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The Mössbauer Effect: A Potentially Ideal Probe into Brownian Motion

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We calculate the Mössbauer spectrum of nuclei embedded in spheres of radius on the order of 1 μm which are suspended in a liquid. We demonstrate that the Mössbauer effect is an ideal means for testing the deductions based upon a generalized Langevin equation which takes into account the effects of acceleration memory on the force and torque of the liquid on a sphere and for studying, generally, the detailed statistical dynamical behavior of Brownian particles. The spectrum is expressed in terms of an integral over an integrand consisting of standard functions. Experimental desiderata are discussed and a list of sample experimental parameters given.

KEY WORDS: Brownian motion; Mössbauer effect; fluctuations; diffusion; generalized Langevin equation; acceleration memory; linearized hydrodynamics; velocity autocorrelation function; angular velocity autocorrelation function; Lorentzian; Gaussian.

1. INTRODUCTION

In 1967 Alder and Wainwright[1] performed computer simulation experiments on a "gas" of hard spheres and found that the velocity autocorrelation function behaved asymptotically as $t^{-3/2}$ as the time t approached infinity. To some, this result was quite unexpected insofar as it disagreed with the standard classical behavior of Brownian motion found in standard treatises,[2]

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which predicts *exponential* long-time decay. Widom[3] and Zwanzig and Bixon[4] subsequently pointed out that the computer result could be understood on the basis of an extension of classical results to the case when the mass density of a Brownian particle ρ_0, which is typically on the order of 1 g/cm^3, is comparable to the fluid mass density ρ, rather than much larger, as is required for the classical result to obtain. Hauge and Martin-Löf,[5] in a statistical hydrodynamical paper on the problem, have noted that this result was conjectured by Lorentz[6] in 1911–12. We feel quite incompetent to judge who was first with what in this problem and leave it to the historians to study its history. In any case, quite a number of theoretical papers have appeared on the subject since the Alder and Wainwright paper.[7–11]

What is annoyingly lacking is *experimental* confirmation of the predicted behavior of the velocity autocorrelation function in a *real* system of Brownian particles. What is being tested is the assumption that linearized hydrodynamics of a dense viscous fluid fully describes the fluctuations in the velocity of a Brownian particle. We have every reason to believe in the validity of this assumption. What makes the search for an experimental probe of Brownian motion exciting is the prospect of being able to observe the detailed behavior of a particle which is on the order of 1 μm in diameter and suspended in a fluid. This range of particle size—which lies midway between the "fully" macroscopic and atomic domains—seems to have been neglected by physicists. Such knowledge could be very valuable in many areas of science and technology. Foremost on our minds at the moment are biophysics, computer science, and pollution control.

The purpose of this paper is to demonstrate that the Mössbauer effect may be the ideal method[2] to examine the detailed behavior of a particle undergoing Brownian motion. The reasons for our optimism will become apparent in the course of this paper. Since we have a complete theory of this motion, we are not content to obtain merely the width and peak magnitude of the spectrum. We expect to obtain a detailed comparison of the experimental and theoretically predicted Mössbauer spectra.

The system we will be considering is a suspension of spherically shaped particles of radius R on the order of 1 μm and mass m, containing a spherically symmetric distribution of Mössbauer nuclei, in a viscous liquid of mass density ρ and viscosity η. We will treat the fluid as if it were incompressible

[2] Harris[12] has proposed the study of the decay of an electric current of ions in solution. This method is quite difficult and, given available experimental techniques, could at best reveal only the long-time behavior of the velocity autocorrelation function. Second, it is not so clear to what extent an ion can be treated as a Brownian particle. In particular, it seems clear that its motion on a short time scale—less than the order of the characteristic time t_1 of the text—is not describable by the generalized Langevin equation.

