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Time-dependent transport coefficients: an effective macroscopic description of small scale dynamics?

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Abstract

Situations where particles taken from a thermal reservoir are immersed at some initial time in a fluid are considered. The diffusion model is the Ornstein–Uhlenbeck process. It is proven that particle transport in physical space can be described exactly at all times with the help of a time dependent diffusion coefficient; the result is, in particular, valid outside of the hydrodynamic regime. The use of time-dependent transport coefficients in other contexts in also discussed. *To cite this article: F. Debbasch, J.-P. Rivet, C. R. Physique 9 (2008).*
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Résumé

Coefficients de transport dépendant du temps : vers une description macroscopique des dynamiques à petite échelle. On considère des situations où des particules extraites d'un réservoir à l'équilibre thermique sont immergées, à un instant donné, dans un fluide. Le model utilisé est le processus d'Ornstein–Uhlenbeck. On prouve que le transport de particules dans l'espace physique peut se décrire exactement et à tout instant à l'aide de coefficients de diffusion dépendant du temps. Ce résultat est valide, en particulier, en dehors du régime hydrodynamique. On discute également l'utilisation, dans d'autres contextes, de coefficients de transport non constants. *Pour citer cet article : F. Debbasch, J.-P. Rivet, C. R. Physique 9 (2008).*
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1. Introduction

The first historical descriptions of transport phenomena are purely macroscopic. They are based on the assumption that fluxes are proportional, with constant coefficient, to the gradients of the associated densities. The prototypical

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transport equation is the diffusion equation; it can be derived from Fick's law, which states that the matter flux is proportional to the gradient of the matter density.

All historic macroscopic equations [1–3] can now be derived from microscopic transport equations by assuming that the local state describing the system varies on space and time scales much larger than a microscopic collision time between particles and an associated mean free path [4]. These conditions correspond to the so-called hydrodynamic limit. When either of them is violated, the dynamics prescribed by the macroscopic equations fails to reproduce the microscopic dynamics fixed by transport equations.

Obtaining macroscopic equations which correctly describe transport outside the range of validity of the hydrodynamic limit is still a challenging issue [5]. Indeed, a large body of work has been devoted to developing such new macroscopic descriptions [5–7]. The most popular theories are perhaps those commonly called Extended Thermodynamics [8,9], which can be obtained from the transport equations via Grad expansions [10]. These theories are however plagued with serious difficulties [8,11]; thus, the problem of building purely macroscopic descriptions of continuous media with larger application domains than conventional hydrodynamical theories is still an open one.

The aim of this Note is to suggest a possible new approach to this problem. We focus on the simplest transport phenomenon, namely matter diffusion, and consider situations in which an observer "creates" the system at time $t = 0$ by immersing diffusing particles in a given fluid. We restrict to situations where the diffusing particles are extracted from a thermal bath and use the standard Ornstein–Uhlenbeck process [12,13] as fundamental microscopic model. We prove that the particle current is then exactly proportional to the spatial density gradient, at all times, even for short times where the hydrodynamic limit is not yet reached. This extension to short times of the usual Fick's law requires the proportionality coefficient to be time-dependent. As expected, this time-dependent coefficient tends towards a constant for long times.

2. The stochastic model

The Ornstein–Uhlenbeck Process is defined by the following system of stochastic differential equations [12,13]:

$$d\mathbf{x} = \mathbf{v}\,dt, \qquad d\mathbf{v} = -\alpha\mathbf{v}\,dt + \sqrt{2D}\,d\mathbf{W}_t \tag{1}$$

where $\mathbf{W}_t$ is the 3-D Wiener process. The system (1) can be interpreted as the equations of motion of a particle of mass m under the action of a deterministic force $-\alpha\mathbf{v}$ and a stochastic Gaussian force.

