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STOCHASTIC MODELS OF THERMODIFFUSION

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New stochastic models of thermodiffusion are constructed and their hydrodynamical limits are studied through a first-order Chapman–Enskog expansion. These models differ from earlier ones by taking into account all first-order contributions proportional to the temperature gradient and, thus, allow for both positive and negative Soret coefficients, in accordance with observations.

Keywords: Stochastic processes; classical transport.

1. Introduction

Stochastic process theory is one of the most popular tools used in modeling timeasymmetric phenomena, with applications as diverse as economics,^{1,2} traffic management,^{3,4} biology,^{5,6} physics and chemistry⁷ and cosmology.⁸ Stochastic models of thermodiffusion⁹ have been proposed in the late $80s^{10,11}$ and have been recently reconsidered.¹² These are based on generalizations of the Langevin equation and model the microscopic motion of a colloidal particle undergoing Brownian motion in a fluid with non-uniform temperature field. The most elaborate description^{11,12} assumes that the colloidal particle diffuses under the influence of three forces. The first one is the thermophoresis force, independent of the particle velocity and directly proportional to the temperature gradient. The second force is a viscous fluid force and the third one is stochastic, proportional to a Gaussian white noise. The friction and noise coefficients are allowed to depend on position through the temperature field and they obey a local fluctuation-dissipation relation. An expansion in the inverse friction coefficient then predicts that the particle current contains a contribution linear in the temperature gradient, as in traditional macroscopic models of thermodiffusion.

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Observations of thermodiffusion reveal however that these models are not fully realistic. For example, these models predict that Soret coefficients can only take positive values, whereas both positive and negative values have been measured experimentally.¹³⁻¹⁶ Also, the orders of magnitude of observed coefficients¹² often differ substantially from theoretical predictions based on these models.¹¹ Explanations for these discrepancies have been proposed¹² but an important and simple one seems to have been overlooked. In a non-uniform temperature field, friction and noise coefficients generally depend on position, not only through the temperature field, but also through its derivatives. For small enough temperature inhomogeneities, the friction and noise coefficients thus contain contributions directly proportional to the temperature gradient. These terms, which are *a priori* of the same order of magnitude as the thermophoresis force, have until now been ignored in the literature.

This letter remedies the problem by presenting new stochastic models of thermodiffusion. These are fully consistent and take into account all first-order corrections induced by temperature gradients. The traditional macroscopic description of thermodiffusion is recovered from these new models by a Chapman–Enskog expansion. The new stochastic models are much more flexible than the previous ones¹¹ and allow for example, for positive as well as negative values of Soret coefficients.

2. General Stochastic Models

Let us consider a Brownian^a particle 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 following form:

$$\begin{cases} dx_t = \frac{p_t}{m} dt, \\ dp_t = -\kappa(x_t, p_t) \frac{d\theta}{dx} dt - \alpha^{(S)}(x_t, p_t) p_t dt + \sqrt{2D(x_t, p_t)} dB_t. \end{cases}$$
(1)

Here, B_t is a standard Brownian motion and the superscript (s) indicates that these equations are to be understood in the Stratonovich sense.¹⁸ The term proportional to the temperature gradient is a generalized thermophoresis force. It coincides with the traditional velocity-independent thermophoresis force if κ is a constant. The density f(t, x, p) of the process with respect to the phase-space measure dxdp obeys the forward Kolmogorov equation,

$$\partial_t f + \partial_x \left(\frac{p}{m}f\right) = \partial_p \left(\kappa(x, p)\frac{d\theta}{dx}f\right) + Lf, \qquad (2)$$

 $^{\rm a}{\rm A}$ particle whose size is much larger than the microscopic scale of the surrounding medium, but much smaller than any macroscopically relevant scale.

where $\alpha(x,p) = \alpha^{(S)}(x,p) + \frac{1}{2p}\partial_p D(x,p)$ and

$$Lf = \partial_p \left(\alpha(x, p) p f + D(x, p) \partial_p f \right).$$
(3)

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

$$n(t,x) = \int_{\mathbb{R}} f(t,x,p)dp.$$
(4)

3. Hydrodynamic Limit

3.1. 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 the Maxwellian local equilibrium distribution of density n(t, x), temperature $\theta(x)$ and vanishing mean velocity:

$$f_0(t,x,p) = n(t,x) \frac{\exp\left(-\frac{p^2}{2mk_B\theta(x)}\right)}{\sqrt{2\pi mk_B\theta(x)}}.$$
(5)