since in the significant regime of frequencies $\omega \sim 6\pi\eta R/m$ (which is on the order of the inverse of the characteristic time for velocity decay) the penetration depth[(13)] $(2\eta/\rho\omega)^{1/2}$ of the velocity flow into the fluid is much less than the distance $c_s m/6\pi\eta R$, where c_s is the speed of sound in the fluid. We will use linear hydrodynamics since the typical Reynolds number is on the order of $\rho R(kT/m)^{1/2}/\eta$, where k is Boltzmann's constant and T is the absolute temperature.[3] The suspension will be assumed to be so dilute and free from electric charge effects that we will neglect correlations between the particles. Finally, along with previous treatments of this problem, we will assume that "stick" boundary conditions hold—namely that the tangential velocity component of the particle at a point on its surface is equal to that in the fluid.

In Section 2 we briefly review the theory of the generalized Langevin equation—generalized to include the effects of particle acceleration on the force of the fluid on the particle—and its connection with the velocity autocorrelation function and comment on the reasons for the reliability of the theory. A key step in the calculation of the Mössbauer spectrum involves a major assumption—whose validity we discuss—namely that the Fourier components of the velocity fluctuations of a particle are Gaussian distributed. We end with a summary of the corresponding results regarding the *angular velocity* autocorrelation function, which also contributes to the Mössbauer spectrum. In Section 3, we develop the theory of the Mössbauer spectrum of a suspension of such Brownian particles. We end up with an expression for the Mössbauer spectrum in terms of a Fourier transform of a function which is easily calculated by a computer. Finally, we discuss experimental desiderata.

To help give the reader a feeling for the important parameters in the theory, we have listed the basic and derived parameters in Appendix A, along with a sample set of their values. In Appendix B we provide some of the essential properties of the complex error function $w(z)$,[(14)] a function which is of fundamental importance in the theory—analogous to the exponential function in the classical Langevin equation.

2. THE VELOCITY AND ANGULAR VELOCITY AUTOCORRELATION FUNCTIONS

The generalized Langevin equation[4] for a solid sphere moving in a fluid is given by

$$m\dot{v}(t) = -6\pi\eta R v(t) - \tfrac{2}{3}\pi\rho R^3\dot{v}(t) - 6R^2(\pi\eta\rho)^{1/2}\int_{-\infty}^{t} dt'\dot{v}(t')/(t-t')^{1/2} + F_{\text{ext}}(t) + f(t) \qquad (1)$$

[3] This point was made by Chow and Hermans.[(9)]

[4] See Ref. 3 and, for a general treatment, Kubo.[(7)]

where $v(t)$ is the velocity component of the sphere at time t and $\dot{v}(t)$ is its time derivative. The first three terms represent the force of the fluid on the sphere calculated directly from the linearized Navier–Stokes equation[13] of hydrodynamics. The first of these terms is the Stokes force, while the second and third are neglected when the fluid is dilute (so that $\rho \sim 0$), leading to the classical Langevin equation. The second term is a result of the mass of fluid dragged by the sphere and the third term is the "*acceleration memory*" term, which takes into account the fact that it takes time for the fluid to develop a steady-state flow pattern for a given velocity. It vanishes when the velocity is constant and is a force which depends upon the entire history of the motion of the sphere. It is interesting, from a partly mathematical and partly philosophical point of view, that there is no physically meaningful solution to the homogeneous equation obtained by setting $f + F = 0$ in the equation. [This is not the case when the memory term is absent, in which case a physically significant homogeneous solution exists but can be replaced by an inhomogeneous solution which represents the response of $v(t)$ to an external force; cf. below.] The function $F_{\text{ext}}(t)$ is any external force which may be acting on the sphere (e.g., a gravitational force) and is also present in the hydrodynamical description of the motion. *We will henceforth set* $F_{\text{ext}} = 0$. The function $f(t)$ is the fluctuating force of the fluid on the sphere, present whether or not the sphere is in motion. It introduces fluctuations into the equation and its average over time vanishes. Henceforth, we will also assume that the fluid and sphere are in equilibrium, so that, in addition, the thermal average velocity $\langle v \rangle$ vanishes. The inhomogeneous solution (the only physically significant solution) to Eq. (1) is