Let $\Pi(t, \mathbf{x}, \mathbf{v})$ be the particle distribution in phase-space, normalized to unity with respect to $d^3x\,d^3p$. This distribution obeys the so-called Kramers or forward Kolmogorov equation [13,14]:

$$\partial_t \Pi + \nabla_{\mathbf{x}}(\mathbf{v}\Pi) + \nabla_{\mathbf{v}}(-\alpha\mathbf{v}\Pi) = \frac{D}{m^2}\Delta_{\mathbf{v}}\Pi \tag{2}$$

In a finite volume $\mathcal{V}$, this transport equation (2) admits the following uniform equilibrium solution:

$$\Pi_e(t, \mathbf{x}, \mathbf{v}) = \frac{1}{\mathcal{V}}\left(\frac{2\pi D}{m^2\alpha}\right)^{-3/2}\exp\left[-\frac{m^2\alpha}{2D}\mathbf{v}^2\right] \tag{3}$$

It is natural to identify this distribution with the Maxwellian associated to the temperature T_e of the fluid surrounding the particle. One thus has the following fluctuation–dissipation theorem [13]:

$$k_B T_e = \frac{D}{m\alpha} \tag{4}$$

where k_B is the Boltzmann constant.

3. Exact resolution of the forward Kolmogorov equation

What follows is inspired by [15–18]. We start from the transport equation (2), and use the fluctuation–dissipation theorem (4) to rewrite it in terms of the equilibrium temperature T_e. We introduce the Fourier transform $\hat{\Pi}(t, \mathbf{k}, \mathbf{u})$ of the distribution function $\Pi(t, \mathbf{x}, \mathbf{v})$:

$$\hat{\Pi}(t, \mathbf{k}, \mathbf{u}) = \frac{1}{\sqrt{2\pi}^6}\int_{\mathbb{R}^6} \Pi(t, \mathbf{x}, \mathbf{v})\exp\left[-i(\mathbf{k}\cdot\mathbf{x} + \mathbf{u}\cdot\mathbf{v})\right]d^3x\,d^3v \tag{5}$$

If $\hat{\Pi}$ does not vanish anywhere, Eq. (2) implies:

$$\partial_t(\ln \hat{\Pi}) = (\mathbf{k} - \alpha\mathbf{u}) \cdot \nabla_\mathbf{u}(\ln \hat{\Pi}) - \frac{k_B T_e \alpha}{m}\mathbf{u}^2 \tag{6}$$

We now introduce the new function $\lambda(t, \mathbf{k}, \mathbf{u}) \equiv \partial_t(\ln \hat{\Pi})$, so that:

$$\ln \hat{\Pi}(t, \mathbf{k}, \mathbf{u}) = \ln \hat{\Pi}_0(\mathbf{k}, \mathbf{u}) + \int_0^t \lambda(\tau, \mathbf{k}, \mathbf{u})\, d\tau \tag{7}$$

where $\hat{\Pi}_0(\mathbf{k}, \mathbf{u})$ stands for $\hat{\Pi}(0, \mathbf{k}, \mathbf{u})$. Eq. (6) imposes that $\lambda(t, \mathbf{k}, \mathbf{u})$ verify:

$$\lambda(t, \mathbf{k}, \mathbf{u}) = (\mathbf{k} - \alpha\mathbf{u}) \cdot \left(\nabla_\mathbf{u}(\ln \hat{\Pi}_0) + \int_0^t \nabla_\mathbf{u}\lambda(\tau, \mathbf{k}, \mathbf{u})\, d\tau \right) - \frac{k_B T_e \alpha}{m}\mathbf{u}^2 \tag{8}$$

which, for $t = 0$, leads to:

$$\lambda(0, \mathbf{k}, \mathbf{u}) = (\mathbf{k} - \alpha\mathbf{u}) \cdot \left(\nabla_\mathbf{u}(\ln \hat{\Pi}_0) \right) - \frac{k_B T_e \alpha}{m}\mathbf{u}^2 \tag{9}$$

Deriving Eq. (8) with respect to t yields the following partial differential equation for λ:

$$\partial_t \lambda(t, \mathbf{k}, \mathbf{u}) = (\mathbf{k} - \alpha\mathbf{u}) \cdot \nabla_\mathbf{u}\lambda(t, \mathbf{k}, \mathbf{u}) \tag{10}$$

