x,p)$  and D(x,p) by imposing that there exist also two quantities  $\alpha_{\star}$  and  $D_{\star} = mk_B \alpha_{\star} \theta_{\star}$ , such that  $|\alpha(x,p) - \alpha_{\star}| \ll \alpha_{\star}$  and  $|D(x,p) - D_{\star}| \ll D_{\star}$ , for any value of the particle position x and for any value of the momentum p, accessible with non-vanishing probability.

It is then possible to define a microscopic time-scale  $\tau = 1/\alpha_{\star}$ , which can be interpreted as a mean free-flight time. In the same manner, a microscopic momentum typical scale  $\rho$  can be defined as  $\rho = (D_{\star}/\alpha_{\star})^{\frac{1}{2}}$ . Consequently, the typical length scale  $\lambda = \tau \rho/m$  emerges naturally, and can be interpreted as the mean free path of the diffusing particle.

Let us now suppose (i) that the temperature field varies on a typical length scale  $\lambda/\tilde{\epsilon}$  much larger than the mean free path and (ii) that the distribution function *f* varies on the same length scale as  $\theta$  and on a time-scale  $\tau/v$  much larger than the mean flight time. The infinitesimals  $\tilde{\epsilon}$  and *v* are at this stage *a priori* unrelated to each other and to  $\epsilon$ .

The transport equation (27) is then best solved by introducing the dimensionless time and space variables  $T = vt/\tau$  and  $X = \tilde{\epsilon}x/\lambda$ as well as the dimensionless momentum  $P = p/\rho$ . We also define a dimensionless density N(T,X) as:

$$N(T,X) = \frac{\lambda}{\tilde{\epsilon}} n\left(\frac{T\tau}{\nu}, \frac{X\lambda}{\tilde{\epsilon}}\right),\tag{33}$$

and a dimensionless phase space density F(T,X,P) as:

$$F(T, X, P) = \frac{\lambda \rho}{\tilde{\epsilon}} f\left(\frac{T\tau}{\nu}, \frac{X\lambda}{\tilde{\epsilon}}, \rho P\right),$$
(34)

so that the following simple normalization relations hold:

$$\int_{\mathbb{R}} N(T, X) dX = 1, \tag{35}$$

$$\int_{\mathbb{R}^2} F(T, X, P) dX dP = 1.$$
(36)

In terms of the dimensionless variables, the Kolmogorov equation (27) reads:

$$v \partial_T F + \tilde{\epsilon} \partial_X (PF) = \tilde{\epsilon} \partial_P \left( K(X, P) \frac{d\Theta}{dX} F \right) + \mathcal{L}F, \qquad (37)$$

where

$$K(X,P) = \frac{\kappa(\frac{X\lambda}{\tilde{\epsilon}}, P\rho)}{k_B} \quad \text{and} \quad \Theta(X) = \frac{\theta(\frac{X\lambda}{\tilde{\epsilon}})}{\theta_{\star}}.$$
(38)

The linear operator  $\mathcal{L}$  is defined by:

$$\mathcal{L}F = \partial_P(\mathcal{A}(X, P)PF + \mathcal{D}(X, P)\partial_P F), \tag{39}$$

with

$$\mathcal{A}(X,P) = \frac{\alpha(\frac{X\lambda}{\epsilon},P\rho)}{\alpha_{\star}} \tag{40}$$

and

$$\mathcal{D}(X,P) = \frac{D(\frac{\chi_{\lambda}}{\epsilon}, P\rho)}{D_{\star}}.$$
(41)

The first two moments of (37) read:

$$\begin{cases} v\partial_T N + \tilde{\epsilon}\partial_X J = \mathbf{0}, \\ v\partial_T J + \tilde{\epsilon}\partial_X S = -\tilde{\epsilon}K(X,P)\frac{d\Theta}{dX}N - \int_{\mathbb{R}}\mathcal{A}(X,P)PFdP + \int_{\mathbb{R}}\partial_P\mathcal{D}(X,P)FdP, \end{cases}$$
(42)

where *J* is the dimensionless particle current  $\int_{\mathbb{R}} PF dP$ , and *S* is  $\int_{\mathbb{R}} P^2 F dP$ . Since all odd-order momenta of the Maxwell distribution vanish, all odd-order momenta of the distribution *F* given by (31) are  $\mathcal{O}(\epsilon)$ . Thus, *J* and the integrals in the right-hand side of (42) are  $\mathcal{O}(\epsilon)$ , but *S* is  $\mathcal{O}(1)$ . The first equation in (42) thus implies that  $v = \tilde{\epsilon}\epsilon$  but the second one does not enforce any particular relation between  $\epsilon$  and  $\tilde{\epsilon}$ . Three types of scalings are thus compatible with (42). The first one is  $\tilde{\epsilon} < \epsilon$ , the second one is  $\tilde{\epsilon} > \epsilon$  and the third one is evidently  $\tilde{\epsilon} = \epsilon$ . Solutions which obey this last scaling law will exhibit a richer macroscopic physics because the choice  $\tilde{\epsilon} = \epsilon$  maximizes the number of term of equal order in (42). We, therefore, focus on this scaling law and thus retain:

$$\tilde{\epsilon} = \epsilon \quad \text{and} \quad v = \epsilon^2$$
(43)

for the remainder of this contribution. Note that these scaling laws are identical to those obeyed by the hydrodynamic regimes of the Ornstein–Uhlenbeck process in uniform temperature fields.

#### 3.2.2. First order Chapman–Enskog expansion

We now write down the Kolmogorov equation at first order in  $\epsilon$ . According to (37), we need *K* at zeroth order and  $\mathcal{L}$ , *i.e.*  $\mathcal{A}$  and  $\mathcal{D}$ , at first order. We suppose that *K*, at zeroth order in  $\epsilon$ , is a constant  $K_0$  independent of *x* and *p*. The force proportional to  $\frac{d\theta}{dr}$  is then exactly identical to the standard thermophoresis force. The friction and noise coefficients are expanded into:

$$\mathcal{A}(X,P) = \mathcal{A}_0(X,P^2) + \epsilon \mathcal{A}_1(X,P^2) P \frac{d\Theta}{dX},$$
(44)

and

$$\mathcal{D}(X,P) = \mathcal{D}_0(X,P^2) + \epsilon \mathcal{D}_1(X,P^2) P \frac{d\Theta}{dX}.$$
(45)

We further assume that  $A_0$  and  $D_0$  obey the *local* fluctuation-dissipation relation:

$$\frac{\mathcal{D}_0(X, P^2)}{\mathcal{A}_0(X, P^2)} = \Theta(X), \quad \text{for all } P \text{ and } X.$$
(46)

The terms  $A_1$  and  $D_1$  have been omitted by previous authors but are clearly necessary if one wants to ensure the consistency of the first order treatment.

The Kolmogorov equation then reads, at first order in  $\epsilon$ :

$$\epsilon \partial_X (PF) - \epsilon K_0 \frac{d\Theta}{dX} \partial_P F = \mathcal{L}_0 F + \epsilon \frac{d\Theta}{dX} \mathcal{L}_1 F$$
(47)

with

)

$$\mathcal{L}_0 F = \partial_P (\mathcal{A}_0(X, P^2) P F + \mathcal{D}_0(X, P^2) \partial_P F)$$
(48)

and

$$\mathcal{L}_1 F = \partial_P (\mathcal{A}_1(X, P^2) P^2 F + \mathcal{D}_1(X, P^2) P \partial_P F).$$
(49)

The dimensionless local equilibrium distribution:

$$F_0(T, X, P) = N(T, X) \frac{\exp(-P^2/2\Theta(X))}{(2\pi\Theta(X))^{\frac{1}{2}}}$$
(50)

solves (47) at order zero in  $\epsilon$ . The first order terms of (47) collect into:

$$\mathcal{L}_0 F_1 = \partial_X (PF_0) - \frac{d\Theta}{dX} (K_0 \partial_P F_0 + \mathcal{L}_1 F_0),$$
(51)

where  $F_1$  is the dimensionless version of  $f_1$ , the first order term of the Chapman–Enskog expansion (31). Equation (51) can be integrated over *P* to deliver:

$$\mathcal{A}_{0}(X,P^{2})PF_{1} + \mathcal{D}_{0}(X,P^{2})\partial_{P}F_{1} = -\partial_{X}(\Theta(X)F_{0}(T,X,P)) - \frac{d\Theta}{dX}(K_{0}F_{0} + \mathcal{A}_{1}(X,P^{2})P^{2}F_{0} + \mathcal{D}_{1}(X,P^{2})P\partial_{P}F_{0}).$$
(52)

The function  $H_1(T,X,P)$ , defined by:

$$H_1(T, X, P) = F_1(T, X, P) \frac{(2\pi \Theta(X))^{\frac{1}{2}}}{\exp(-P^2/2\Theta(X))},$$
(53)

for all *T*, *X*, and *P*, verifies:

$$\partial_{P}H_{1} = -\frac{\Theta(X)}{\mathcal{D}_{0}(X,P^{2})}\partial_{X}N - \left(\frac{\frac{1}{2} + K_{0} + P^{2}\mathcal{A}_{1}(X,P^{2})}{\mathcal{D}_{0}(X,P^{2})}\right)N\frac{d\Theta}{dX} - \left(\frac{\frac{1}{2} - \mathcal{D}_{1}(X,P^{2})}{\mathcal{D}_{0}(X,P^{2})}\right)P^{2}\frac{N}{\Theta(X)}\frac{d\Theta}{dX}.$$
(54)

