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PARTICLE MOTIONS INDUCED BY CAPILLARY FLUCTUATIONS OF A FLUID-FLUID INTERFACE

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Abstract—The motion of a Brownian particle in the presence of a deformable interface is studied by considering the random distortions of interface shape due to spontaneous thermal impulses from the surrounding fluid. The fluctuation-dissipation theorem is derived for the spontaneous fluctuations of interface shape using the method of normal modes in conjunction with a Langevin type equation of motion for a Brownian particle, in which the fluctuating force arises from the continuum motions induced near the particle by the fluctuation of interface shape. The analysis results in the prediction of autocorrelation functions for the location of the dividing surface, for the random force acting on the particle, and for the particle velocity. The particle velocity correlation, in turn, yields the effective diffusion coefficient due to random fluctuations of the interface shape.

Key words: *Brownian Particle and Diffusion, Interface Fluctuations, Capillary Wave, Velocity Autocorrelation, Langevin Equation, Normal Mode Decomposition*

INTRODUCTION

We consider in this paper motions of Brownian particles near a fluctuating interface due to the thermal agitations of the nearby fluids. Interest in this problem stems from its relevance to Brownian motion or diffusion near a fluid-fluid interface. The difficulties experienced in trying to model the motions of Brownian particles near an interface are many and mainly attributable to the deformation of the interface. Most of preceding investigations so far pertain to the case in which the interface remains precisely flat, in spite of the random motions induced in the two contiguous fluids by the thermal agitations [cf. Brenner and Leal, 1977, 1982; Gotoh and Kaneda, 1982; Lee et al., 1979; Lee and Leal, 1980; Yang and Leal, 1983, 1984; and Yang and Hong, 1987]. It is, of course, that a real interface cannot remain precisely flat except for the limiting case of a rigid wall. As a matter of fact, the interface will fluctuate around the equilibrium flat configuration due to the thermal agitation of the surrounding fluids, even in the absence of Brownian particles, and these random changes in the interface shape will produce fluctuating velocity fields and so induce random motions of Brownian particles in the vicinity of the interface. These random motions are in addition to the random motions caused by direct interactions between the Brownian particles and the molecules of the surrounding fluid. Thus, the interface effects on the motion of Brownian particles are due to the fluctuating velocity fields caused by the random changes in the interface shape.

Whilst considerable progress has been made over the last decade in understanding the equilibrium properties of the liquid-vapor interface [cf. Buff et al., 1965; Evans, 1981], the macroscopic structure and thermodynamical properties of an interface between two immiscible fluids are relatively less well understood. One approach, in principle, to understanding the structure of the fluid-fluid interface would be to use the same type of detailed *microscopic* molecular theory that has been used widely in the study of liquid-vapor interface [cf. Teletzke et al., 1982]. In the present study, however, we approach the problem from a macroscopic statistical framework in order to develop physically appealing and mathematically tractable theory for systems of this type. Philosophically similar macroscopic statistical methods have been very successful in determining macroscopic properties of gases (e.g., the relationship between pressure and temperature in the system) that are identical to the results from the molecular kinetic theory. Further, essentially the same macroscopic method that we describe here has been the cornerstone of theoretical descriptions of the relevant dynamics of Brownian motion. In particular, we adopt the conceptual idea of separating the phenomenon into two parts: one associated with rapid fluctuations with time scales characteristic of molecular motion, and the other associated with a much slower response time characteristic of viscous relaxation of the system.

In the present work, we examine the interface fluctuations due to random thermal impulses, and evaluate the corresponding velocity fields in order to determine the induced particle motions. This is done by employing nonequilibrium thermodynamics in conjunction with a capillary-wave model to describe the interface dynamics. The objective of our study is to determine the statistical properties of near equilibrium fluctuations of an interface between two immiscible fluids based on macroscopic statistical mechanics coupled with the concept of a fluctuation-dissipation principle as developed by Landau and Lifshitz [1959]. According to the fluctuation-dissipation principle, the statistical properties of ***nonequilibrium*** fluctuations, linear in the external forces from a macroscopic point of view, can be related to equilibrium self-correlations. We thus begin our analysis by determining the ***equilibrium*** self-correlations of interface fluctuations.

EQUILIBRIUM FLUCTUATIONS

We begin by considering a system which consists of two immis-

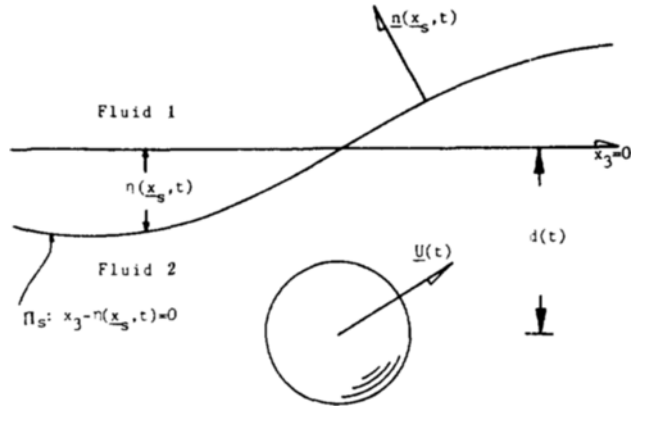

Fig. 1. Schematic sketch of the fluctuating interface and a Brownian sphere. In the absence of the fluctuations, the interface is designated by the plane $x_3=0$.

cible Newtonian fluids 1 and 2 that are separated by an interface, as depicted in Fig. 1. We assume that the interface can be designated by the plane $x_3=0$ in the absence of the fluctuations. The surface of the interface is denoted as Π_S defined by

$$\Pi_S = x_3 - \eta(\mathbf{x}_s,\ t) = 0 \tag{1}$$

where $\mathbf{x}_s$ is a position vector representing points lying in a plane parallel to the undeformed, flat interface. In our model system, the interface shape function $\eta(\mathbf{x}_s, t)$ is envisioned as fluctuating around equilibrium, i.e., $\eta(\mathbf{x}_s, t)=0$, due to the spontaneous random impulses from the surrounding fluids. Indeed, our objective in this section is to evaluate the autocorrelation function $\langle\eta^2(\mathbf{x}_s, t)\rangle$ of the interface fluctuation by determining the probability distribution of interface distortion, $\eta(\mathbf{x}_s, t)$, and utilizing the general theory of statistical physics. The autocorrelation function $\langle\eta^2(\mathbf{x}_s, t)\rangle$ will in turn provide the statistical properties of the system at equlibrium necessary to calculate the random velocity field induced by the spontaneous fluctuations in interface shape. In order to determine the probability distribution of $\eta(\mathbf{x}_s, t)$, we thus need to be able to evaluate the entropy change due to the interface fluctuations.