$$v(t) = \int_{-\infty}^{t} dt'\, \phi(t - t')f(t') \tag{2}$$

where $\phi(t)$ is the response function obtained by Laplace-transforming Eq. (1) and using the fact that

$$\mathrm{ILT}\left\{\frac{1}{\sqrt{s} - z}\right\} = (\pi t)^{-1/2} + zw(-iz\sqrt{t}) \tag{3}$$

where ILT symbolizes the inverse Laplace transform, z is the complex number $x + iy$, and w is the complex error function (cf. Appendix B). In terms of the parameters $\lambda \equiv \rho/2\rho_0$, $\alpha \equiv \frac{3}{2}[\lambda/(1 + \lambda)]^{1/2}$, $m^* \equiv m(1 + \lambda)$, $t_1 \equiv m^*/6\pi\eta R$, $\tau \equiv t/t_1$, and $\theta \equiv \sin^{-1} \alpha$, we obtain

$$\phi(t) = (1/m^*)\{\mathrm{Re}\, w[e^{i\theta}\sqrt{\tau}] - \tan\theta\, \mathrm{Im}\, w(e^{i\theta}\sqrt{\tau})\} \tag{4}$$

The time t_1 is the characteristic time of velocity fluctuation and (cf. Appendix A) is on the order of 10^{-2} μsec for spheres of 1 μm radius in glycol. The force

$f(t)$ which is taken into account is a result of a huge number of collisions. This approximation can be viewed as a coarse graining in time over a period $\ll t_1$ but much greater than the time t_c between collisions[5] or simply as being valid only when $t \gg t_c$. Because many collisions, $\sim t_1/t_c \gtrsim 10^{10}$ in a time interval t_1, are responsible for producing a significant force $f(t)$, we can assume that the Fourier components f_ω of $f(t)$ are Gaussian distributed. In concrete terms, the probability distribution function of $f(t)$ is assumed to be given by

$$P_f = C_f \prod_\omega \exp(-|f_\omega|^2/\langle|f_\omega|^2\rangle) \tag{5}$$

where C_f is a normalization constant, the subscript ω here and henceforth signifies the ω Fourier component of the function subscripted, $\langle\ \rangle$ represents a thermal average, and $\prod_\omega$ is a product over all frequencies ω. Furthermore, by Fourier transforming Eq. (2), we obtain the relation

$$v_\omega = \phi_\omega f_\omega \tag{6}$$

Explicitly,

$$\phi_\omega = (1/6\pi\eta R)[1 + 2\alpha(-i\omega t_1)^{1/2} - i\omega t_1]^{-1} \tag{7}$$

From Eqs. (5) and (6) we obtain the probability distribution function of $v(t)$:

$$P_v = C_v \prod_\omega \exp(-|v_\omega|^2/\langle|v_\omega|^2\rangle) \tag{8}$$

where C_v is a normalization constant and

$$\langle|v_\omega|^2\rangle = |\phi_\omega|^2\langle|f_\omega|^2\rangle \tag{9}$$

On the other hand, linear response theory[(7)] predicts that

$$\langle v(t)v(0)\rangle = kT\phi(|t|) \tag{10}$$

[Note that the function $\phi(t)$ is regarded as vanishing when $t < 0$.] By Fourier transforming Eq. (10), we obtain

$$\langle|v_\omega|^2\rangle = 2kT \operatorname{Re} \phi_\omega \tag{11}$$

From Eqs. (9) and (11) we obtain the important relation

$$\langle|f_\omega|^2\rangle = 2kT \operatorname{Re}(1/\phi_\omega) \tag{12}$$

Equation (12) shows us that $\langle|f_\omega|^2\rangle$ is *uniquely determined* by the macroscopic, hydrodynamic viscous force, a point which has not always been recognized.[6]

[5] The time t_c can be estimated as (molecular mass)$^{3/2}/\rho R^2(kT)^{1/2} = 10^{-18}$–$10^{-19}$ sec.