The first order contribution  $J_1$  to the particle current can be expressed in terms of the function  $H_1$  as:

$$J_{1}(T,X) = \int_{\mathbb{R}} H_{1}(T,X,P) \frac{\exp(-P^{2}/2\Theta(X))}{(2\pi\Theta(X))^{\frac{1}{2}}} P dP$$
$$= \Theta(X) \int_{\mathbb{R}} \partial_{P} H_{1}(T,X,P) \frac{\exp(-P^{2}/2\Theta(X))}{(2\pi\Theta(X))^{\frac{1}{2}}} dP.$$
(55)

Taking into account expression (54) for  $\partial_P H_1$ , the first order contribution to the particle current can be related as follows to the gradients of the particle density and of the temperature:

$$J_1(T,X) = -\Phi(X)\frac{\partial N}{\partial X} - \Psi(X)N(T,X)\frac{d\Theta}{dX},$$
(56)

where the diffusion coefficient  $\Phi$  and the thermal diffusion coefficient  $\Psi$  have the following expressions:

$$\begin{split} \Phi &= \Theta^{2}(X) \int_{\mathbb{R}} \frac{1}{\mathcal{D}_{0}(X,P^{2})} \frac{\exp(-P^{2}/2\Theta(X))}{(2\pi\Theta(X))^{\frac{1}{2}}} dP, \\ \Psi &= \Theta(X) \int_{\mathbb{R}} \frac{\frac{1}{2}+K_{0}}{\mathcal{D}_{0}(X,P^{2})} \frac{\exp(-P^{2}/2\Theta(X))}{(2\pi\Theta(X))^{\frac{1}{2}}} dP + \\ \Theta(X) \int_{\mathbb{R}} \frac{A_{1}(X,P^{2})}{\mathcal{D}_{0}(X,P^{2})} \frac{\exp(-P^{2}/2\Theta(X))}{(2\pi\Theta(X))^{\frac{1}{2}}} P^{2} dP + \\ \int_{\mathbb{R}} \frac{\frac{1}{2}-\mathcal{D}_{1}(X,P^{2})}{\mathcal{D}_{0}(X,P^{2})} \frac{\exp(-P^{2}/2\Theta(X))}{(2\pi\Theta(X))^{\frac{1}{2}}} P^{2} dP. \end{split}$$
(57)

The first term in (56) is the usual contribution of the particle density gradient to the particle current (Fick's law). The second is the traditional macroscopic description of the Ludwig–Soret effect. Previous stochastic models [10] neglect the  $A_1$  and  $D_1$  contributions to  $\Psi$  and also assume that  $D_0$  is independent of  $P^2$ . It is clear that the new models are much more flexible and allow, for example, for positive as well as negative values of the Soret coefficient.

To fully test these new models, one should have experimental access, not only to Soret coefficients and to  $A_0$  and  $D_0$  coefficients, but also to  $A_1$  and  $D_1$  coefficients. To the best of our knowledge, no  $A_1$  and  $D_1$  coefficient has yet been measured, if only because previous theoretical efforts had not taken these coefficients into account and thus, presumably, drawn the attention of experimentalists away from measuring them. A less satisfactory alternative would be to compute these coefficients from molecular dynamics models. Unfortunately, no such computation exists at present in the literature.

#### 4. Conclusion

We have used the Boltzmann equation to obtain new effective stochastic descriptions of dilute gas diffusions in the presence of temperature gradients. These new descriptions have then been used as templates to construct new, more general Markov processes of thermodiffusion and the Ludwig–Soret coefficient has been computed for these models. Our main results are that temperature gradients induce new contributions to the friction coefficient and noise tensor acting on the diffusing particle and that these contributions must be taken into account if one wants to achieve a realistic theoretical prediction of the Ludwig–Soret coefficient.

This work can be prolonged in various directions. First and foremost, one should compute the new contributions to the friction coefficient and noise tensor outside the dilute gas regime; this will be probably best achieved through molecular dynamics simulations. One also wonders how the results presented in this article are modified if the temperature gradient driving the diffusion depends on time. For dilute gases, the first step in addressing this problem would be to find non-stationary solutions of the Boltzmann equation describing the evolution of the solvent under the time-dependent temperature gradient. Finally, a relativistic extension of this work is also mandatory, if only to develop realistic stochastic models of diffusions in relativistic stars [16]; this extension should be based upon the purely kinetic description of relativistic thermodiffusion presented in [17–19].

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