The entropy change $\Delta S\{\eta(\mathbf{x}_s, t)\}$ associated with the interface distortion can be related to the free energy functional $A\{\eta(\mathbf{x}_s, t)\}$ corresponding to the distortion $\eta(\mathbf{x}_s, t)$ as

$$\Delta S\{\eta(\mathbf{x}_s,\ t)\} = -\frac{A\{\eta(\mathbf{x}_s,\ t)\}}{T} \tag{2}$$

and thus the derivative of the entropy change with respect to the free energy is just $-1/T$, where T is the temperature of the system; the temperatures of fluids 1 and 2 are the same, since the system is assumed to be in equilibrium. The free energy functional $A\{\eta(\mathbf{x}_s, t)\}$ associated with the distortion $\eta(\mathbf{x}_s, t)$ is defined to be the isothermal reversible work necessary at equilibrium to impose the disturbance, i.e.,

$$A\{\eta(\mathbf{x}_s,\ t)\} = \frac{1}{2}\int_{x_s}[(\Delta\rho)g\eta^2(\mathbf{x}_s,\ t) + \gamma|\nabla_s\eta(\mathbf{x}_s,\ t)|^2]\ d\mathbf{x}_s \tag{3}$$

Here, $\Delta\rho(=\rho_2-\rho_1)$ is the density difference between fluids 1 and 2, ∇_s denotes the two-dimensional gradient operator on the plane defined by $\mathbf{x}_s$ and γ is the surface tension between the two fluids. The first term in the integrand represents the free energy associated with the external acceleration due to gravity g and the second is associated with an increase in surface area. The required probability distribution for $\eta(\mathbf{x}_s, t)$ is thus

$$W\{\eta(\mathbf{x}_s,\ t)\} = \Omega\exp\left[-\frac{1}{2k_BT}\int_{x_s}\{(\Delta\rho)g\eta^2(\mathbf{x}_s,\ t) + \gamma|\nabla_s\eta(\mathbf{x}_s,\ t)|^2\}\ d\mathbf{x}_s\right] \tag{4}$$

in which k_B is the Boltzmann constant and Ω denotes the normalization constant. The distribution (4) is a Gibbs (or canonical) distribution for the interface distortion [Buff et al., 1965; Landau and Lifshitz, 1980]. We now determine the autocorrelation function $\langle\eta^2(\mathbf{x}_s, t)\rangle$ using the probability distribution (4). Since the integrand of (4) contains $|\nabla_s\eta(\mathbf{x}_s, t)|^2$, however, it is convenient to resolve the arbitrary fluctuation $\eta(\mathbf{x}_s, t)$ into independent modes of a two dimensional Fourier-transform

$$\eta(\mathbf{x}_s,\ t) = \int_k \hat{\eta}(\mathbf{k},\ t)\exp(i\mathbf{k}\cdot\mathbf{x}_s)d\mathbf{k} \tag{5}$$

in which $\mathbf{k}$ is the wave vector (i.e., the wave number $k=|\mathbf{k}|$). In this formulation, the disturbed surface is represented as a collective coordinate of decoupled surface *harmonic waves*. Further, the entropy change can also be expressed in terms of the Fourier-tranform variables. It is now simple matter to evaluate the autocorrelation of the fluctuations for two different wave vectors $\mathbf{k}$ and $\mathbf{k}'$. The result is given by

$$\langle\hat{\eta}(\mathbf{k},\ t)\hat{\eta}(\mathbf{k}',\ t)\rangle = (2\pi)^{-2}k_BT[(\Delta\rho)g - \gamma\mathbf{k}\cdot\mathbf{k}']\ \delta(\mathbf{k}+\mathbf{k}') \tag{6}$$

where $\delta(\mathbf{k}+\mathbf{k}')$ is the two-dimensional Dirac delta function. The correlation function in terms of the position vector $\mathbf{x}_s$ can then be evaluate by Fourier transformation of (6). The result is

$$\langle\eta(\mathbf{x}_s,\ t)\eta(\mathbf{x}_s',\ t)\rangle = k_BT\int_{k_{min}}^{k_{max}}\frac{kJ_0(rk)}{(\Delta\rho)g+\gamma k^2}\,dk \tag{7}$$

in which $r=|\mathbf{x}_s-\mathbf{x}_s'|$ and J_0 is the Bessel function of the first kind of order 0. The lower limit, k_{min}, of possible wave numbers is inversely proportional to the largest length scale of the system and thus $k_{min}\to0$ if the interface is unbounded. The choice for an upper cutoff on wave number, k_{max}, is somewhat arbitrary, and the present continuum treatment cannot make a rigorous identification of this quantity. However, in a theoretical treatment of a liquid-vapor interface, Buff et al. [1965] selected k_{max} as being inversely proportional to the interface width, L_ρ, across which a sharp discontinuity in density may occur. In addition, thermodynamic perturbation theories have been developed by Evans [1981] for the study of a planar interface, which show that the order of magnitude of L_ρ is approximately the same as the intermolecular length scale σ of surrounding molecules, and in fact $L_\rho\approx1.5\sigma$-3.0σ.

The mean-square fluctuation, which provides a measure of the magnitude of interface distortion via spontaneous fluctuations, can be obtained readily from (7) with $r=0$ and $k_{min}=0$:

$$\langle\eta^2(\mathbf{x}_s,\ t)\rangle = \frac{k_BT}{4\pi\gamma}\ln\left[1+\frac{\gamma}{(\Delta\rho)g}k_{max}^2\right] \tag{8}$$

It can be noted from (8) that the mean-square fluctuation $\langle\eta^2(\mathbf{x}_s, t)\rangle$ becomes ***magnified*** as either the density difference or the surface tension between the two fluids becomes smaller. In fact, in the limit $\Delta\rho\to0$, the autocorrelation function of $\eta(\mathbf{x}_s, t)$ diverges logarithmically. This ***weak*** divergence is related to the fact that $\eta(\mathbf{x}_s, t)$ characteristic of distortions of the interface is a symmetry breaking collective coordinate in terms of decoupled harmonic surface waves (i.e., the Fourier decomposition, (5), breaks down in this particular case of $\Delta\rho=0$), which was also noted by Jhon et al. [1978]. They have developed the so-called memory function approach for interface dynamics and found that, associated with the symmetry breaking variable, $\eta(\mathbf{x}_s, t)$ is a propagating mode whose long-wave length dispersion relation is identical to the famous result for capillary waves, i.e., $\omega(k)=\{\gamma k^3/(\Delta\rho)\}^{1/2}$ in which ω is the frequency of capillary waves. It then follows that capillary waves must always exist if a nonuniform density distribution exists (i.e., $\Delta\rho\neq 0$), even if $\gamma=0$. It is noteworthy, in this context, that the mean square fluctuation $\langle\eta^2(\mathbf{x}_s, t)\rangle$ approaches a finite limiting value, $k_B T k_{max}^2/4\pi(\Delta\rho)g$, as the surface tension between the two fluids vanishes (i.e., $\gamma\rightarrow 0$).

So far we have dealt only with fluctuations around the equlibrium state of the system using Gibbs *ensembles*, i.e., we have derived the equilibrium correlation functions for the interface distortion in terms of ensemble averages. According to the ergodic hypothesis by Landau and Lifshitz [1980], however, ensemble averages yield the same results as *long-time* averages over the history of a single system providing the system is statistically stationary. Thus, we can regard the correlation functions in (6)-(8) as limiting time-average values with $t\rightarrow\infty$. In the next section, the time-dependent interface fluctuations and the corresponding velocity fields will be considered explicitly. The time-averages from these detailed time-dependent fluctuating fields must have the same long-time values (or forms) as calculated in the present section using the concept of an ensemble of near-equilibrium fluctuations [Landau and Lifshitz, 1980; Kreuzer, 1984].

