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LETTER TO THE EDITOR

BROWNIAN MOTION AND HYDRODYNAMIC FLUCTUATIONS NEAR THE CONVECTIVE INSTABILITY POINT

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We consider the effect of the enhanced hydrodynamic fluctuations in a fluid near the convective instability point on the motion of suspended brownian particles. Using Faxén's theorem it is found that the diffusion coefficient of the brownian particles increases when the instability point is approached. The divergent part of the diffusion coefficient depends on the difference, between the Rayleigh number R and its critical value R_c as $|R_c - R|^{-3/2}$. The feasibility to observe this effect experimentally is considered.

Recently there has been a growing interest in pre-transitional effects in hydrodynamic regime transitions[1-3]), with particular emphasis on the analogies with pretransitional phenomena near second-order phase transition points[4]). One of the simplest examples of a hydrodynamic instability is the Rayleigh–Bénard or convective instability[5]) of a plane horizontal fluid layer heated from below. When the temperature gradient exceeds a certain critical value stationary convection sets on spontaneously. Using a set of linear stochastic hydrodynamic equations, Zaitsev and Shliomis[1]) found that near the convective instability point the velocity and temperature fluctuations are strongly enhanced. It has been suggested[3]) that light scattering would be a possible tool to investigate these pretransitional effects. However, the modes, the fluctuation intensities of which are strongly enhanced near the instability, have wavelengths of the order of the thickness of the fluid layer *i.e.* typically 0.1–1 cm. This implies that to observe these modes with light scattering requires scattering angles of 10^{-2}–10^{-3} degrees and so far no experimental evidence for anomalous fluctuations near the convective instability has been produced[6])[+]. In this letter we show that the study of the dynamics of brownian

[+] In certain electrohydrodynamical instabilities in nematics the wavelength of the unstable mode is relatively short and an increase in the intensity of scattered light near the instability has been observed.

motion could yield valuable information on the fluctuating fluid velocity field and that such a study appears to be experimentally feasible.

We first derive a relation between the diffusion coefficient of a spherical brownian particle and the fluid velocity fluctuations that prevail in the absence of the brownian particle. We start from the well-known expression

$$D_i = \int_0^\infty \mathrm{d}t \, \langle u_i(0) \, u_i(t) \rangle \qquad (i = x, y, z), \tag{1}$$

where $\boldsymbol{u}$ is the fluctuating velocity of the brownian particle. Using the usual Langevin equation

$$m \frac{\mathrm{d}}{\mathrm{d}t} \boldsymbol{u}(t) = -(6\pi\eta a) \, \boldsymbol{u}(t) + \boldsymbol{F}(t),$$

one readily obtains from eq. (1) that

$$D_i = \frac{1}{(6\pi\eta a)^2} \int_0^\infty \mathrm{d}t \, \langle F_i(0) \, F_i(t) \rangle \qquad (i = x, y, z), \tag{2}$$

where η is the shear viscosity of the fluid, a is the radius of the brownian particle and $\boldsymbol{F}$ is the fluctuating force exerted on the brownian particle by the molecules in the surrounding fluid. To connect $\boldsymbol{F}$ to the fluid velocity fluctuations we use Faxén's theorem[7]). According to this theorem the force $\boldsymbol{K}$ exerted on a sphere at rest in a viscous fluid in stationary motion is given by

$$\boldsymbol{K} = 6\pi\eta a \, (4\pi a^2)^{-1} \int_S \boldsymbol{V}(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} = 6\pi\eta a \bar{\boldsymbol{V}}^{\mathrm{s}}, \tag{3}$$

where the integral is taken over the surface of the sphere and $\boldsymbol{V}(\boldsymbol{r})$ is the velocity field of the fluid in the absence of the sphere. Recently Faxén's theorem was generalized by Mazur and Bedeaux[8]) to the case of non-stationary flows, in which case additional terms are present in eq. (3). However, these terms are zero at zero-frequency. Now since it follows from the Wiener–Khinchin theorem that eq. (2) relates the diffusion coefficient to the spectral density of the random force at zero-frequency the latter quantity can be calculated from eq. (3) where the velocity field is now the fluctuating fluid velocity field $\boldsymbol{v}(\boldsymbol{r}, t)$; one obtains

$$D_i = \int_0^\infty \mathrm{d}t \, \langle \bar{v}_i^{\mathrm{s}}(0) \, \bar{v}_i^{\mathrm{s}}(t) \rangle, \tag{4}$$

where $\bar{v}_i^{\mathrm{s}}(t)$ is the average of $v_i(\boldsymbol{r}, t)$ over the surface of the brownian particle. Notice the striking similarity between eqs. (1) and (4) for the diffusion coefficient.