We thus introduce an infinitesimal parameter ϵ and a collection of functions $f_k(t, x, p)$ for k > 0 such that the solution of the Kolmogorov equation (2) reads:

$$f(t,x,p) = \sum_{k=0}^{\infty} \epsilon^k f_k(t,x,p) \,. \tag{6}$$

We treat Eq. (6) as a Chapman–Enskog expansion and therefore impose that the f_k s for k > 0 do not contribute to the particle density,

$$\int_{\mathbb{R}} f_k(t, x, p) dp = 0, \quad \text{for } k > 0.$$
(7)

The functions f_k will be obtained by solving the transport equation (2) and condition (7) implies that the all f_k s depend on n and θ 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 θ_{\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 α_{\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 ρ can be defined as $\rho = \sqrt{D_{\star}/\alpha_{\star}}$. 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 θ and on a time-scale τ/ν much larger than the mean flight time. The infinitesimals $\tilde{\epsilon}$ and ν are at this stage a priori unrelated to each other and to ϵ .

The transport equation (2) is then best solved by introducing the dimensionless time and space variables $T = \nu t/\tau$ and $X = \tilde{\epsilon}x/\lambda$ as well as the dimensionless momentum $P = p/\rho$. We also define a dimensionless density N(T, X) and a dimensionless phase space density F(T, X, P) as

$$N(T,X) = \frac{\lambda}{\tilde{\epsilon}} n\left(\frac{T\tau}{\nu}, \frac{X\lambda}{\tilde{\epsilon}}\right) \quad \text{and} \quad F(T,X,P) = \frac{\lambda\rho}{\tilde{\epsilon}} f\left(\frac{T\tau}{\nu}, \frac{X\lambda}{\tilde{\epsilon}}, \rho P\right), \tag{8}$$

so that the following simple normalization relations hold:

$$\int_{\mathbb{R}} N(T, X) dX = 1 \quad \text{and} \quad \int_{\mathbb{R}^2} F(T, X, P) dX dP = 1.$$
(9)

In terms of the dimensionless variables, the Kolmogorov equation (2) reads

$$\nu \partial_T F + \tilde{\epsilon} \partial_X \left(P F \right) = \tilde{\epsilon} \partial_P \left(K(X, P) \frac{d\Theta}{dX} F \right) + \mathcal{L} F \,, \tag{10}$$

where

$$K(X,P) = \frac{\kappa\left(\frac{X\lambda}{\tilde{\epsilon}}, P\rho\right)}{k_B} \quad \text{and} \quad \Theta(X) = \frac{\theta\left(\frac{X\lambda}{\tilde{\epsilon}}\right)}{\theta_{\star}}.$$
 (11)

The linear operator \mathcal{L} is defined by

$$\mathcal{L}F = \partial_P \left(\mathcal{A}(X, P) \, P \, F + \mathcal{D}(X, P) \partial_P F \right), \tag{12}$$

with

$$\mathcal{A}(X,P) = \frac{\alpha\left(\frac{X\lambda}{\tilde{\epsilon}}, P\rho\right)}{\alpha_{\star}} \quad \text{and} \quad \mathcal{D}(X,P) = \frac{D\left(\frac{X\lambda}{\tilde{\epsilon}}, P\rho\right)}{D_{\star}}.$$
 (13)

The first two moments of Eq. (10) reads

$$\begin{cases}
\nu \partial_T N + \tilde{\epsilon} \partial_X J = 0 \\
\nu \partial_T J + \tilde{\epsilon} \partial_X S = -\tilde{\epsilon} K(X, P) \frac{d\Theta}{dX} N \\
- \int_{\mathbb{R}} \mathcal{A}(X, P) P F dP + \int_{\mathbb{R}} \partial_P \mathcal{D}(X, P) F dP,
\end{cases}$$
(14)

where J is the dimensionless particle current $\int_{\mathbb{R}} P F dP$, 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 Eq. (6) are $\mathcal{O}(\epsilon)$. Thus, J and the integrals on the right-hand side of Eq. (14) are $\mathcal{O}(\epsilon)$, but S is $\mathcal{O}(1)$. The first equation in (14) thus implies that $\nu = \tilde{\epsilon}\epsilon$ but the second one does not enforce any particular relation between ϵ and $\tilde{\epsilon}$. We choose to investigate the case $\tilde{\epsilon} = \epsilon$. Solutions which obey this scaling law exhibit a richer macroscopic physics than solutions associated to other scalings because the choice $\tilde{\epsilon} = \epsilon$ maximizes the number of term of equal order in (14). We thus focus on this scaling law and therefore retain $\tilde{\epsilon} = \epsilon$ and $\nu = \epsilon^2$ for the remainder of this letter. 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. First-order Chapman–Enskog expansion