TIME CORRELATIONS AND THE VELOCITY FIELD INDUCED BY INTERFACE FLUCTUATIONS

The impulsive motion of a body surrounded by a "viscous" fluid is accompanied by frictional processes, which ultimately bring the motion to a stop. The kinetic energy of a Brownian particle, contributed by thermal *fluctuations* of the surrounding medium, is thereby converted into heat and is said to be *dissipated.* This is the basic concept of the fluctuation-dissipation theorem developed by Landau and Lifshitz [1959]. A rigorous, purely mechanical treatment of such a motion is clearly impossible. Since the energy of macroscopic motion is converted to thermal energy of the molecules of the suspending fluid, such a treatment would require a solution of the equations of motion for all of these molecules. The problem of setting up an equivalent description, with a macroscopic scale of resolution proportional to the Brownian particle dimensions, is therefore a problem of statistical physics.

In the present system, it is the interface that fluctuates around the equilibrium flat configuration, and thereby generates velocity fields in fluids 1 and 2. In the presence of fluctuations, however, there are also spontaneous local stresses in the bulk fluids 1 and 2, which are not related to the velocity gradient; Landau and Lifshitz [1959] determined the statistical properties of these *random* stresses, including formulae for the correlation between the components of the stress tensor. Hauge and Martin-Löf [1973] and Hinch [1975] showed that the macroscopic framework with fluctuating stresses could provide a self-consistent theoretical description of Brownian motion. In their theories, the fluctuating stress acts on the particle through its divergence, which drives fluctuations in the ***bulk*** fluid and thence fluctuations in the viscous stress on the particle and relates the white noise $\mathbf{A}(t)$ in the bulk fluid to the fluctuating stress in the surrounding fluid. It is the white noise contribution to the motion of Brownian particles, i.e., $\mathbf{A}(t)$, that will continue to be present even when the particle is far removed from the interface. The random force contribution on a Brownian particle due to interface fluctuations is in *addition* to the white noise $\mathbf{A}(t)$ that derives from the fluctuating stresses in the bulk fluids. In the present section, we thus determine the statistical properties of the fluctuating velocity fields in fluids 1 and 2 caused solely by spontaneous random changes in the interface shape. In our analysis, we introduce a fluctuating forcing function $y(\mathbf{x}_s, t)$ in the normal stress balance for the interface as the "energy source" for interface shape fluctuations.

The energy of the interface imparted by thermal impulses decays via viscous dissipation in the surrounding fluids, and this process is governed by a fluctuation-dissipation theorem developed by Landau and Lifshitz [1959]. The construction of this fluctuation-dissipation theorem begins from a purely macroscopic description of the system, based upon the equations of motion for the fluctuating quantities, e.g., the interface position $\eta(\mathbf{x}_s, t)$, and the velocity and pressure fields ($\mathbf{u}^{(j)}$, $p^{(j)}$) in fluids j(=1 and 2). The equations describing the fluid motions are simply the Navier-Stokes equations with appropriate boundary conditions. Provided the order of magnitude of the fluctuating velocity $\mathbf{u}^{(j)}$ is sufficiently small, as we shall assume here, we can neglect the convective inertia terms in these equations, and we thus find that the fluid motion is described by the unsteady Stokes' equation plus the equation of continuity for each fluid j(=1 and 2)

$$\rho_j\frac{\partial \mathbf{u}^{(j)}}{\partial t}=-\nabla p^{(j)}+\mu_j\nabla^2\mathbf{u}^{(j)} \tag{9}$$

$$\nabla\cdot\mathbf{u}^{(j)}=0 \tag{10}$$

Here, μ_j is the viscosity of fluid j. The boundary conditions to be satisfied in dimensional form are the following:

$$\mathbf{u}^{(j)}\rightarrow 0 \text{ as } x_3\rightarrow\pm\infty \tag{11a}$$

At the surface of the interface, defined by $\Pi_S=x_3-\eta(\mathbf{x}_s, t)=0$

$$\mathbf{u}^{(1)}=\mathbf{u}^{(2)} \tag{11b}$$

$$\mathbf{n}\cdot\mathbf{u}^{(1)}=\mathbf{n}\cdot\mathbf{u}^{(2)}=\frac{1}{|\nabla\Pi_S|}\frac{\partial\eta}{\partial t} \tag{11c}$$

$$[|t_i n_j T_{ij}|]=0 \tag{11d}$$

and

$$[|n_i n_j T_{ij}|]=\gamma(\nabla\cdot\mathbf{n})+(\Delta\rho)g\eta+y(\mathbf{x}_s, t) \tag{11e}$$

The parameters appearing in (11c)-(11e) are the unit outward pointing normal vector $\mathbf{n}$ from fluid 2 (i.e., $\mathbf{n}=\nabla\Pi_S/|\nabla\Pi_S|$), the unit tangential vector, $\mathbf{t}$ in the interface and a fluctuating forcing function $y(\mathbf{x}_s, t)$ which is introduced in this "macroscopic theory" as the source of the interface fluctuations. The statistical properties of this *white noise* function $y(\mathbf{x}_s, t)$ will be discussed in detail shortly. Eqs. (11b) and (11d) are the conditions of continuity of velocity and tangential stress, respectively, while (11c) is the kinematic condition which relates the rate of change of the random displacement, $\eta(\mathbf{x}_s, t)$, to the normal velocities at the interface. The objective of the present analysis is to derive from Eqs. (9)-(11e) a Langevin-type *stochastic* equation for the unknown fluctuation function $\eta(\mathbf{x}_s, t)$ which is driven by random forcing function $y(\mathbf{x}_s, t)$. A correct formulation of the stochastic equations ultimately requires that this forcing function (i.e., white noise) $y(\mathbf{x}_s, t)$ be chosen so that the interface fluctuations exhibit the correct equilibrium correlations (i.e., those from the equilibrium fluctuation theory of the preceding section) on taking the limit $t \to \infty$. The procedure for determining $y(\mathbf{x}_s, t)$ is very similar to the method used to specify the statistical properties of the white noise function A(t) in the Langevin equation from the assumption of equipartition of energy at equilibrium [Batchelor, 1976].

The problem represented by (9)-(11e) is, of course, both time-dependent and highly nonlinear due to the fact that $\eta(\mathbf{x}_s, t)$ is unknown. As noted from (8), however, the magnitude of η is very small and we can therefore linearize the terms in (11c) and (11e) to proceed analytically. The most effective approach to solving the resulting linearized problem is to apply the method of *normal modes*, whereby the small fluctuations $\eta(\mathbf{x}_s, t)$ are resolved into a complete set of normal modes. In particular, we resolve the arbitrary fluctuation $\eta(\mathbf{x}_s, t)$ into independent modes of the form:

$$\eta(\mathbf{x}_s, t)=\int_k\int_\omega \hat{\eta}(\mathbf{k}, \omega)e^{i(\mathbf{k}\cdot \mathbf{x}_s-\omega t)}d\mathbf{k}d\omega \tag{12}$$

and it follows from this and Eqs. (9)-(11e) that

$$(\mathbf{u}^{(j)}, p^{(j)})=\int_k\int_\omega \{\hat{\mathbf{u}}^{(j)}(x_3;\ \mathbf{k}, \omega), \hat{p}^{(j)}(x_3;\ \mathbf{k}, \omega)\}e^{i(\mathbf{k}\cdot \mathbf{x}_s-\omega t)}d\mathbf{k}d\omega \tag{13}$$

In this formulation, the fluctuating variables $\eta(\mathbf{x}_s, t)$ and $(\mathbf{u}^{(j)}, p^{(j)})$ in the problem are being expanded in terms of the same Fourier-transform normal modes, $\hat{\eta}(\mathbf{k}, \omega)$ and $(\hat{\mathbf{u}}^{(j)}, \hat{p}^{(j)})$, that are usually employed in theories of linear dispersive wave motion and hydrodynamic stability [Whitham, 1974]. It can be seen that the normal mode, as usual, has an exponential dependence on time with a complex exponent.

