Tracer diffusivity in a time or space dependent temperature field

Ramin Golestanian\textsuperscript{1,2,3} and Armand Ajdari\textsuperscript{2}

\textsuperscript{1}Institute for Advanced Studies in Basic Sciences, Zanjan, 45195-159, Iran
\textsuperscript{2}Laboratoire de Physico-Chimie Théorique, UMR CNRS 7083, E.S.P.C.I., 75231 Paris Cedex 05, France
\textsuperscript{3}Institute for Studies in Theoretical Physics and Mathematics, P.O. Box 19395-5531, Tehran, Iran

to appear in Europhys. Lett.)

The conventional assumption that the self-diffusion coefficient of a small tracer can be obtained by a local and instantaneous application of Einstein’s relation in a temperature field with spatial and temporal heterogeneity is revisited. It is shown that hydrodynamic fluctuations contribute to the self-diffusion tensor in a universal way, i.e. independent of the size and shape of the tracer. The hydrodynamic contribution is anisotropic—it reflects knowledge of the global anisotropy in the temperature profile, leading to anisotropic self-diffusion tensor for a spherical tracer. It is also retarded—it creates memory effects during the diffusion process due to hydrodynamic interactions.

\textbf{PACS:} 05.40.-a, 66.10.Cb, 05.60.Cd

\textbf{Introduction} - Motion of particles in thermal gradients is a relatively old subject, of both fundamental and applied interest. The net directed motion in a steady gradient (usually referred to as the Soret effect or thermophoresis) has been observed and quantified for various systems (polymer molecules, solid particles or bubbles in a fluid) but often through indirect measurements. However, the microscopic mechanisms responsible for this motion are far from clear in many cases (see e.g. Ref. \textsuperscript{2}).

The resulting collective motion is usually rationalized through Onsager-like relations, with kinetic coefficients that are often empirically deduced from indirect measurements. The corresponding experiments are often difficult to set up due, in particular, to the buoyancy driven convective effects induced by thermal gradients.

In principle, the development of microfluidics (see \textsuperscript{3,4} and references therein) should allow to create fluidic environment less prone to such convective instabilities, where temperature gradients can be induced and controlled, and that should allow direct measurement of particle motion. Various fluorescence techniques have indeed been developed that allow a rather precise detection of temperature \textsuperscript{3}, and a laser in the IR range can offer a versatile tool for this motion are far from clear in many cases (see e.g. Ref. \textsuperscript{2}).

Hence, the net directed motion in a steady space dependent temperature profile will be reflected in the self-diffusion of a tracer \textsuperscript{3}. The Einstein formula for the self-diffusion tensor takes on the form

\[ D_{ij}(\mathbf{r}, t) = \mu_{ij} k_B T(\mathbf{r}, t) + \delta D_{ij}(\mathbf{r}, t), \]

with a (usually small) correction term that is universal, i.e. independent of the shape of the tracer particle. This term is caused by an interplay between the long-ranged hydrodynamic interactions and the spatial or temporal heterogeneity of the temperature field. For a steady space dependent temperature profile \( T(\mathbf{r}) \), we find

\[ \delta D_{ij}(\mathbf{r}) = \frac{1}{32\pi\eta} \int d^3r' \frac{k_B T(r')}{|\mathbf{r} - \mathbf{r}'|^2} \times \left[ \delta_{ij} + 2 \frac{(r_i - r_i')(r_j - r_j')}{|\mathbf{r} - \mathbf{r}'|^2} \right], \]

which implies that a global anisotropy in the temperature profile will be reflected in the self-diffusion of a tracer. For the case of a temporally varying temperature \( T(t) \), on the other hand, we obtain

\[ \delta D_{ij}(t) = \frac{\rho^{1/2} \delta_{ij}}{4(2\pi\eta)^{3/2}} \int_{-\infty}^{t} dt' \frac{k_B T(t')}{(t - t')^{3/2}}. \]
which manifests a memory effect corresponding to retardation in hydrodynamic flows.

