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Rate theory for solids. IV. Classical Brownian-motion model*

J. H. Weiner and R. E. Forman†
Brown University, Providence, Rhode Island 02912
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In order to gain insight into classical and quantum-rate theories for solids, a model for interstitial diffusion is presented in which the impurity atom is regarded as a Brownian particle constrained to move in a single direction and subject to a periodic potential. The classical behavior of this model is studied in this paper by the use of computer-simulation techniques; the study of the behavior of this model in the quantum regime is deferred to the following paper. Particular emphasis is placed here on the effect of the magnitude of the Brownian friction coefficient upon the persistence of motion of the impurity atom and how this persistence, in turn, affects the diffusion coefficient.

I. INTRODUCTION

The previous papers in this series[1-3] have dealt with the general problem of rate theory in solids from both the classical and quantum viewpoints. In the last of these[3] a rate theory was presented which may be regarded as a generalization to the quantum regime of the classical Vineyard theory,[4] in the sense that the derivation is in the same general spirit and in that the quantum-rate formula reduces[5] to the Vineyard rate formula in the limit of high temperature and large particle mass. This quantum theory makes use of minimum-uncertainty wave packets and incorporates both quantum-statistical and quantum-dynamical (tunneling) effects. Another approach to the quantum theory of diffusion, together with a survey of other treatments of this problem, may be found in the paper by Sussmann.[6] For a comprehensive treatment of point defects and diffusion in solids the reader is referred to the recent book by Flynn.[7]

The classical Vineyard theory[4] and its quantum generalization[3] both utilize phase spaces of huge dimensionality. For example, if we consider the case of impurity-atom diffusion in a crystal, then the coordinates of the impurity atom and those of the host atoms, both those near and far from the impurity, are accorded equal status in the phase-space description. This procedure leads to a treatment which, from a formal viewpoint, appears clearcut with a minimum of assumptions. However, there remains the possibility that effects associated with the huge dimensionality of the phase space are not clearly revealed by this formalism and that, in fact, it may not be advantageous for maximum insight into the process to treat the coordinates of atoms far from the impurity, which physically act only as a heat bath, on the same footing as those of the impurity atom itself. Also, when the many-dimensional viewpoint is employed, it is difficult to examine the system's history after it has left a given equilibrium configuration and moved on to an adjacent one. This aspect of the process plays a significant role even in the classical regime[8] and may, as has been recently emphasized by Sussmann and Weissman,[9] play an even more important role in the quantum regime.

In this paper, and the one immediately following it,[10] we attempt to gain insight into these questions by moving to the other extreme and considering an idealized model for interstitial diffusion in a crystal lattice in which only a single degree of freedom of the impurity atom is considered explicitly and all other degrees of freedom of the system are treated as an interacting heat bath. Specifically, the model, which we study from both the classical and quantum[10] viewpoints, may be described as follows: We consider that the impurity atom has been restricted to move in only a single direction, denoted by x [Fig. 1(a)]. Assume next that the impurity atom is moved quasistatically along x from one equilibrium position S to an adjacent equilibrium position S' with the host atoms allowed to assume their equilibrium positions appropriate to the instantaneous position of the impurity atom. During such motion the host atoms will exert a force on the impurity atom which may be regarded as derived from a potential $V(x)$. This potential will be periodic with stable equilibrium positions S and S' separated by a distance equal to the lattice parameter b, Fig. 1(b). In the case of the thermally activated motion of the impurity, the host atoms will not be at the equilibrium positions appropriate to the instantaneous position of the impurity atom, but will be in thermal motion in the vicinity of these positions. Therefore, in addition to the forces derived from the potential $V(x)$ (called here the deterministic force) the impurity atom is subject to an additional force (called here the thermal force). A basic assumption of the model here employed is that

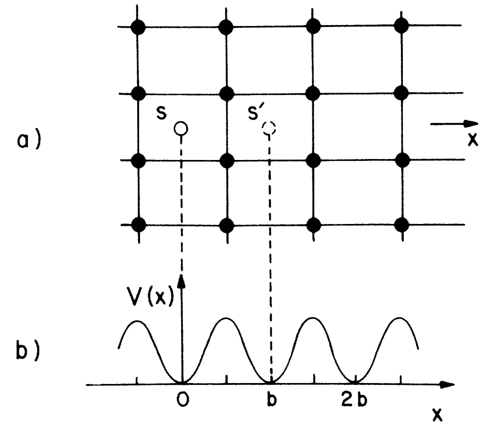


FIG. 1. (a) Schematic of crystal lattice containing an impurity atom, shown in two possible adjacent equilibrium sites S and S'. (b) Potential function $V(x)$ whose derivative yields deterministic force exerted by host atoms on impurity atom as it moves in x direction.