Let us introduce the new variable $\mathbf{p} \equiv \mathbf{k} - \alpha\mathbf{u}$ and the new function $\tilde{\lambda}(t, \mathbf{k}, \mathbf{p}) \equiv \lambda(t, \mathbf{k}, (\mathbf{k} - \mathbf{p})/\alpha)$. By Eq. (10), $\tilde{\lambda}$ satisfies:

$$\partial_t \tilde{\lambda} = -\alpha \mathbf{p} \cdot \nabla_\mathbf{p} \tilde{\lambda} \tag{11}$$

which implies that $\tilde{\lambda}(t, \mathbf{k}, \mathbf{p})$ is to depend on t and $\mathbf{p}$ only through the combination $\mathbf{p}e^{-\alpha t}$. According to Eq. (9), the initial value of $\tilde{\lambda}$ is:

$$\tilde{\lambda}(0, \mathbf{k}, \mathbf{p}) = \mathbf{p} \cdot \left(\nabla_\mathbf{u}\left(\ln \hat{\Pi}_0(\mathbf{k}, \mathbf{u}) \right) \right)\Big|_{(\mathbf{k}, \frac{(\mathbf{k}-\mathbf{p})}{\alpha})} - \frac{k_B T_e}{m\alpha}(\mathbf{k} - \mathbf{p})^2 \tag{12}$$

where the subscript $(\mathbf{k}, (\mathbf{k} - \mathbf{p})/\alpha)$ means that the expression between parentheses is to be taken for $(\mathbf{k}, \mathbf{u})$ equal to $(\mathbf{k}, (\mathbf{k} - \mathbf{p})/\alpha)$. Since the dependence of $\tilde{\lambda}$ on t and $\mathbf{p}$ must only involve $\mathbf{p}e^{-\alpha t}$, an exact expression for $\tilde{\lambda}(t, \mathbf{k}, \mathbf{p})$ can be obtained by changing $\mathbf{p}$ into $\mathbf{p}e^{-\alpha t}$ in Eq. (12). This yields:

$$\tilde{\lambda}(t, \mathbf{k}, \mathbf{p}) = \mathbf{p}e^{-\alpha t} \cdot \left(\nabla_\mathbf{u}\left(\ln \hat{\Pi}_0(\mathbf{k}, \mathbf{u}) \right) \right)\Big|_{(\mathbf{k}, \frac{(\mathbf{k}-\mathbf{p}e^{-\alpha t})}{\alpha})} - \frac{k_B T_e}{m\alpha}(\mathbf{k} - \mathbf{p}e^{-\alpha t})^2 \tag{13}$$

It is now straightforward to use Eq. (7) to get an exact expression for $\hat{\Pi}(t, \mathbf{k}, \mathbf{u})$ in terms of $\hat{\Pi}_0$:

$$\hat{\Pi}(t, \mathbf{k}, \mathbf{u}) = \hat{\Pi}_0\left(\mathbf{k}, \mathbf{u}e^{-\alpha t} + \frac{\mathbf{k}}{\alpha}(1 - e^{-\alpha t}) \right) \times \exp\left[-\frac{k_B T_e}{m\alpha} \int_0^t \left(\mathbf{k} - (\mathbf{k} - \alpha\mathbf{u})e^{-\alpha\tau} \right)^2 d\tau \right] \tag{14}$$

It is convenient to introduce the following time-dependent quantities:

$$\eta(t) = \frac{k_B T_e}{m\alpha^2}\left(\alpha t - \frac{3}{2} + 2e^{-\alpha t} - \frac{1}{2}e^{-2\alpha t} \right), \quad \mu(t) = \frac{k_B T_e}{m\alpha}(1 - e^{-\alpha t})^2, \quad \nu(t) = \frac{k_B T_e}{m}(1 - e^{-2\alpha t}) \tag{15}$$