On substituting the expressions (12) and (13) into Eqs. (9) and (11) [i.e., applying the Fourier transform directly to Eqs. (9) and (11)], we obtain a system of ordinary differential equations for $(\hat{\mathbf{u}}^{(j)}, \hat{p}^{(j)})$ and $\hat{\eta}(\mathbf{k}, \omega)$. Then, the solution can be obtained straightforwardly by utilizing the Squire transformation [Squire, 1933]. To determine the stochastic Langevin-type equation for $\hat{\eta}(\mathbf{k}, \omega)$, in terms of the random forcing function $y(\mathbf{k}, \omega)$, we therefore substitute expressions for the stress components calculated from $(\hat{\mathbf{u}}^{(j)}, \hat{p}^{(j)})$ into (11e). The result is

$$[\hat{H}_I(\mathbf{k}, \omega)]\ \hat{\eta}(\mathbf{k}, \omega)=\hat{y}(\mathbf{k}, \omega) \tag{14}$$

If the function $\hat{H}_I(\mathbf{k}, \omega)$ is specified, the response $\hat{\eta}(\mathbf{k}, \omega)$ of the interface to the random force $\hat{y}(\mathbf{k}, \omega)$ is completely determined. The functional quantity $\hat{H}_I(\mathbf{k}, \omega)$, which is known as the generalized *susceptibility* (or system function), plays a fundamental part in the theory described below and is given by

$$\hat{H}_I(\mathbf{k}, \omega)=\frac{i\omega}{k}\{\rho_2\Phi_2(\mathbf{k}, \omega)+\rho_1\Phi_1(\mathbf{k}, \omega)\} -2(\mu_2-\mu_1)\{k\Phi_2(\mathbf{k}, \omega)+\alpha_2\Psi_2(\mathbf{k}, \omega)\}-\{(\Delta\rho)g+\gamma k^2\} \tag{15}$$

in which

$$\Phi_j(\mathbf{k}, \omega)=\frac{i\omega\lambda^{-1}\nu_j(k+\alpha_j)+\nu_q(\alpha_q-k)\{2k^2\nu_j(\lambda-1)(-1)^j+i\omega\lambda^{2-j}\}}{\nu_1(k-\alpha_1)+\lambda\nu_2(k-\alpha_2)} \tag{16a}$$

$$\Psi_j(\mathbf{k}, \omega)=\frac{2i\omega k\lambda^{-1}-2\nu_1\nu_2k^2(\lambda-1)(-1)^j(\alpha_q-k)}{\lambda\nu_2(\alpha_2-k)+\nu_1(\alpha_1-k)} \tag{16b}$$

Here, $\lambda=\mu_1/\mu_2$, $\nu_j=\mu_j/\rho_j$, $\alpha_j=(k^2-i\omega/\nu_j)^{1/2}$ and the subscript q is defined by $q=j-(-1)^j$.

The statistical properties of the fluctuating forcing function $\hat{y}(\mathbf{k}, \omega)$ must now be specified so that the statistical properties of the interface normal modes, $\hat{\eta}(\mathbf{k}, \omega)$, at equilibrium are the same as those derived in the preceding section via equilibrium fluctuation theory, i.e., Eqs. (6)-(8). Thus, for the fluctuating random force $\hat{y}(\mathbf{k}, \omega)$, the following principal assumptions are made:

(i) $\hat{y}(\mathbf{k}, \omega)$ is independent of $\hat{\eta}(\mathbf{k}, \omega)$,

(ii) $\hat{y}(\mathbf{k}, \omega)$ varies extremely rapidly compared to the variations of $\hat{\eta}(\mathbf{k}, \omega)$.

The second assumption implies that time intervals of duration Δt_I exist such that the expected variations in $\hat{\eta}(\mathbf{k}, \omega)$ in period Δt_I are very small while the number of fluctuations in $\hat{y}(\mathbf{k}, \omega)$ is still very large. Thus, the fluctuating force $\hat{y}(\mathbf{k}, \omega)$ appears as white noise (i.e., random and uncorrelated) on the time scale characteristic of variations of $\hat{\eta}(\mathbf{k}, \omega)$:

$$\langle \hat{y}(\mathbf{k}, \omega)\rangle=0 \tag{17}$$

However, it is evident from (14) and (6) that the self-correlation of $\hat{y}(\mathbf{k}, \omega)$ cannot be zero but must take the general form:

$$\langle y(\mathbf{x}_s, t)y(\mathbf{x}_s', t')\rangle=R_y(\mathbf{x}_s, \mathbf{x}_s')\ \delta(t-t') \tag{18a}$$

or

$$\langle \hat{y}(\mathbf{k}, \omega)\ \hat{y}(\mathbf{k}', \omega')\rangle=\hat{R}_y(\mathbf{k}, \mathbf{k}')\ \delta(\omega-\omega') \tag{18b}$$

The unknown function R_y (or $\hat{R}_y$), which specifies the intensity of fluctuations in $y(\mathbf{x}_s, t)$ [or $\hat{y}(\mathbf{k}, \omega)$], must be chosen so that we obtain the correct equilibrium correlation results. The very drastic nature of the *ad hoc* assumptions implicit in (17) and (18) lies in the presumption that the forces that the surrounding fluid molecules exert on the interface can be divided into two parts; one associated with *rapid* fluctuations $y(\mathbf{x}_s, t)$ with time scales characteristic of molecular motion, and the other associated with a much *slower* response time characteristic of viscous relaxation of the system. They are, however, made with reliance on physical intuition and an *a posteriori* justification based on the success of the hypothesis, which will be shown shortly.

In order to determine the functions R_y and $\hat{R}_y$ by comparison with the equilibrium correlation function, (6), from the preceding section, we must solve (14) together with (15). Using white noise $\hat{y}(\mathbf{k}, \omega)$ with properties (17) and (18a, b) as input into (14), we can evaluate the correlation function $\langle \hat{\eta}(\mathbf{k}, \omega)\ \hat{\eta}(\mathbf{k}', \omega')\rangle$ in terms of $\hat{R}_y(\mathbf{k}, \mathbf{k}')$ and $\hat{H}_I(\mathbf{k}, \omega)$. Then, from the Fourier inversion formula, it follows that $\langle \hat{\eta}(\mathbf{k}, t)\hat{\eta}(\mathbf{k}, t+t^0)\rangle$ can be expressed in the form:

$$\langle \hat{\eta}(\mathbf{k}, t)\hat{\eta}(\mathbf{k}', t+t^0)\rangle=\hat{R}_y(\mathbf{k}, \mathbf{k}')\int_{-\infty}^{\infty}\frac{e^{i\omega t^0}d\omega}{\hat{H}_I(\mathbf{k}, \omega)\ \hat{H}_I(\mathbf{k}', -\omega)} \tag{19}$$

It can be seen from (19) that the correlation function for $\hat{\eta}(\mathbf{k}, t)$ is independent of the present time t but depends only on the time difference t^0, and thus satisfies the *invariance* of the equilibrium state under a time translation $t \to t'$ which is expected as a consequence of the hypothesis of microscopic reversibility in statistical physics. The unknown function $\hat{R}_y(\mathbf{k}, \mathbf{k}')$ can now be determined from (19) by setting $t^0=0$ and comparing the result with the equilibrium self-correlation function given by (6). From this, we see

$$\hat{R}_y(\mathbf{k}, \mathbf{k}')=\frac{k_BT\{(\Delta\rho)g-\gamma\mathbf{k}\cdot\mathbf{k}'\}^{-1}\delta(\mathbf{k}+\mathbf{k}')}{(2\pi)^2\int_{-\infty}^{\infty}\frac{d\omega}{\hat{H}_I(\mathbf{k}, \omega)\ \hat{H}_I(\mathbf{k}', -\omega)}} \tag{20}$$