**Model** - We consider an incompressible fluid at low Reynolds number that is subject to a thermal random stirring force (density) \( f(r, t) \). The stochastic dynamics of the velocity field \( \mathbf{v}(r, t) \), which is subject to the incompressibility constraint \( \nabla \cdot \mathbf{v} = 0 \), is then governed by the linearized Navier-Stokes equation

\[
\rho \partial_t \mathbf{v} = -\nabla p + \eta \nabla^2 \mathbf{v} + \mathbf{f},
\]

where \( \eta \) is the viscosity and \( p \) is the pressure field, and the density \( \rho \) is taken to be temperature independent. The noise in the above equation is assumed to be Gaussian, with \( \langle f_i(r, t) \rangle = 0 \) and

\[
\langle f_i(r, t) f_j(r', t') \rangle = 2\eta k_B T(r, t) \delta_{ij} \langle -\nabla^2 \rangle \delta^3(\mathbf{r} - \mathbf{r}') \delta(t - t'),
\]

where the noise correlator is chosen so as to ensure local and instantaneous thermal equilibrium for a sufficiently slowly varying temperature field \( T \). Note that the structure of the noise term should be such that it only induces vorticity-free velocity fluctuations, so that the system is not driven far from equilibrium by the noise \( \mathbf{f} \). The velocity field correlation function can then be calculated in a straightforward way. We obtain

\[
\langle v_i(r, t) v_j(r', t') \rangle = 2\eta \int dt_1 d^3 r_1 k_B T(r_1, t_1) \nabla G_{ij}(\mathbf{r} - \mathbf{r}_1, t - t_1) \cdot \nabla G_{kj}(\mathbf{r}' - \mathbf{r}_1, t' - t_1),
\]

where \( G_{ij} \) is the Green’s function for Eq.(1) above, i.e. in Fourier space \( \hat{G}_{ij}(\mathbf{q}, \omega) = (\delta_{ij} - \hat{q}_i \hat{q}_j)/(\omega - i\nu \omega + \eta q^2) \).

Using the result for the velocity correlation function, we can extract the diffusion coefficient of a tracer by assuming that the velocity fluctuations of an immersed particle would follow that of the fluid at the particle’s location by way of no-slip boundary condition. This assumption is reasonable as long as we are probing the long time behavior of the motion. We thus define the self-diffusion tensor via

\[
D_{ij}(r, t) \equiv \int_0^\infty dt' \langle v_i(r, t) v_j(r, t') \rangle,
\]

where it should be clear that this Eulerian velocity autocorrelation function decays rapidly.

Examining the expression in Eq.(3) then shows that the diffusion tensor, as defined above, is decomposed as in Eq.(1) in which \( \mu_{ij} = \int d^3 r (\delta_{ij} - \hat{k}_i \hat{k}_j)/(\eta k^2) \) involves a diverging integral that is sensitive to the details at short length scales, whereas \( \delta D_{ij} \) is a long-ranged convolution of a hydrodynamic response function and the temperature field. Note that \( \delta D_{ij} = 0 \) for a constant temperature profile. One can easily see that in fact \( \mu_{ij} \) corresponds to the mobility tensor of the particle, which we would obtain if we treated the proper hydrodynamic problem of flow past a body, as the form of the integral expression suggests if we use a cutoff of the order of the size of the particle [1]. In short, we can say that the diffusivity tensor \( D_{ij}(r, t) \) obtained from Eqs. (1) and (3) consists of two contributions: (1) a term that is sensitive to short length-scale features and thus to the geometry and size of the tracer, which depends only locally on temperature, and (2) a term that is sensitive to the non-local features in the temperature profile, and is thus independent of the size and shape of the tracer as long as these features have characteristic length-scales that are much larger than the size of the tracer. While the closed form expression for \( \delta D_{ij}(r, t) \) can be obtained for an arbitrary temperature profile, we choose to report here separately the results for space dependent temperature as in Eq.(1) and for time dependent temperature as in Eq.(2) above.

**Steady non-uniform temperature** - Let us now try to elaborate on the meaning of the above results. For a non-uniform temperature, Eq.(1) implies that a spherical particle should undergo anisotropic diffusive motion, with the anisotropy being inherited from the structure of the temperature profile [2]. For example, a harmonically modulated temperature profile \( T(r) = T_0 + \delta T \cos(\mathbf{k} \cdot \mathbf{r}) \), yields \( \delta D_{ij}(r) = -\hat{k}_B \delta T k/(64\eta) (\delta_{ij} + \hat{k}_i \hat{k}_j) \cos(\mathbf{k} \cdot \mathbf{r}) \) that predicts an anisotropy of \( \delta D_{ij}/\delta D_{11} = 4/3 \) for the ratio between the corrections to the diffusion constant in the parallel and perpendicular directions respectively. It also shows that for a small tracer of size a the correction is typically weaker than the usual term in (1) by a factor of order \( \sim (ka)/|\delta T|/T_0 \), with both terms typically smaller than 1.