We now write down the Kolmogorov equation at first-order in ϵ . According to Eq. (10), 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 ϵ , is a constant K_0 independent of x and p. The force proportional to $\frac{d\theta}{dx}$ is then exactly identical to the standard thermophoresis force. The friction and noise coefficients are expanded into

$$\mathcal{A}(X,P) = \mathcal{A}_0(X,P^2) + \epsilon \mathcal{A}_1(X,P^2) P \frac{d\Theta}{dX}, \qquad (15)$$

and

$$\mathcal{D}(X,P) = \mathcal{D}_0(X,P^2) + \epsilon \mathcal{D}_1(X,P^2) P \frac{d\Theta}{dX}.$$
 (16)

We further assume that \mathcal{A}_0 and \mathcal{D}_0 obey the *local* fluctuation-dissipation relation,

$$\frac{\mathcal{D}_0(X, P^2)}{\mathcal{A}_0(X, P^2)} = \Theta(X), \quad \text{for all } P \text{ and } X, \qquad (17)$$

The terms \mathcal{A}_1 and \mathcal{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 ϵ ,

$$\epsilon \partial_X (PF) - \epsilon K_0 \frac{d\Theta}{dX} \partial_P F = \mathcal{L}_0 F + \epsilon \frac{d\Theta}{dX} \mathcal{L}_1 F, \qquad (18)$$

with

$$\mathcal{L}_0 F = \partial_P \left(\mathcal{A}_0(X, P^2) P F + \mathcal{D}_0(X, P^2) \partial_P F \right), \tag{19}$$

and

$$\mathcal{L}_1 F = \partial_P \left(\mathcal{A}_1(X, P^2) P^2 F + \mathcal{D}_1(X, P^2) P \partial_P F \right).$$
⁽²⁰⁾

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The dimensionless local equilibrium distribution,

$$F_0(T, X, P) = N(T, X) \frac{e^{-\frac{P^2}{2\Theta(X)}}}{\sqrt{2\pi\Theta(X)}},$$
(21)

solves Eq. (18) at order zero in ϵ . The first-order terms of Eq. (18) collect into

$$\mathcal{L}_0 F_1 = \partial_X (P F_0) - \frac{d\Theta}{dX} (K_0 \partial_P F_0 + \mathcal{L}_1 F_0), \qquad (22)$$

where F_1 is the dimensionless version of f_1 , the first-order term of the Chapman– Enskog expansion (6). Equation (22) can be integrated over P to deliver

$$\mathcal{A}_0(X, P^2)PF_1 + \mathcal{D}_0(X, P^2)\partial_P F_1$$

= $-\partial_X(\Theta(X)F_0(T, X, P))$
 $-\frac{d\Theta}{dX}(K_0F_0 + \mathcal{A}_1(X, P^2)P^2F_0 + \mathcal{D}_1(X, P^2)P\partial_P F_0).$ (23)

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

$$H_1(T, X, P) = F_1(T, X, P) \frac{\sqrt{2\pi\Theta(X)}}{e^{-\frac{P^2}{2\Theta(X)}}},$$
(24)

for all T, X and P, verifies

$$\partial_P H_1 = -\frac{\Theta(X)}{\mathcal{D}_0(X, P^2)} \partial_X N - \left(\frac{\frac{1}{2} + K_0 + P^2 \mathcal{A}_1(X, P^2)}{\mathcal{D}_0(X, P^2)}\right) N \frac{d\Theta}{dX} - \left(\frac{\frac{1}{2} - \mathcal{D}_1(X, P^2)}{\mathcal{D}_0(X, P^2)}\right) P^2 \frac{N}{\Theta(X)} \frac{d\Theta}{dX}.$$
(25)