In order to calculate D from eq. (4) we have to know the fluctuating fluid velocity field. For a fluid near the convection instability this was calculated for the first time in ref. 1. For the sake of simplicity we consider a fluid layer with free boundaries. In that case the (vertical) z component of the velocity field can be written as

$$v_z(\boldsymbol{r}, t) = \sum_{n=1}^{\infty} \int \mathrm{d}\boldsymbol{\kappa} v_{z,n}(\boldsymbol{\kappa}, t)\, \mathrm{e}^{\mathrm{i}\boldsymbol{\kappa}\cdot\boldsymbol{x}} \sin(n\pi z/\mathrm{d}).$$

Here $\boldsymbol{\kappa} = (\varkappa_x, \varkappa_y)$ is the horizontal wavevector, $\boldsymbol{x} = (x, y)$ is the horizontal position vector and d is the thickness of the fluid layer. Near the instability threshold only modes with $n = 1$ develop anomalous fluctuations. Following essentially the treatment of Zaitsev and Shliomis one obtains near the instability point[9])

$$\langle v_{z,1}(\boldsymbol{\kappa}, 0)\, v_{z,1}(\boldsymbol{\kappa}', t)^* \rangle = \left(\frac{\chi}{\chi + \nu}\right)^2 \frac{Q}{\lambda_1(\varkappa)}\, \mathrm{e}^{-\lambda_1(\varkappa)t}\, \delta(\boldsymbol{\kappa} - \boldsymbol{\kappa}'). \tag{5}$$

Here χ is the thermal diffusivity, ν is the kinematic viscosity, $\lambda_1(\varkappa)$ is the damping factor of the fluid velocity fluctuations with vertical wavenumber π/d and horizontal wavenumber $\varkappa$ and Q is the intensity of the fluctuating stress tensor in the momentum equation which in the notation used here is given by $Q = k_B T\nu\varkappa^2/\varrho 2\pi^2 d$.

The instability sets in when the damping factor $\lambda_1(\varkappa)$ becomes equal to zero. This happens for the critical Rayleigh number $R_c = 27\pi^4/4$ and for the critical horizontal wavenumber $\varkappa_c = \pi/\sqrt{2}\, d$. For R just below R_c and for $\varkappa$ close to $\varkappa_c$ one can expand $\lambda_1(\varkappa)$ in a series in $\varepsilon = (R_c - R)/R_c$ and $(\varkappa - \varkappa_c)$. For the first non-zero terms one obtains

$$\lambda_1(\varkappa) = \frac{\chi\nu}{\chi + \nu} k_c^2 \varepsilon + 4 \frac{\chi\nu}{\chi + \nu} (\varkappa - \varkappa_c)^2, \tag{6}$$

where $k_c^2 = \varkappa_c^2 + (\pi/d)^2$.

We now calculate the contribution of the modes with $n = 1$ to the diffusion coefficient. Since these are the modes that develop critical fluctuations near the instability point we shall denote their contribution to the diffusion constant by D^{crit}. Using eq. (4) the surface average of v_z can be written as

$$\bar{v}_z^{\mathrm{s}} = \sum_{n=1}^{\infty} \int \mathrm{d}\boldsymbol{\kappa} \sin \frac{n\pi Z}{d} \frac{\sin k_n a}{k_n a} v_{z,n}(\boldsymbol{\kappa}), \tag{7}$$

where $k_n = [\varkappa^2 + (n\pi/d)^2]^{\frac{1}{2}}$, Z is the z-coordinate of the brownian particle and the origin of the x and y axis is taken at the center of the sphere. Substituting eq. (7) in eq. (4) and using eq. (5) for the critical fluid velocity fluctuations we obtain after carrying out the time integration

$$D_z^{\text{crit}} = \left(\sin\frac{\pi Z}{d}\right)^2 \int_0^\infty \varkappa\, \mathrm{d}\varkappa \int_0^{2\pi} \mathrm{d}\phi \left(\frac{\sin k_1 a}{k_1 a}\right)^2 \left(\frac{\chi}{\chi + \nu}\right)^2 \frac{Q}{\lambda_1(\varkappa)^2}. \tag{8}$$