[6] This point had also previously been noted by Kubo.[(7)] [Note that the spectrum of $f(t)$, $\langle|f_\omega|^2\rangle$, is automatically white if the velocity autocorrelation function decays exponentially.]

An analysis similar to that above leads to the following results for the autocorrelation function of a component $\Omega(t)$ of the angular velocity of a sphere[5,13]:

$$\langle\Omega(t)\Omega(0)\rangle = (kT/8\pi\eta R^3)\,\mathrm{ILT}\{[1 + 3(\lambda t_0 s)^{1/2}] \times [1 + 3(\lambda t_0 s)^{1/2} + \tfrac{3}{10}(1 + 10\lambda)t_0 s + \tfrac{9}{10}\sqrt{\lambda}(t_0 s)^{3/2}]^{-1}\} \tag{13}$$

where

$$t_0 \equiv m/6\pi\eta R = t_1/(1 + \lambda) \tag{14}$$

is the characteristic time for velocity fluctuations in the limit that ρ approaches zero. If we let $I = \frac{2}{5}mR^2$ be the moment of inertia of the sphere,

$$z_0 \equiv \tfrac{1}{3}[(1 + \lambda)/\lambda]^{1/2}$$

and $z_{1,\pm}$ be the three roots of the equation[7]

$$1 + 3\left(\frac{\lambda}{1 + \lambda}\right)^{1/2} z + \frac{3}{10}\,\frac{1 + 10\lambda}{1 + \lambda}\,z^2 + \frac{9}{10}\,\frac{\sqrt{\lambda}}{(1 + \lambda)^{3/2}}\,z^3 = 0$$

we have

$$\langle\Omega(t)\Omega(0)\rangle = \frac{kT}{I}\left\{\frac{\mathrm{Im}[z_+ w(-iz_+\sqrt{\tau})]}{\mathrm{Im}\, z_+} + \frac{z_0 + z_1}{\mathrm{Im}\, z_+}\,\mathrm{Im}\,\frac{z_+ w(-iz_+\sqrt{\tau}) - z_1 w(-iz_1\sqrt{\tau})}{z_+ - z_1}\right\} \tag{15}$$

Equations (4) and (15) and the fact that $|v_\omega|^2$ and $|\Omega_\omega|^2$ are Gaussian distributed are all we need to proceed to calculate the Mössbauer spectrum.

3. CALCULATION OF THE MÖSSBAUER SPECTRUM

Let $\mathbf{x}(t)$ be the displacement of the center of mass of a sphere in a time t. Then the displacement of a Mössbauer nucleus located at the position $\mathbf{r}$ relative to the center of mass of the sphere is given to first order (which is adequate to take into account position fluctuations) by

$$\mathbf{x}(t, \mathbf{r}) = \mathbf{x}(t) + \boldsymbol{\theta}(t) \times \mathbf{r} \tag{16}$$

where $\boldsymbol{\theta}(t)$ is the angular rotation of the sphere in time t. If we now let $n(\mathbf{r})$ be the density of Mössbauer nuclei at position $\mathbf{r}$ in a sphere, the Mössbauer

[7] This equation is obtained from the denominator in Eq. (13) if we set $z = (st_1)^{1/2}$. In particular, when $\rho_0 = \rho$, so that $\lambda = 1/2$, $z_1 = -1.341$ and $z_\pm = -1.062 \pm 1.013i$. We will henceforth assume that $z_\pm$ are a pair of complex conjugate roots.

spectrum is given by[15]

$$I(\omega) = (1/\pi)\int_0^\infty dt \cos(\omega t)\int_{sp} d\mathbf{r}\, n(\mathbf{r})I(\mathbf{q}, t, \mathbf{r}) \exp(-\Gamma t/2) \tag{17}$$

where Γ is the natural linewidth of the Mössbauer γ-ray,

$$I(\mathbf{q}, t, \mathbf{r}) = \langle \exp[i\mathbf{q}\cdot\mathbf{x}(t, \mathbf{r})]\rangle \tag{18}$$

where the symbol sp indicates that the integral is over the volume of a sphere and $\mathbf{q}$ is the wave vector of the Mössbauer γ-ray.