To make connection with experiments, we need to consider realistic temperature profiles. Non-uniform temperature can be achieved by locally heating the fluid, and the profile can be obtained through the heat equation

\[
-\kappa \nabla^2 T(r) = Q(r),
\]

where \( \kappa \) is the thermal conductivity and \( Q(r) \) is the volume density of heat generated by external sources per unit time. The heating can originate from Ohmic loss if, for example, a wire carrying electric current is placed in the fluid, or from optical heating with an IR laser light focused into a spot within the fluid. Note, however, that in the latter case we need to make sure that the dielectric constant of the tracer particle matches that of the fluid at the wavelength of the beam, or that the particle is sufficiently far from the spot, so that optical trapping of the dielectric particle does not interfere with the effect that we are studying here. We choose a source with the anisotropic Gaussian profile \( Q(r) = P_0/(\ell^2 \epsilon_z) \exp(-\pi(x^2 + y^2)/\ell^2 - \pi z^2/\ell_z^2) \), in which \( P_0 \) is the total dissipation power, and find a variety of different asymptotic regimes: (i) For \( \ell_z \ll r \), where the tracer is sufficiently far from a point-like heat-
ing source, we find $T(r) = T_0 + P_0/(4\pi \kappa r)$, and
\[ \delta D_{ij}(r) = -\frac{1}{64\pi^2} \left( \frac{P_0 k_B}{\kappa \eta r^2} \right) (2\delta_{ij} - \hat{r}_i \hat{r}_j), \quad (8) \]
to the leading order. Note that $\delta D$ has a different (faster) power law decay with $r$ as compared to that of $T$. Moreover, we find an anisotropy $\delta D_{rr}/\delta D_{\perp \perp} = 1/2$. (ii) For $\ell \ll r \ll \ell_z$, where we have a linear source, we find $T(r) = T_0 - (P_0/2\pi \kappa \ell_z) \ln |r|$, and corrections to the diffusion tensor as
\[ \delta D_{zz}(r) = -\frac{3}{128\pi} \left( \frac{P_0 k_B}{\kappa \eta r} \right) \left( \frac{r_\perp}{r} \right), \]
\[ \delta D_{ij}(r) = -\frac{1}{128\pi} \left( \frac{P_0 k_B}{\kappa \eta r^2} \right) (4\delta_{ij} - \hat{r}_i \hat{r}_j), \quad (9) \]
and $\delta D_{\perp \perp}(r) = 0$ to the leading order. Since in this case the temperature variations in space is very weak compared to the variations in $\delta D$, it may be a good candidate for experimental observation of the space dependency of $\delta D$. We also find an anisotropy $\delta D_{zz}/\delta D_{\perp \perp} = 3/4$ in terms of the components in cylindrical coordinates. (iii) For $\ell_z \ll r \ll \ell$, where we have a planar source, we find $T(z) = T_0 - (P_0/2\kappa \ell^2) |z|$, and the corrections as
\[ \delta D_{zz}(z) = -\frac{1}{16\pi} \left( \frac{P_0 k_B}{\kappa \eta \ell^2} \right) \ln |z|, \]
\[ \delta D_{ij}(z) = -\frac{3}{64\pi} \left( \frac{P_0 k_B}{\kappa \eta \ell^2} \right) \ln |z| \delta_{ij}, \quad (10) \]
and $\delta D_{\perp \perp}(z) = 0$ to the leading order. This case also corresponds to a temperature profile with a constant gradient, and is expected to have the strongest effects in terms of magnitude as compared to other regimes. The anisotropy in this case is found as $\delta D_{zz}/\delta D_{\perp \perp} = 4/3$, similar to the harmonically modulated case. (iv) Finally, for $\ell_z \gg r$, where we have an extended anisotropic source with an aspect ratio $\alpha = \ell_z/\ell$, we find $T(r) = T_0 + (P_0/2\pi \kappa \ell) \ln \left[ \frac{\sqrt{1 - \alpha^2}}{\alpha^2} \right] / \sqrt{\alpha^2 - 1}$, and
\[ \delta D_{ij}(r) = -\frac{1}{128\pi^2} \left( \frac{P_0 k_B}{\kappa \eta \ell^2} \right) \Lambda_z \delta_{ij}, \quad (11) \]
to the leading order, where $\Lambda_z = \frac{4 - 3\alpha^2}{\sqrt{\alpha^2} - \sqrt{1 - \alpha^2}} - \frac{\sqrt{1 - \alpha^2}}{(1 - \alpha^2)^{3/2}}$, and $\Lambda_\perp = \frac{(6 - 7\alpha^2)}{\sqrt{1 - \alpha^2}} \frac{\sqrt{1 - \alpha^2}}{(1 - \alpha^2)^{3/2}}$. This is a very interesting case in the sense that both temperature and diffusion tensor have constant profiles to the leading order, and yet the diffusing tracer feels the large-scale anisotropy in the temperature profile, as manifest in Eq. (11). The anisotropy in this case is found as
\[ \frac{\delta D_{zz}}{\delta D_{\perp \perp}} = \frac{2(4 - 3\alpha^2) \tanh^{-1}(\sqrt{1 - \alpha^2}) - 2\sqrt{1 - \alpha^2}}{(6 - 7\alpha^2) \tanh^{-1}(\sqrt{1 - \alpha^2}) + \sqrt{1 - \alpha^2}}, \quad (12) \]
which depends on the aspect ratio, as plotted in Fig. 1. Note that Eq. (12) shows that the anisotropy asymptotes to 4/3 in the limit $\ell_z \ll \ell$, similar to the planar and the harmonically modulated cases. Moreover, it reveals that oblate profiles lead to stronger anisotropy than the prolate cases. This trend is in agreement with diminished anisotropy in the case of linear sources ($\delta D_{zz}/\delta D_{\perp \perp} = 1$)