The central importance of the fluctuation-dissipation theorem can now be grasped from Eq. (20). The left-hand side of (20) involves a correlation function which is a measure of the magnitude of *spontaneous fluctuations* about the equilibrium state, i.e., of the ever-present thermal noise $y(\mathbf{x}_s, t)$. The response function on the

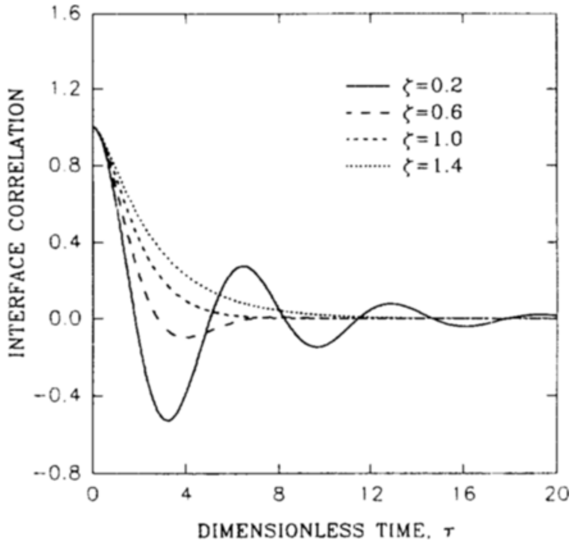

Fig. 2. Dimensionless correlation function $\frac{\langle \hat{\eta}(\mathbf{k},\ t)\hat{\eta}(\mathbf{k},\ t)\rangle}{k_B T\delta(\mathbf{k}+\mathbf{k}')/[(2\pi)^2\{(\Delta\rho)g+\gamma k^2\}]}$**, as a function of the dimensionless time difference** τ**.**

right-hand side incorporates the macroscopic mechanical (i.e., dynamical) response when the system has been removed from equilibrium by the imposition of external forces or constraints. The fluctuation-dissipation theorem then says that the time-correlations of the ***nonequilibrium*** fluctuations, linear in the external forces, are related to and can, indeed, be calculated from equilibrium self-correlations. Finally, with $\hat{R}_y$ determined, we have all the statistical properties that are necessary to specify the system from a macroscopic point of view. In particular,

$$\langle \hat{\eta}(\mathbf{k},\ \omega)\hat{\eta}(\mathbf{k}',\ \omega')\rangle = \frac{\hat{R}_y(\mathbf{k},\ \mathbf{k}')\ \delta(\omega+\omega')}{\hat{H}_I(\mathbf{k},\ \omega)\ \hat{H}_I(\mathbf{k}',\ \omega')} \tag{21}$$

The statistical properties of the random velocity field $\hat{\mathbf{u}}^{(j)}=(\hat{u}_1^{(j)}, \hat{u}_2^{(j)}, \hat{u}_3^{(j)})$ associated with the interface disturbances can be evaluated readily from (9)-(11e):

$$\hat{u}_1^{(j)}=(-1)^{j-1}\left\{i\mathbf{\Phi}_j(\mathbf{k},\ \omega)e^{(-1)^j kx_3}+i\frac{\alpha_j}{k}\mathbf{\Psi}_j(\mathbf{k},\ \omega)e^{(-1)^j\alpha_j x_3}\right\}\hat{\eta}(\mathbf{k},\ \omega) \tag{22a}$$

$$\hat{u}_3^{(j)}=\{\mathbf{\Phi}_j(\mathbf{k},\ \omega)e^{(-1)^j kx_3}+\mathbf{\Psi}_j(\mathbf{k},\ \omega)e^{(-1)^j\alpha_j x_3}\}\hat{\eta}(\mathbf{k},\ \omega) \tag{22b}$$

Obviously, $\hat{u}_2^{(j)}=\hat{u}_1^{(j)}$. So far we have developed a general theory for the spontaneous "thermal" fluctuations of shape which occur in a real fluid interface, and determined the statistical properties of the fluctuating flow field ($\hat{\mathbf{u}}^{(j)}$, $\hat{p}^{(j)}$) driven by the random boundary fluctuations, $\hat{\eta}(\mathbf{k},\ \omega)$.

Before concluding this section, we turn, for illustrative purposes, to a detailed evaluation of the correlation function, given by (21). Here, we consider a general case in which viscous effects on the interface relaxation cannot be neglected. In this case it can be easily seen from (15) that the interface fluctuations are governed by two independent time scales

$$\tau_I=\omega_0^{-1}=\sqrt{\frac{\rho_1+\rho_2}{(\Delta\rho)gk+\gamma k^3}} \tag{23a}$$

and

$$\tau_R=\frac{\rho_1+\rho_2}{k^2(\mu_1+\mu_2)} \tag{23b}$$

Here, ω_0 is the ***natural*** frequency for interface oscillation and thus $2\pi\tau_I$ represents the period of oscillation in the absence of viscous friction. Meanwhile, τ_R denotes the viscous relaxation time scale for the interface displacement on which the initial amplitude due to the impulse decays ***exponentially.*** The same exponential attenuation of capillary waves at the free surface of a body of liquid (i.e., $\mu_1=0$ and $\rho_1=0$) was predicted by Lamb [1932] from the fact that the loss of total energy (kinetic plus potential) of the liquid over one cycle is necessarily equal to the rate of viscous dissipation of energy per cycle, provided the net flux of energy into the volume of liquid concerned is zero. In Fig. 2, the correlation function $\langle\hat{\eta}(\mathbf{k},\ t)\hat{\eta}(\mathbf{k}',\ t')\rangle$ given by Fourier transformation of (21) is illustrated as a function of the dimensionless time difference $\tau[=(t-t')/\tau_R]$ for $\zeta=0.2$, 0.6, 1.0 and 1.4. Here, $\zeta=\tau_I/\tau_R$. It can be seen that the restoring process which drives the system back to a flat configuration exhibits three particular modes depending on the ratio ζ, of viscous forces to capillary elastic response forces: an oscillatory damping ($\zeta<1$), a critical damping ($\zeta=1$) and underdamping ($\zeta>1$).

This completes our study of the spontaneous fluctuations of interface shape that are caused by the thermal agitation in the surrounding fluids. In the next section, we shall consider motions of spherical Brownian particles due to the random flow field that is induced by these interface fluctuations.