Because the fluctuations of $\mathbf{x}(t)$ and $\boldsymbol{\theta}(t)$ are independent,

$$I(\mathbf{q}, t, \mathbf{r}) = \langle \exp[i\mathbf{q}\cdot\mathbf{x}(t)]\rangle\langle \exp[i\mathbf{q}\cdot\boldsymbol{\theta}(t) \times \mathbf{r}]\rangle \tag{19}$$

Because $\mathbf{v}(t)$ and $\boldsymbol{\Omega}(t)$ are Gaussian distributed, so are $\mathbf{x}(t)$ and $\boldsymbol{\theta}(t)$ Gaussian distributed, so that

$$I(\mathbf{q}, t, \mathbf{r}) = \exp[-q^2\langle x(t)^2\rangle/2] \exp[-(\mathbf{q} \times \mathbf{r})^2\langle \theta(t)^2\rangle/2] \tag{20}$$

where $x(t)$ and $\theta(t)$ are the components of $\mathbf{x}(t)$ and $\boldsymbol{\theta}(t)$ along the directions $\mathbf{q}$ and $\mathbf{q} \times \mathbf{r}$, respectively.

We next relate $\langle x(t)^2\rangle$ and $\langle \theta(t)^2\rangle$ to the velocity and angular velocity autocorrelation functions, respectively. From the relations

$$x(t) = \int_0^t dt'\, v(t') \tag{21}$$

and

$$\theta(t) = \int_0^t dt'\, \Omega(t') \tag{22}$$

and the stationarity of the ensemble [which gives us the relation $\langle v(t + t')v(t')\rangle = \langle v(t)v(0)\rangle$], we have

$$\langle x(t)^2\rangle = 2\int_0^t dt'\, (t - t')\langle v(t')v(0)\rangle \tag{23}$$

and

$$\langle \theta(t)^2\rangle = 2\int_0^t dt'\, (t - t')\langle \Omega(t')\Omega(0)\rangle \tag{24}$$

Using Eq. (B.5) of Appendix B, we obtain

$$\langle x(t)^2\rangle = 2Dt_1\tau^{3/2} \sec\theta \operatorname{Im} g(ie^{i\theta}\sqrt{\tau}) \tag{25}$$

and

$$\langle\theta(t)^2\rangle = \frac{2kTt_1{}^2\tau^{3/2}}{I\,\mathrm{Im}\,z_+}\left\{\mathrm{Im}\,g(z_+\sqrt{\tau}) + (z_0 + z_1)\,\mathrm{Im}\,\frac{g(z_+\sqrt{\tau}) - g(z_1\sqrt{\tau})}{z_+ - z_1}\right\} \tag{26}$$

where $D \equiv kT/6\pi\eta R$ is the translational diffusion constant and where

$$g(z) \equiv z^{-3}[-z^2 + w(-iz) - 1 - 2z/\sqrt{\pi}] \tag{27}$$

When $t \ll t_1$,

$$\langle x(t)^2\rangle \sim \langle v(0)^2\rangle t^2 = kTt^2/m^* \tag{28}$$

and

$$\langle\theta(t)^2\rangle \sim \langle\Omega(0)^2\rangle t^2 = kTt^2/I \tag{29}$$

In the first case, Eq. (28), the only effect of the fluid on the particle in time t is that of the fluid dragged instantaneously by the particle due to the assumed incompressibility of the fluid. Equation (28) is valid (cf. discussion in the introduction) as long as $\eta/\rho c_s{}^2 \ll t \ll t_1$. In the second case, Eq. (29), there is no effect of the fluid on the particle for times $t \ll t_1$.