Near the instability point where ε is small the integrand of eq. (8) is sharply peaked around $\varkappa_c$ due to the behavior of $\lambda_1(\varkappa)$ [see eq. (6)]. Therefore to a good approximation‡ we may set the functions $(\sin k_1 a)/k_1 a$ and Q equal to their values at $\varkappa = \varkappa_c$ and take them outside the integral. For the same reason we may extend the remaining integral over $\varkappa$ from $-\infty$ to $+\infty$. Assuming that $d \gg a$ we may set $(\sin k_c a)/k_c a = 1$. Finally upon averaging from $Z = 0$ to $Z = d$ we obtain

$$D_z^{\text{crit}} = k_B T / 24\sqrt{3}\, \eta d \varepsilon^{3/2}. \tag{9}$$

We can carry out the same treatment as given above to obtain the x and y components of the diffusion coefficient. Using the same approximations one finds for $D_{x,y}^{\text{crit}}$ the same expression as for D_z^{crit}.

The modes with $n \geqslant 2$ are only very slightly affected by the non-equilibrium constraints of the system and their fluctuations are virtually the same as under equilibrium conditions. It then follows from eq. (4) that their contribution to the diffusion coefficient, yields essentially the regular Stokes–Einstein expression for the diffusion coefficient. Thus the diffusion coefficient can be written as

$$D_i = D_i^{\text{reg}} + D_i^{\text{crit}} \simeq \frac{k_B T}{6\pi\eta a} + \frac{k_B T}{24\sqrt{3}\, \eta d \varepsilon^{3/2}}. \tag{10}$$

The numerical factor $24\sqrt{3}$ appears as a result of the computation for a system with free boundaries and is expected to be different for the physically more realistic situation of rigid boundaries.

As is well known with photon correlation spectroscopy[10]) it is possible to probe the dynamics of brownian motion and the method allows one to determine diffusion coefficients with an accuracy of about 1%.

As can be seen from eq. (10) the ratio of D^{crit} to D^{reg} is determined by $a/d\varepsilon^{3/2}$. Consider $a = 10^3$ Å and $d = 1$ cm; then for $\varepsilon = 10^{-3}$, D^{crit} is of the order of 10% of D^{reg} and for $\varepsilon = 10^{-4}$, D^{crit} is of the order of 10 times D^{reg}. Given the fact that the temperature difference between the lower and upper boundary at which the instability occurs is typically of the order of 10°C, it follows that ε values down to 10^{-4} are definitely within experimental reach. Thus there should be no problem to observe the increase in the diffusion coefficient but whether it will be possible to extract the value of the critical exponent with any accuracy remains to be seen.

‡ These approximations were checked numerically by Mrs. C. Perin and for $\varepsilon < 10^{-2}$ the error is less than 5%.

We note that the results presented in this letter are not expected to be valid in the immediate vicinity of the instability point due to the neglect of nonlinear effects. On the one hand the treatment given here is based upon eq. (5) for the fluctuating velocity field which was obtained from linear stochastic hydrodynamic equations[1,9]). When ε is small the fluctuations become large and one has to take nonlinear terms in the hydrodynamic equations into account. Graham and Pleiner[11]) have shown that the width of the region where the linear description breaks down is small. (Typically $\varepsilon \leqslant 10^{-5}$.) On the other hand in calculating $\langle \bar{v}_i^s(0)\, \bar{v}_i^s(t)\rangle$ we have as usual neglected the motion of the sphere itself[8]). Taking the motion of the sphere into account leads to nonlinear effects that are numerically negligible in equilibrium fluids but do become important near a hydrodynamic instability point where the diffusion coefficient becomes large and the decay constant of the fluctuating fluid velocity field becomes small. This limits the treatment given here for typical cases to $\varepsilon \geqslant 10^{-4}$.

Finally it appears to us that it would be of interest to extend the treatment presented here for brownian motion near the convective instability point to other hydrodynamic instabilities. It has been argued[1]) that in general near hydrodynamic instability points the hydrodynamic fluctuations will be enhanced and thus in view of the result obtained here one expects a concomitant increase in the diffusion coefficient of suspended brownian particles. For example we think that the dramatic increase in the linewidth of laser light scattered from brownian particles suspended in a Poiseuille flow near the critical Reynolds number[12]) might be due to a sharp increase in the diffusion coefficient caused by the enhancement of the intensity of fluid velocity fluctuations. In collaboration with J.P. Boon, this problem is being studied in detail at the moment.

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