BROWNIAN MOTION NEAR A SPONTANEOUSLY FLUCTUATING INTERFACE

In the previous section, we studied and derived a fluctuation-dissipation theorem for spontaneous fluctuations of a fluid interface around its equilibrium configuration. In this section, we will consider the motions of a nearby Brownian particle which occur as a consequence of the velocity field, (22a, b), that is generated by these fluctuations. In general, a Brownian particle near an interface will undergo random motions due to random fluctuating forces of two types: the first, which we shall denote as $\mathbf{F}_R(\mathbf{x};\ t)$, is caused by the boundary-driven random velocity field associated with spontaneous interface fluctuations, and the second, which we shall denote as $\mathbf{A}(t)$, is caused by random fluctuations in the molecular environment immediately adjacent to the particle. It is this latter contribution which will continue to be present even when the particle is far removed from the interface. In this section, we consider the motion of a spherical Brownian particle of radius a that is located in fluid 2 near a fluid interface. The separation distance between the particle center and the undeformed flat interface is d. The usual supposition is that, for sufficiently small fluctuations, the independent random forces and the macroscopic time-evolution of particle momentum have to obey a linear law or a macroscopic rate equation of the Langevin type, i.e.,

$$\frac{dU}{dt}+\mathbf{B}\cdot\mathbf{U}=\mathbf{F}_R(\mathbf{x};\ t)+\mathbf{A}(t) \tag{24}$$

in which $\mathbf{B}$ is a linear operator (called the Boussinesq operator) determined from the unsteady Stokes' equation such that $\mathbf{B}\cdot\mathbf{U}$ represents the time dependent viscous forces including the virtual mass and Basset memory contributions.

In the present section, we consider the motion which results from the random force $F_R(\mathbf{x};\ t)$ that results from the fluctuating velocity field (22a, b). The random force corresponding to the velocity field (22a, b) can be calculated from the Faxen's law generalized to an arbitrary time-dependent flow by Yang [1987]. We begin by taking the Fourier transform of the Langevin Eq. (24) to obtain

$$[\hat{H}_u(\omega)]\ \hat{U}_i(d;\ \mathbf{k},\ \omega)=\hat{F}_{Ri}(d;\ \mathbf{k},\ \omega)+\hat{A}_i(\omega) \tag{25}$$

in which the susceptibility for the particle motion is given by

$$\hat{H}_u(\omega)=-\omega i+\frac{6\pi\mu_2 a}{m}\{1+a\sqrt{\omega/(2\nu_2)}(1-i)\}-\frac{2\pi\rho_2 a^3\omega}{3m}\,i \tag{26}$$

Here, m is the mass of the particle. The Fourier component of the random force $\hat{F}_{Ri}(d;\ \mathbf{k},\ \omega)$ determined from the generalized Faxen's law, is given by

$$\hat{F}_{Ri}(\omega)=\frac{6\pi\mu_2 a}{m}\{1+a\sqrt{\omega/(2\nu_2)}(1-i)\}[\hat{u}_i^{(2)}]_0^S-\frac{2\pi\rho_2 a^3\omega}{3m}\,i[\hat{u}_i^{(2)}]_0^V \tag{27}$$

Here, $[\cdot]_0^S$ and $[\cdot]_0^V$ denote the average values of the quantity in the bracket over the sphere surface and volume, respectively, and each component of the undisturbed velocity $\hat{u}_i^{(2)}$ is defined by (22a, b).

Since the random fluctuating forces $\hat{F}_{Ri}$ and $\hat{A}_j$ are not correlated (i.e., $\langle\hat{F}_{Ri}\hat{A}_j\rangle=0$) and the problem is linear, we can consider the contribution of the random force $\hat{F}_{Ri}$ in (25) independently of the white noise $\hat{A}_i$. We thus examine the net effect of random fluctuations of the interface configuration on the motions of a spherical Brownian particle by determining the velocity correlation of a Brownian sphere that is freely immersed in the fluctuating velocity field driven by the spontaneous interface distortions. Then, the particle velocity correlation function will, in turn, determine the net diffusion coefficient of the Brownian particle associated with the random force F_{Ri} from (25). First, we now evaluate the particle velocity correlation function $\hat{Q}_{ij}(d;\ \mathbf{k},\ \mathbf{k}',\ \omega,\ \omega')=\langle\hat{U}_i(d;\ \mathbf{k},\ \omega)\ \hat{U}_j(d;\ \mathbf{k}',\ \omega')\rangle$ by solving the Langevin Eq. (25) for each mode of random force $\hat{F}_{Ri}(d;\ \mathbf{k},\ \omega)$ of (27).

$$\hat{Q}_{ij}(d;\ \mathbf{k},\ \mathbf{k}',\ \omega,\ \omega')=\frac{\hat{P}_{ij}(d;\ \mathbf{k},\ \mathbf{k}',\ \omega,\ \omega')}{\hat{H}_u(\omega)\ \hat{H}_u(\omega')} \tag{28}$$

and then relating the required statistics of the random force (i.e., the correlation function $\hat{P}_{ij}$ for the random force $\hat{F}_{Ri}$) to the statistical property (21) of the interface fluctuations. The correlation function $\hat{P}_{ij}$ for the random force can be determined from the generalized Faxen's law of (27) together with the random velocity field (22a, b) which is related to the random stochastic fluctuations $\hat{\eta}(\mathbf{k},\ \omega)$ by (21). The resulting expression in terms of the correlation function for $\hat{\eta}(\mathbf{k},\ \omega)$ is simply

$$\begin{aligned}\hat{P}_{ij}(d;\ \mathbf{k},\ \mathbf{k}',\ \omega,\ \omega')&=\langle\hat{F}_{Ri}(d;\ \mathbf{k},\ \omega)\ \hat{F}_{Ri}(d;\ \mathbf{k}',\ \omega')\rangle\\&=\hat{G}_{ij}(d;\ \mathbf{k},\ \omega)\langle\hat{\eta}(\mathbf{k},\ \omega)\hat{\eta}(\mathbf{k}',\ \omega')\rangle\end{aligned} \tag{29}$$

in which each component of the tensor $\hat{G}_{ij}$ can be obtained from (21)-(22b) combined with (27). Taking the inverse Fourier transformation of (29) with respect to k_i and k_i', and utilizing the properties of the Dirac δ-function, we get

$$\hat{P}_{ij}(d;\ \omega,\ -\omega)=2\pi\int_0^\infty\hat{G}_{ij}(d;\ \mathbf{k},\ \omega)\langle\hat{\eta}(\mathbf{k},\ \omega)\hat{\eta}(\mathbf{k}',\ -\omega)\rangle k\,dk \tag{30}$$

Thus, the particle velocity correlation function $\langle U_i(d;t)\ U_j(d;t+t^0)\rangle$, which relates the present particle velocity to its velocities at other times, can be determine from (28) and (30), i.e.,

$$Q_{ij}(d;\ t^0)=\langle U_i(d;\ t)\ U_j(d;\ t+t^0)\rangle=\int_{-\infty}^{\infty}\frac{\hat{P}_{ij}(d;\ \omega,\ -\omega)e^{i\omega t^0}}{|\hat{H}_u(\omega)|^2}d\omega \tag{31}$$

It can be seen from (31) that the velocity correlation function $Q_{ij}(d;\ t^0)$ is independent of the present time t and depends only on the time difference t^0 between the present time and other times as a consequence of the time-translational invariance of the equilibrium state [Kreuzer, 1984]. In order to proceed analy-

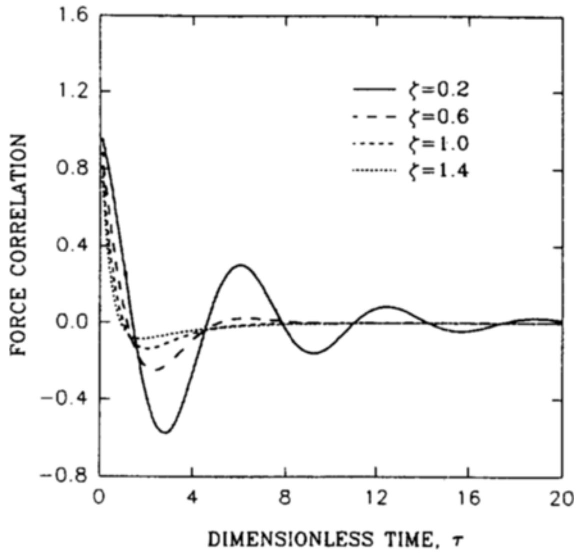

Fig. 3. Dimensionless correlation function $\dfrac{\langle\hat{F}_{R3}(d;\ \mathbf{k},\ t)\hat{F}_{R3}(d;\ \mathbf{k}',\ t+\tau)\rangle}{9k_BT\mu_2^2a^2k\delta(\mathbf{k}+\mathbf{k}')e^{-2dk}/[m^2(\rho_1+\rho_2)]}$, as a function of the dimensionless time difference τ.