Asymptotically, as $t \to \infty$,

$$\langle v(t)v(0)\rangle \to (kT\rho^{1/2}/12)(\pi\eta t)^{-3/2} \tag{30}$$

and

$$\langle\Omega(t)\Omega(0)\rangle \to (\pi kT\rho^{3/2}/32)(\pi\eta t)^{-5/2} \tag{31}$$

which contrasts sharply with the long-time, exponential behavior [$\sim\exp(-6\pi\eta Rt/m)$ and $\sim\exp(-5\pi\eta Rt/2m)$, respectively] which obtains if we set ρ equaı to zero in Eq. (1) and its counterpart for $\Omega(t)$.[8] On the other hand, as $t \to \infty$,

$$\langle x(t)^2\rangle \to 2Dt_1[\tau - 4\alpha(\tau/\pi)^{1/2}\cdots] \tag{32}$$

and

$$\langle\theta(t)^2\rangle \to \frac{kTt_1}{4\pi\eta R^3}\left\{\tau - 6\left(\frac{\tau}{\pi}\right)^{1/2}\left[\left(\frac{\lambda}{1+\lambda}\right)^{1/2} - \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\right]\cdots\right\} \tag{33}$$

so that acceleration memory effects die out relatively in these two quantities which determine the Mössbauer spectrum, and we need to study time scales on the order of t_1 to see the effect of acceleration memory on the Mössbauer spectrum.

[8] The $t^{-5/2}$ long-time behavior of $\langle\Omega(t)\Omega(0)\rangle$ for the molecules of a molecular fluid was derived in Ref. 16.

We see from Eqs. (20), (32), and (33) that $-\ln I(\mathbf{q}, t, \mathbf{r})$ scales, for $r \sim R$, as $\beta^2 \equiv Dq^2 t_1$ multiplied by a function of τ which becomes linear as $\tau \to \infty$. Therefore, to see acceleration memory effects in the Mössbauer spectrum, it is best to have β on the order of unity and, because of the exponential time factor $\exp(-\Gamma t/2)$, to have $\Gamma \lesssim t_1^{-1}$. In addition, if we use a source of Mössbauer nuclei embedded in a solid and a suspension of Brownian particles as an absorber, it is very desirable to have $\Gamma \ll t_1^{-1}$, so that the observed Mössbauer absorption or transmission will directly give us the function $I(\omega)$ of Eq. (17). This function $I(\omega)$ is determined by Eqs. (20), (25), (26), and (27) once $n(\mathbf{r})$ and the basic parameters [cf. Appendix A] are known. When $\beta \sim 1$ and $\Gamma \ll t_1^{-1}$, $I(\omega)$ will be a function intermediate in character between a Gaussian and a Lorentzian and with a width on the order of t_1^{-1}.

A group from Tufts University and the National Magnet Laboratory of MIT are currently undertaking this experiment.

APPENDIX A. A LIST OF RELEVANT PARAMETERS

Below is a list of basic and derived parameters which are relevant in the Mössbauer spectrum of a liquid suspension of spherical Brownian particles. The numbers following the definitions represent a sample set of values which obtain when 1-μm spheres containing Fe^{57} are suspended in glycol[17] at room temperature and $\rho_0 = \rho$.