\[ \delta D_{zz} = \frac{\delta D_{\perp \perp}}{2(4 - 3\alpha^2) \tanh^{-1}(\sqrt{1 - \alpha^2}) - 2\sqrt{1 - \alpha^2}} \]

\[ \delta D_{\perp \perp} = \frac{(6 - 7\alpha^2) \tanh^{-1}(\sqrt{1 - \alpha^2}) + \sqrt{1 - \alpha^2}}{2(4 - 3\alpha^2) \tanh^{-1}(\sqrt{1 - \alpha^2}) - 2\sqrt{1 - \alpha^2}} \]

\[ \delta D(t) = \frac{k_B T}{4\pi \sqrt{2} \eta} \frac{P_0 \omega_0}{\sqrt{2}} \cos(\omega_0 t - 3\pi/4). \quad (13) \]

The above result shows a systematic phase lag of $3\pi/4$ for the hydrodynamic correction to the diffusion constant, with respect to the temperature. The characteristic length in the above equation is set by the kinematic viscosity $\eta/\rho$ (that has the dimension of a diffusion constant) and the frequency $\omega$ as $\alpha T = \sqrt{\eta/\rho \omega_0}$, and is of the order of 1.3 mm for water at $\omega_0/(2\pi) = 0.1$ Hz.

**Discussion** - The above results are interesting from a fundamental point of view because they reveal that hydrodynamic interactions reflect on a diffusing particle the global knowledge of the temperature heterogeneity and
anisotropy. They may appear though to be difficult to verify experimentally, because in typical cases the correction will be considerably smaller than the conventional value given by Einstein’s relation. However, we would like to point out that due to the anisotropy in the diffusion tensor, one can choose to probe a quantity such as $D_{xy}$, by direct measurements of $(\Delta x(t)\Delta y(t))/2t$, in a non-symmetrical coordinate system. Since this quantity is always zero for a spherical tracer in the local picture, it would provide a feasible experimental test of this effect.

The structure of the stochastic forcing in Eqs. (1) and (3) has a crucial role in determining the form of the above results. While we are studying systems that are only slightly away from equilibrium (by choosing a noise correlator that is a smooth perturbation of the one that ensures thermal equilibrium), other noise structures could drastically change the results so that for example the decomposition in Eq. (2) could be blurred and the scaling with length could be altered.