The expression for $\hat{\Pi}$ now takes the simpler form:

$$\hat{\Pi}(t, \mathbf{k}, \mathbf{u}) = \hat{\Pi}_0\left(\mathbf{k}, \mathbf{u}e^{-\alpha t} + \frac{\mathbf{k}}{\alpha}(1 - e^{-\alpha t}) \right) \times \exp\left[-\frac{1}{2}\mathbf{k}^2\eta(t) - \mathbf{k} \cdot \mathbf{u}\mu(t) - \frac{1}{2}\mathbf{u}^2\nu(t) \right] \tag{16}$$

which leads to:

$$\Pi(t, \mathbf{x}, \mathbf{v}) = \frac{1}{\sqrt{2\pi}^6} \int_{\mathbb{R}^6} \hat{\Pi}_0\left(\mathbf{k}, \mathbf{u}e^{-\alpha t} + \frac{\mathbf{k}}{\alpha}(1 - e^{-\alpha t})\right)$$

$$\times \exp\left[-\frac{1}{2}\mathbf{k}^2\eta(t) - \mathbf{k} \cdot \mathbf{u}\mu(t) - \frac{1}{2}\mathbf{u}^2\nu(t) + i(\mathbf{k} \cdot \mathbf{x} + \mathbf{u} \cdot \mathbf{v})\right] d^3k \, d^3u \tag{17}$$

The particle density $n(t, \mathbf{x}) \equiv \int_{\mathbb{R}^3} \Pi \, d^3v$ then admits the following integral expression:

$$n(t, \mathbf{x}) = \int_{\mathbb{R}^3} \hat{\Pi}_0\left(\mathbf{k}, \frac{\mathbf{k}}{\alpha}(1 - e^{-\alpha t})\right) \exp\left[-\frac{1}{2}\mathbf{k}^2\eta(t) + i\mathbf{k} \cdot \mathbf{x}\right] d^3k \tag{18}$$

Eq. (17) also yields the following expression for the particle current $\mathbf{j}(t, \mathbf{x}) \equiv \int_{\mathbb{R}^3} \mathbf{v}\Pi \, d^3v$:

$$\mathbf{j}(t, \mathbf{x}) = \int_{\mathbb{R}^3} i\nabla_{\mathbf{u}}\left(\hat{\Pi}_0\left(\mathbf{k}, \mathbf{u}e^{-\alpha t} + \frac{\mathbf{k}}{\alpha}(1 - e^{-\alpha t})\right) \exp\left[-\mathbf{k} \cdot \mathbf{u}\mu(t) - \frac{1}{2}\mathbf{u}^2\nu(t)\right]\right)\Big|_{\mathbf{u}=0}$$

$$\times \exp\left[-\frac{1}{2}\mathbf{k}^2\eta(t) + i\mathbf{k} \cdot \mathbf{x}\right] d^3k \tag{19}$$

4. Exact generalized Fick's law

We now focus on initial conditions whose phase space distribution function is factorized into a density distribution in physical space times a Maxwell–Boltzmann distribution in the momentum space. However, we do not restrict the discussion to the hydrodynamic regime: the initial density distribution in physical space can thus have space scales smaller or comparable to the mean free path of the surrounding fluid. Our approach will indeed be particularly useful in this very case. Practical situations for which this class of initial conditions is relevant are discussed in Section 5.

We thus choose as initial condition the following distribution:

$$\Pi_0(\mathbf{x}, \mathbf{v}) = n_0(\mathbf{x})\left(\frac{m}{2\pi k_B T_0}\right)^{3/2} \exp\left[-\frac{m(\mathbf{v} - \mathbf{v}_0)^2}{2k_B T_0}\right] \tag{20}$$

where T_0 is the temperature of the diffusing particles, and $\mathbf{v}_0$ is their initial uniform drift velocity. The form (20) is clearly very general and can serve as a good approximation to most physically realistic initial conditions. The Fourier transform of Π_0 is:

$$\hat{\Pi}_0(\mathbf{k}, \mathbf{u}) = \hat{n}_0(\mathbf{k})\frac{1}{\sqrt{2\pi}^3} \exp\left[-\frac{1}{2}\mathbf{u}^2\frac{k_B T_0}{m} - i\mathbf{u} \cdot \mathbf{v}_0\right] \tag{21}$$