Basic parameters

R	radius of sphere, 1 μm
ρ_0	mass density of sphere, 1.11 g/cm^3
ρ	mass density of fluid, 1.11 g/cm^3[17]
η	viscosity of fluid, 19.9 cP[17]
T	absolute temperature, 293°K
Γ	natural linewidth of the Mössbauer γ-ray, 0.71×10^7 sec^{-1}
E_γ	energy of the Mössbauer γ-ray, 14.4 keV
c_s	speed of sound in fluid, 1.67×10^5 cm/sec[17]

Derived parameters

m	$\equiv 4\pi\rho_0 R^3/3$; mass of sphere, 4.65×10^{-12} g
I	$\equiv 2mR^2/5$; moment of inertia of sphere, 1.86×10^{-20} g-cm^2
D	$\equiv kT/6\pi\eta R$; translational diffusion constant, 1.08×10^{-10} cm^2/sec
t_1	$\equiv m(1 + \rho/2\rho_0)/6\pi\eta R$; characteristic time for velocity decay, 1.86×10^{-8} sec; the dynamical effects of the fluid on the particle are negligible for time scales $\ll t_1$; On the other hand, the effects of acceleration memory at a time scale $\gg t_1$ do not significantly affect the Mössbauer spectrum

q $\equiv E_\gamma/\hbar c$; magnitude of the wave vector of the Mössbauer γ-ray, $7.27 \times 10^8\ \mathrm{cm}^{-1}$

β $\equiv (Dq^2t_1)^{1/2}$; a dimensionless parameter, which if $\ll 1$, ~ 1, or $\gg 1$ indicates that the velocity autocorrelation function in the time regime $\gg t_1$, $\sim t_1$, or $\ll t_1$, respectively, will have the dominant effect on the Mössbauer spectrum; ideally, β should be on the order of unity to study acceleration memory effects; 1.03

γ $\equiv 2Dq^2$, addition to the linewidth of the Mössbauer spectrum when $\beta \ll 1$; the spectrum remains Lorentzian; $1.14 \times 10^8\ \mathrm{sec}^{-1}$

γ' $\equiv q(kT/2m^*)^{1/2}$; qualitative addition to the linewidth of the Mössbauer spectrum when $\beta \gg 1$; the spectrum is given by $\mathrm{Re} \times w[(\omega - i\Gamma)/4\gamma']/(2\gamma'\sqrt{\pi})$, which becomes a Gaussian when $\Gamma \ll \gamma'$; $3.91 \times 10^7\ \mathrm{sec}^{-1}$

$2\eta/\rho c_s^2$ characteristic time such that for time scales greater than this time, the fluid may be regarded as incompressible; 1.29×10^{-11} sec

APPENDIX B. SOME PROPERTIES OF THE COMPLEX ERROR FUNCTION $w(z)$—THE "FUNDAMENTAL" FUNCTION OF THE THEORY

$$w(z) = (\exp -z^2)\left[1 + (2i/\sqrt{\pi})\int_0^z dt \exp t^2\right] \tag{B.1}$$

$$w(z^*) = w(-z^*) \tag{B.2}$$

$$\mathrm{Re}\, w(z = x) = \exp -x^2 \tag{B.3}$$

$$dw/dz = -2zw(z) + 2i/\sqrt{\pi} \tag{B.4}$$

$$\int_0^x dx'\, w(\sqrt{x'}) = 1 - w(\sqrt{x}) + 2i\sqrt{x}/\sqrt{\pi} \tag{B.5}$$

$$w(z) = \sum_{n=0}^{\infty} (iz)^n/\Gamma(\tfrac{1}{2}n + 1) \tag{B.6}$$

$$w(z) = \frac{i}{\sqrt{\pi}z}\left\{1 + \sum_{m=1} \frac{1\cdot 3\cdots(2m-1)}{(2z^2)^m}\right\} \tag{B.7}$$

Relations (B.1)–(B.4) and (B.6) were taken directly from Ref. 14. Relation (B.7) follows straightforwardly from relation (7.1.23) of Ref. 14 and is an asymptotic expansion. The relation (B.5), which follows from (B.4) should be compared (cf. body of paper) with the relation which holds for the corresponding function, $\exp -x$, which is fundamental when the Langevin equation is adequate:

$$\int_0^x dx' \exp -x' = 1 - \exp(-x) \tag{B.8}$$

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