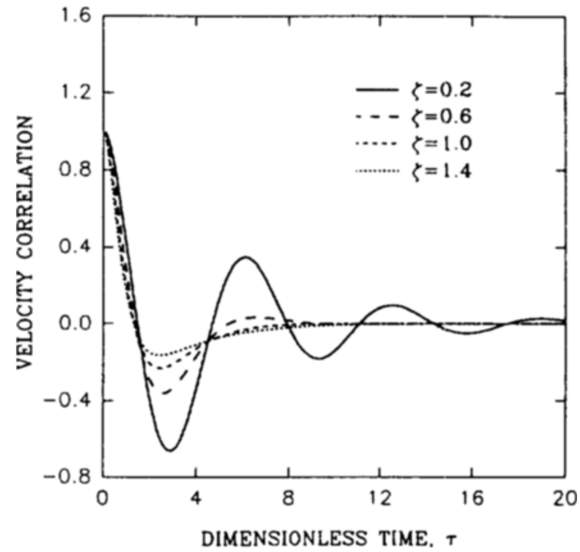

Fig. 4. Dimensionless correlation function $\dfrac{\langle\hat{U}_3(d;\ \mathbf{k},\ t)\hat{U}_3(d;\ \mathbf{k}',\ t+\tau)\rangle}{9k_BT\mu_2^2a^2\delta(\mathbf{k}+\mathbf{k}')e^{-2dk}/[m^2\{(\Delta\rho)g+\gamma k^2\}(2\lambda_{\alpha\omega}\zeta+\lambda_{\alpha\omega}^2+1)]}$ as a function of the dimensionless time difference τ for $\lambda_{\alpha\omega}=2.0$.

tically, there are two possible asymptotic limits corresponding to the relative importance of viscous damping forces on the interface relaxation compared to the capillary forces (i.e., $k^2 \gg \omega/\nu_i$ or $k^2 \ll \omega/\nu_j$). In the weak dissipation limit (i.e., $k^2 \ll \omega/\nu_j$), however, the amplitude of interface fluctuations caused by an initial impulse sustains and does not decay since the viscous damping effects are negligible. In the asymptotic limit, $k^2 \gg \omega/\nu_j$, there exist two limiting cases depending upon the relative magnitude of the particle radius a compared to the length scale of vorticity penetration generated by the particle motions, i.e $\nu_2/(\omega a^2) \gg 1$ (or $\ll 1$). The nature of the response, in this case can be understood most clearly by plotting (30) and (31) as shown in Figs. 3 and 4, where the correlation functions for $\hat{F}_{R3}$ and $\hat{U}_3$ are given as a function of τ for the same values of the parameter ζ as in the previous Fig. 2. It can be seen from Fig. 3 that the force on the sphere that is generated by the random impulse of the interface decays exponentially on the same viscous dissipation time scale, τ_R, as the amplitude $\hat{\eta}(\mathbf{k}, t)$ of the interface distortion. The viscous damping of the force on the particle can be characterized by three typical modes depending on ζ (i.e., the ratio of viscous forces to elastic-response forces) as can be seen in section 3, and the *frequency* of the oscillatory damping case ($\zeta<1$) is exactly the same as the frequency of the interface oscillation. The force correlation lags behind the interface fluctuation. The phase lag φ_F is always negative

$$\varphi_F = -2\tan^{-1}\left(\frac{\zeta}{\sqrt{1-\zeta^2}}\right) \tag{32}$$

and dependent on the ratio of the two intrinsic forces of the system [i.e., $\varphi_F(\zeta\to 0)=0$ and $\varphi_F(\zeta\to 1)=-\pi$]. The velocity correlation function indicates that the energy imparted to a particle by each thermal impulse on the interface decays exponentially on the two independent time scales, τ_R on which the amplitude η and the induced force F_{R3} decay, and $\tau_P[=m/(6\pi\mu_2 a)]$ characteristic of the viscous relaxation time for motions of Brownian particles in an unbounded fluid. Thus the correlation functions of (30) and (31) constitute the fluctuation-dissipation theorem for the motion of a Brownian sphere due to the spontaneous fluctuations of a nearby fluid interface. They relate the spontaneous fluctuations in interface shape caused by the thermal white noise to the viscous dissipation due to the corresponding motions of the surrounding fluids. From (31) we can evaluate the phase lag φ_U for the velocity response of the particle to the interface oscillations

$$\varphi_U = -2\tan^{-1}\left(\frac{\zeta}{\sqrt{1-\zeta^2}}\right) + 2\tan^{-1}\left(\frac{1-\lambda_{a\omega}}{1+\lambda_{a\omega}}\frac{\zeta}{\sqrt{1-\zeta^2}}\right) \tag{33}$$

in which $\lambda_{a\omega}(=\tau_I/\tau_P)$ is the ratio of the time scale for the interface fluctuation (i.e., ω_0^{-1}) to that of the viscous relaxation of the particle velocity. In Fig. 5, the phase lag is plotted as a function of the parameter ζ representing the viscous damping force relative to the elastic-response force. It can be easily seen that when $\lambda_{a\omega}=1$ the correlations of the random force and the particle velocity are in phase. However, the velocity oscillates with the same frequency as the force and interface fluctuations. Chaplin [1984] experimentally measured forces acting on a horizontal cylinder with radius a which is located at a distance d=2a-5a from the undeformed plane of a free surface which is executing wave motions with the range of the dimensionless wave number, ka=0.146-0.824. The existence of phase lags in the fluctuating force and the particle velocity with respect to the phase of the incident waves, which has been predicted in the present analysis, was

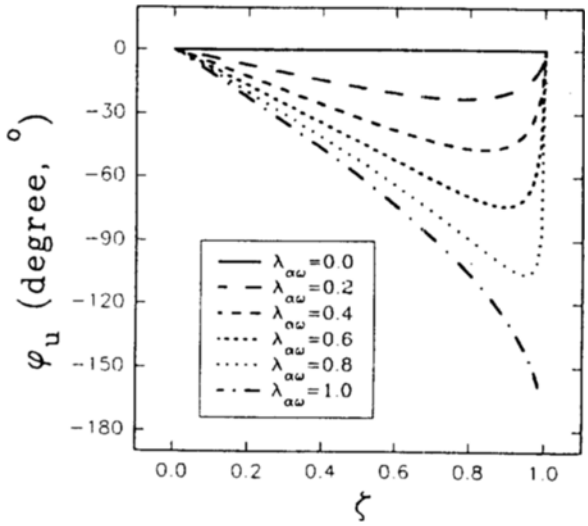

Fig. 5. Phase lag for the velocity response of the particle to the interface oscillations as a function of ζ for various values of $\lambda_{a\omega}$.

demonstrated by the experimental data of Chaplin.