where $\hat{n}_0(\mathbf{k})$ is the spatial Fourier transform of $n_0(\mathbf{x})$. The phase-space distribution function $\Pi(t, \mathbf{x}, \mathbf{v})$ at any positive time is then, according to Eq. (17):

$$\Pi(t, \mathbf{x}, \mathbf{v}) = \frac{1}{\sqrt{2\pi}^9} \int_{\mathbb{R}^6} \hat{n}_0(\mathbf{k}) \exp\left[-\frac{1}{2}\mathbf{k}^2\sigma^2(t) - \mathbf{k} \cdot \mathbf{u}\chi(t) - \frac{k_B}{2m}\mathbf{u}^2 T(t) + i(\mathbf{k} \cdot \mathbf{x}' + \mathbf{u} \cdot \mathbf{v}')\right] d^3k \, d^3u \tag{22}$$

where the quantities σ^2, T, χ, $\mathbf{x}'$ and $\mathbf{v}'$ are defined as follows:

$$\sigma^2(t) = \frac{k_B}{m\alpha^2}\left(T_e\left(\alpha t - \frac{1}{2} + \frac{1}{2}e^{-2\alpha t}\right) - \Delta T\left(1 - 2e^{-\alpha t} + e^{-2\alpha t}\right)\right), \quad T(t) = T_e - \Delta T e^{-2\alpha t}$$

$$\chi(t) = \frac{k_B}{m\alpha}(1 - e^{-\alpha t})(T_e - \Delta T e^{-\alpha t}), \quad \mathbf{x}' = \mathbf{x} - \frac{\mathbf{v}_0}{\alpha}(1 - e^{-\alpha t}), \quad \mathbf{v}' = \mathbf{v} - \mathbf{v}_0 e^{-\alpha t} \tag{23}$$

Here, $\Delta T = T_e - T_0$ is the difference between the equilibrium temperature and the initial temperature.

For the class of initial conditions under consideration, Eq. (18) leads to an exact expression for the particle density $n(t, \mathbf{x})$ in terms of a convolution product of the initial particle density $n_0(\mathbf{x})$ with the following propagator:

$$\Phi(t, \mathbf{x}) = \frac{1}{\sqrt{2\pi\sigma^2(t)}^3} \exp\left[-\frac{\left(\mathbf{x} - \frac{\mathbf{v}_0}{\alpha}(1 - e^{-\alpha t})\right)^2}{2\sigma^2(t)}\right] \tag{24}$$
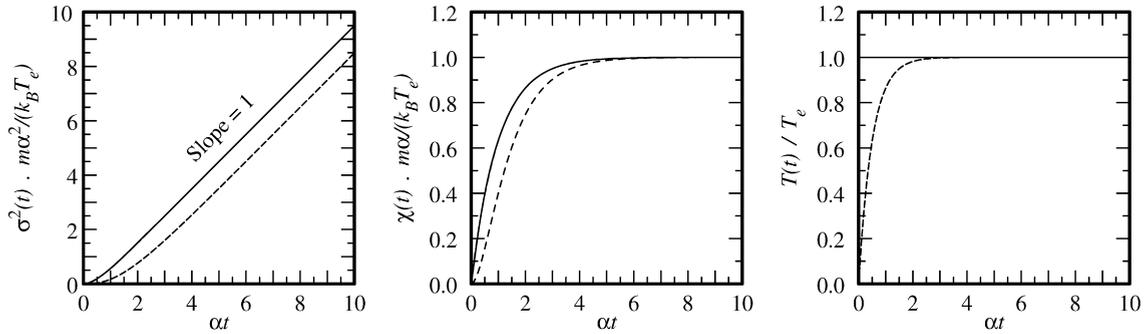
Fig. 1. $\frac{m\alpha^2}{k_B T_e}\sigma^2(t)$, $\frac{m\alpha}{k_B T_e}\chi(t)$, and $\frac{T(t)}{T_e}$ versus αt for $\Delta T = 0$ (solid) and $\Delta T = T_e$ (dashed).