Let us recall that our description of the fluid dynamics is clearly a great simplification, which could be improved by taking into account the temperature dependence of the density (and thus release of the incompressibility assumption) and the viscosity, and also the convection of thermal fluctuations, along the lines of the approach used in Ref. [8] to study fluctuations of a fluid away from equilibrium. With these ingredients, the long-range character of the effects described here should then suffer from screening, but the corresponding screening length will remain large for weakly compressible fluids.

The hydrodynamic contribution to the effective diffusivity is independent of the size and shape of the tracer as long as the shortest length-scale over which the temperature profile varies significantly is considerably larger than the size of the tracer particle. In this regard, a proper account of the tracer geometry for larger particles in strong temperature gradients may become important, when the interplay with Soret effect is expected to appear more clearly. We nevertheless expect that some qualitative features obtained in the present work should remain, i.e. that the fluctuating character of the particle motion should be sensitive to the geometry and history of the temperature field.

Eventually, as pointed out in the introduction, the most important steps to be taken are likely to be on the experimental side with either direct observation of single tracers, of sets of particles in a well-controlled fluidic and thermal environment, or direct probing of the anisotropy in the solvent self-diffusivity (in which case we expect minimal interference due to Soret effect).

We are grateful to D. Bartolo and M. Martin for interesting discussions and comments. One of us (RG) would like to acknowledge ESPCI for hospitality during his visit, and support through the Joliot visiting chair.

[1] G.S. McNab, A. Meisen, J. Coll. Int. Sci., 44, 339 (1973).
[2] M.E. Schimpf, S.N. Semenov, J. Phys. Chem. B, 104, 9935 (2000).
[3] Micro Total Analysis Systems 2000, Eds. A. van den Berg, W. Olthuis, P. Bergveld, Kluwer Academic Publishers, Dordrecht (NL), 2000.
[4] Micro Total Analysis Systems 2001, eds. J.M. Ramsey and A. van den Berg, Kluwer Academic Publishers, Dordrecht (NL), 2001.
[5] A.D. Stroock, G. Whitesides, Physics Today 54, 42-48 (2001).
[6] D. Roos, M. Gaitan, E.L. Locascio, p. 239, in Micro Total Analysis Systems 2001, ed. J.M. Ramsey and A. van den Berg, Kluwer Academic Publishers, Dordrecht (NL), 2001.
[7] This is clearly a much simpler model than the one used to study critical anomalies of thermal diffusivity and kinematic viscosity in: E. Meron, I. Procaccia, Phys. Rev. A, 30, 3221 (1984).
[8] For a recent review on fluctuations in non-equilibrium steady states, see: R. Schmitz, Phys. Rep. 171, 1 (1988).
[9] For the regular term that implies a local and instantaneous application of Einstein’s relation in a temperature field with spatial and temporal heterogeneity, see: E.H. Hauge and A. Martin-Löf, J. Stat. Phys. 7, 259 (1973).
[10] L.D. Landau and E.M. Lifshitz, Fluid Mechanics 2nd edition (Pergamon, Oxford, England, 1987).
[11] For a discussion on other choices of noise correlation in the context of turbulence, see: V. L’vov and I. Procaccia, in: Fluctuating Geometries in Statistical Mechanics and Field Theory, F. David, P. Ginsparg, and J. Zinn-Justin, eds. (Elsevier, Amsterdam, 1996).
[12] The integral expression is also useful to extract symmetry properties of the mobility tensor, such as the (factor of 2) anisotropy in the friction coefficient for a slender object. For related arguments in the analogous case of electrostatic response coefficients such as capacitance and polarizability, see: R. Golestanian, Phys. Rev. E 62, 5242 (2000).
[13] The example focuses on the anisotropic contributions in the universal term caused by global anisotropy in the temperature field. The specific reference is made to spherical tracers only because their regular diffusivity is isotropic and thus they will be good candidates for detecting any possible anisotropy that originates from the non-local term. This, of course, does not mean that the results only apply to the case of spherical tracers.
[14] P. Porion et al., Phys. Rev. Lett., 87, 208302 (2001).