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

$$J_1(T,X) = \Theta(X) \int_{\mathbb{R}} \partial_P H1(T,X,P) \frac{\mathrm{e}^{-\frac{P^2}{2\Theta(X)}}}{\sqrt{2\pi\Theta(X)}} \, dP \,. \tag{26}$$

Taking into account expression (25) 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:

$$J_1(T,X) = -\Phi(X)\frac{\partial N}{\partial X} - \Psi(X)N(T,X)\frac{d\Theta}{dX},$$
(27)

where the diffusion coefficient Φ and the thermal diffusion coefficient Ψ have the following expressions

$$\begin{cases} \Phi = \Theta^{2}(X) \int_{\mathbb{R}} \frac{1}{\mathcal{D}_{0}(X, P^{2})} \frac{e^{-\frac{P^{2}}{2\Theta(X)}}}{\sqrt{2\pi\Theta(X)}} dP, \\ \Psi = \Theta(X) \int_{\mathbb{R}} \frac{\frac{1}{2} + K_{0} + P^{2}\mathcal{A}_{1}(X, P^{2})}{\mathcal{D}_{0}(X, P^{2})} \frac{e^{-\frac{P^{2}}{2\Theta(X)}}}{\sqrt{2\pi\Theta(X)}} dP \\ + \int_{\mathbb{R}} \frac{\frac{1}{2} - \mathcal{D}_{1}(X, P^{2})}{\mathcal{D}_{0}(X, P^{2})} \frac{e^{-\frac{P^{2}}{2\Theta(X)}}}{\sqrt{2\pi\Theta(X)}} P^{2} dP. \end{cases}$$
(28)

The first term is the usual contribution of the particle density gradient to the particle current (Fick's law). The second represents the traditional macroscopic description of the Ludwig–Soret effet.

4. Application to a Simple Class of Thermodiffusion Models

The precise expressions of \mathcal{A} and \mathcal{D} depend on both the diffusing colloidal particle and on the solvent. These may be derived from kinetic collisional models.¹⁷ Let us illustrate the phenomenology of the new stochastic models presented in the previous sections through a simple yet instructive example. Suppose that \mathcal{D}_0 is constant (with \mathcal{A}_0 then given by Eq. (17)) and that $\mathcal{A}_1 = a_1/|p|$ and $\mathcal{D}_1 = d_1/|p|$, where a_1 and d_1 are also constant. This is one of the simplest model for which all coefficients are defined for all values of p and for which the relative corrections $\epsilon \mathcal{A}_1/\mathcal{A}_0$ and $\epsilon \mathcal{D}_1/\mathcal{D}_0$ remain bounded for all p.

A direct computation then delivers

$$\Psi = \theta \frac{(1+K_0)}{D_0} + \frac{\theta^{3/2}}{(2\pi)^{1/2}} a_1 - \frac{2\theta^{1/2}}{\pi^{1/2}D_0}.$$
(29)

This simple result illustrates how the new stochastic models can encompass a lot of physical situations, with positive or negative Soret coefficients and with realistic temperature variations of both the diffusion and Soret coefficients.

5. Conclusion

We have introduced new microscopic stochastic models for the Ludwig–Soret effect. These models are essentially Ornstein–Uhlenbeck processes with position dependent noise and friction coefficients and an additional thermophoresis force term. They differ from the previously introduced models by consistently taking into account all possible contributions generated by a non-vanishing temperature gradient. The hydrodynamic limit of these models has been studied with a first-order Chapman–Enskog expansion. The new models predict that large scale temperature inhomogeneities induce a non-vanishing particle current proportional to the temperature gradient. This prediction concurs with standard macroscopic models from continuous media theories.⁹ The new models are also flexible enough to describe thermodiffusion in a much more realistic way than earlier stochastic approaches, allowing in particular for both positive and negative Soret coefficients.

This work can and should be extended in various directions. A first task is to consider several practically important applications of the Ludwig–Soret effect^{19–23} and to determine, for each of these applications, which model(s) in the class introduced above best fits the experimental situations. Since the new microscopic models contain contributions linear in temperature gradients which are absent form the older models, it is for example natural to wonder if these extra terms suffice to explain all the documented discrepancies between measured values of the Soret coefficients and previous theoretical predictions.

On the more theoretical side, the work presented in this article should be extended to both special and general relativistic realms,^{24–26} if only to model temperature driven diffusions in stars.²⁷

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