Let us now turn to the *general* expression for the velocity correlation function, Eq. (31), in order to consider the effect of interface fluctuations caused by the thermal noise of surrounding molecules on the Brownian diffusion of particles in the vicinity of the interface. As we mentioned earlier, the relaxation of the interface distortion, η, back toward the equilibrium configuration is very rapid and the displacement η after receiving a thermal impulse decays exponentially on the time scale $\tau_R(\sim 10^{-8}$ sec in water). Further, the correlation functions of (30) and (31) show that the relaxation of the particle velocity is exponentially rapid on the time scales τ_P and τ_R characteristic of the viscous relaxation of particle motion and of the interface relaxation. In a time interval Δt which is very large compared to the relaxation time scales τ_R and τ_P (i.e., $\Delta t \gg \tau_R, \tau_P$), the motion of a particle can therefore be viewed as random and the mean square displacement $\langle |x_i(t)\ x_j(t)| \rangle$ and the Brownian diffusivity D_{ij} are related at equilibrium (i.e., $t\to\infty$) according to

$$D_{ij} = \lim_{t\to\infty} \frac{1}{2}\frac{d}{dt}\langle x_i(t)\ x_j(t)\rangle \tag{34}$$

Recalling the fact that the time differential is commutted with the ensemble averaging and the displacements written as integrals of the velocity from the initial zero conditions [i.e., $x_i(0)=0$], it follows that

$$D_{ij}(d) = \int_0^\infty \langle U_i(d;\ t)\ U_j(d;\ t+t^0)\rangle\ dt^0 \tag{35}$$

in which the integrand is the velocity correlation function given by (31). Thus, the diffusivity is immediately recognized as the spectral density function $\hat{Q}_{ij}(d;\ \omega)$ at frequency $\omega=0$. Utilizing (31), we thus have

$$D_{ij}(d) = \lim_{\omega\to 0} \pi\left[\frac{\hat{P}_{ij}(d;\ \omega,\ -\omega)}{|\hat{H}_u(\omega)|^2}\right] \tag{36}$$

In this low frequency limit, the functions $\Phi_j(\mathbf{k}, \omega)=2k^2\nu_j$, $\Psi_j(\mathbf{k}, \omega)=-2k^2\nu_j$, and the susceptibility for the interface fluctuations $\hat{H}_I(\mathbf{k}, \omega)=-[(\Delta\rho)g+k^2\gamma]$. Thus we can readily evaluate the diffusion coefficient by substituting the various functions into (30) and

(31). The result is

$$D_{ij}=k_B T M_{ij} \quad (37)$$

which includes the contribution from the white noise $A_i(t)$. In (37), M_{ij} is the mobility tensor for the particle motion in the presence of a nondeforming flat interface. Thus, the contribution from the random fluctuations of interface shape turns out to be identically equal to zero. This implies that the fluctuating velocity field caused by the random distortion of interface does not produce any *net* rate of change of mean-square particle displacement. One possible explanation of the present result, (37), stems from the linear theory of plane progressive waves which predicts that at any fixed point the fluid speed remains constant, while the direction of fluid displaced by the waves moves through a circular orbit and the time average of *net* displacement is identically zero in the linear theory, since the second order [in the wave amplitude, $O(\eta^2)$] mean Stokes' drift in the direction of the wave propagation can be neglected in the low frequency limit, $\omega\to 0$. In the low frequency limit, which represents almost steady motion, the trajectories of a Brownian sphere are exactly the same as those of the fluid particle [Whitham, 1974].

CONCLUSIONS

We have considered the motions of Brownian particles in the fluctuating velocity field induced by the random spontaneous changes in interface shape owing to thermal impulses from the surrounding fluid. We have, in addition, determined the various covariance functions and the corresponding effect on the diffusion coefficient.

The restoring process which drives the interface back to a flat configuration is governed by two distinct time scales τ_I and τ_R and exhibits three particular modes depending on the ratio ζ ($=\tau_I/\tau_R$), of viscous forces to capillary elastic response forces: an oscillatory damping ($\zeta<1$), a critical damping ($\zeta=1$) and underdamping ($\zeta>1$).

The random force on the sphere that is generated by the random impulse of the interface decays exponentially on the same viscous dissipation time scale, τ_R, as the interface distortion. The viscous damping of the force on the particle can be characterized by three typical modes depending also on ζ, and the *frequency* of the oscillatory damping case ($\zeta<1$) is exactly the same as the frequency of the interface oscillation.

The diffusion coefficient tensor is related by the Stokes-Einstein equation to the mobility tensor for the particle motion in the presence of a nondeforming flat interface. Although the velocity autocorrelation is modified by the interface fluctuation, the random fluctuations of interface shape does not produce any net rate of change of mean-square particle displacement.

NOMENCLATURE

- a : particle radius
- **A** : White noise on the Brownian particle
- A : free energy functional for the interface fluctuations
- **B** : Boussinesq tensor
- d : separation distance between the particle and the plane interface
- D_{ij} : diffusivity tensor
- $\mathbf{F}_R$: force induced by the interface fluctuations on the particle
- g : gravity
- H_I : susceptibility for the interface fluctuations
- H_u : susceptibility for the particle motion
- i : imaginary number $\sqrt{-1}$
- J_0 : Bessel function of the first kind of order 0
- **k**, **k'**: wave vectors
- k, k': magnitudes of the wave vectors **k**, **k'**
- k_B : Boltzmann constant
- L_p : interface width
- m : particle mass
- M_{ij} : mobility tensor
- **n** : unit normal vector on the interface
- $p^{(j)}$: pressure of fluid j
- P_{ij} : force autocorrelation
- Q_{ij} : velocity autocorrelation
- R_y : autocorrelation of y
- S : entropy induced by the interface fluctuations
- **t** : unit tangential vector on the interface
- t : time
- **T** : stress tensor
- T : absolute temperature
- $\mathbf{u}^{(j)}$: velocity of fluid j, $(u_1^{(j)}, u_2^{(j)}, u_3^{(j)})$
- U : Brownian particle velocity
- W : probability function for the interface displacement
- $\mathbf{x}_s$: position vector of a ponit placed on the interface
- x_3 : coordinate perpendicular to the plane interface
- y : White noise on the interface
- γ : interfacial tension
- δ : Dirac delta function
- ζ : τ_I/τ_R
- η : interface displcement from the plane of $x_3=0$
- λ : viscosity ratio, μ_1/μ_2
- $\lambda_{\omega\omega}$: τ_i/τ_p
- μ_j : viscosity of fluid j
- ν_j : kinematic viscosity of fluid j
- Π_S : shape function for the interface
- ρ_j : density of fluid j
- σ : intermolecular length scale
- τ : dimensionless time difference
- τ_I : reciprocal of the natural frequency of the interface oscillation
- τ_p : viscous relaxation time for the particle motion
- τ_R : viscous relaxation time scale for the interface fluctuation
- ϕ_F : phase lag for the force oscillation
- ϕ_U : phase lag for the particle velocity oscillation
- $\mathbf{\Phi}_j$: function defined in (16a)
- $\mathbf{\Psi}_j$: function defined in (16b)
- ω : frequency of the interface oscillation
- ω_0 : natural frequency of the interface oscillation
- Ω : normalization constant

Symbols

- ∇ : gradient operator
- ∇_s : two-dimensional gradient operator on the interface
- $(\hat{\cdot})$: variable $(\cdot)$ in Fourier transformed domain

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