The quantity $\frac{\mathbf{v}_0}{\alpha}(1 - e^{-\alpha t})$ can be interpreted as the position of a point, initially at $\mathbf{x} = 0$, moving with velocity $\mathbf{v}_0 e^{-\alpha t}$. Thus, the propagator Φ involves a uniform drift which is damped exponentially on a time scale α^{-1}, and a diffusive spreading with growing typical width $\sigma(t)$.

Eqs. (18) and (19) show that the particle current obeys the following simple relation:

$$\mathbf{j} = -\chi(t)\nabla_{\mathbf{x}}n + e^{-\alpha t}n\mathbf{v}_0 \tag{25}$$

We identify in the right-hand side of Eq. (25) two contributions to the particle current:

– a diffusion term proportional to the gradient of the particle density with a time-varying coefficient $\chi(t)$,
– an 'advection' term that damps exponentially, and which is a remnant of the initial mean drift at velocity $\mathbf{v}_0$.

The physical meaning of $T(t)$ is more subtle. Indeed, since the distribution function $\Pi(t, \mathbf{x}, \mathbf{v})$ for $t > 0$ cannot be an equilibrium solution when spatially non-uniform, it is not trivial to define a time-dependent temperature. The mean square velocity,[1] that can give some sense to the notion of temperature, is a priori position-dependent in the most general case. However, the *space-averaging* of the mean square velocity is a well-defined quantity that amounts to $3k_B T(t)/m$. The quantity $T(t)$ defined in Eq. (23) can thus be thought of as a space-averaged temperature, characteristic of the distribution Π at time t.

The physically relevant quantities $\sigma^2(t)$, $\chi(t)$ ant $T(t)$ are plotted on Fig. 1. The solid curves correspond to $\Delta T = 0$, that is, the initial condition is at thermal equilibrium with the surrounding fluid. The dashed curves correspond to $\Delta T = T_e$, that is, $T_0 = 0$, so that they describe situations with vanishing initial velocities.

5. Discussion and conclusion

We have investigated particle diffusion through the Ornstein–Uhlenbeck process and considered initial conditions whose phase-space distributions factorize into the product of an arbitrary spatial density by a Maxwell–Boltzmann distribution in momentum space. These initial conditions generate a particle current in physical space which has been shown to be exactly proportional at all times to the density gradient. The proportionality coefficient is time-dependent and relaxes toward the standard Fick value. No Chapman–Enskog expansion is performed, so, no scale separation hypothesis is needed. Consequently our approach is still valid outside of the hydrodynamical regime, to which the usual approach in terms of the diffusion equation is restricted. Namely, situations with space scales comparable or even smaller than the mean free path fall within the scope of our theory.

This class of exact solutions encompasses a lot of experimental situations of practical interest. Our approach is indeed valid when the system {diffusing particle + surrounding fluid} is created at some reference time $t = 0$ by injecting locally and suddenly particles into a fluid, provided these particles are taken out of a reservoir where they are at global equilibrium. In this case, the initial condition is necessarily factorized with no correlation between physical and momentum space. Moreover, the initial density profile is then likely to have well-defined sharp edges

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[1] With uniform damped drift $\mathbf{v}_0 e^{-\alpha t}$ subtracted.

with thickness comparable to the mean free path. The usual model based on the standard diffusion equation cannot address the short-time regime of this problem, since the density distribution only reaches the hydrodynamic limit after the small scales have been smoothed out by the diffusion process.

This result suggests that transport equations with time-dependent coefficients may be helpful to model the short-time non-hydrodynamic evolution of continuous media systems which are "created" or "prepared" at a given reference time $t = 0$, by putting into contact two media which are not at equilibrium with each other, even though each of theses media may be separately in an equilibrium state. For example, fall into this category the sudden contact of two pieces of matter at different initial temperatures, or the mixing layer at the outlet of an injection nozzle.

Note finally that relativistic transport phenomena cannot be described in a coherent manner by partial derivatives equations with constant coefficients [19,11,20]. A relativistic extension of the work presented in this Letter may contribute to solving this problem.

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