the dynamic effect of the thermal force may be represented, as in the theory of Brownian motion, in terms of two separate components: (a) a systematic part proportional to the impurity atom's velocity; and (b) a random fluctuating part which must be described by classical or quantum statistics. In brief, then, this diffusion model represents the impurity atom as a classical or quantum Brownian particle subject to a periodic potential $V(x)$.

The use of the one-dimensional Langevin equation in the study of rate processes appears to have been initiated by Kramers.[11] In his classical work (in both senses of the word) he employed a double-well potential and studied the effect of the strength of coupling to the heat bath in both the overdamped and underdamped regimes. For our present study of diffusion it appears that only the underdamped regime is relevant and we concentrate on sufficiently weak coupling so that it has negligible effect on the jump rate from a given well but does, nevertheless, have a substantial effect on the system's later behavior. Although our primary motivation in the classical study arises from its quantum counterpart, it does have some direct interest as well in connection with the effect of the persistence of impurity atom motion on the diffusion coefficient, an effect first noted in the computer simulation studies of Bennet and Alder[12] on vacancy diffusion in a hard-sphere crystal.

A great deal of effort has been expended in recent years to derive conditions under which the Langevin equation (or a generalization of it) may be used rigorously to describe the behavior of an impurity atom in a crystal lattice.[13] These are, however, concerned with the localized motion of the impurity atom in the vicinity of an equilibrium site and not with the large intersite excursions involved in diffusion. Our use of the one-dimensional Langevin equation with a periodic potential is intended only as a mathematical model for the interstitial diffusion process, not as a formulation which is rigorously equivalent to it.

The plan of this paper which presents a classical discussion of this model is as follows: In Sec. II we present a numerical procedure for the computer simulation of the classical Langevin equation which describes the model in the classical regime. The results of two check examples for which the analytical solution is known are presented in Sec. III in order to demonstrate that the computer-simulation procedure is capable of accurate results. It is applied in Sec. IV to the computer simulation of the model of impurity-atom diffusion in order to investigate the effect of the strength of coupling between the single degree of freedom of the impurity atom and the remainder of the lattice. Concluding remarks are presented in Sec. V.

II. COMPUTER SIMULATION OF THE LANGEVIN EQUATION

As noted in Sec. I, in this one-dimensional model for interstitial diffusion, the impurity atom is treated as a Brownian particle subject to a periodic potential $V(x)$ and therefore, in the classical regime, is described by Langevin's equation in the form

$$m\frac{dv}{dt}=-\frac{dV}{dx}-\beta v+F(t)\,, \tag{2.1}$$

where m is the mass of the impurity atom, $v=dx/dt$ is its velocity, β is the friction constant, and $F(t)$ is the random fluctuating force. As mentioned, the thermal force on the impurity (i.e., the effect of its interaction with the remainder of the crystal acting as a heat bath) is composed of the dynamical friction $-\beta v$ and a random fluctuating part $F(t)$. These two terms thus represent a contracted description of the random aspect of the interaction between the impurity atom and the crystal in the sense that they are specified by only two parameters, the friction constant and temperature T. In addition, these two terms are not independent of each other as is seen in the following description of the statistical characteristics of $F(t)$. [Although more sophisticated descriptions of Brownian motion in the terminology of the mathematical theory of stochastic processes may be given, we follow here the mode of description of the statistical characteristics of $F(t)$ as given by Chandrasekhar,[14] because it provides more physical insight and leads most naturally to the numerical procedure employed.]

Let Δt be a time interval sufficiently short such that during it the position and velocity change very little but $F(t)$ suffers many fluctuations. Let

$$B(\Delta t) = \int_t^{t+\Delta t} F(\tau)\, d\tau \tag{2.2}$$

be the impulse (assumed independent of t) imparted to the impurity atom during this time interval by the fluctuating force. Then the probability of occurrence of different values of $B(\Delta t)$ is governed by the distribution function

$$\rho_B(B(\Delta t)) = \frac{1}{(2\pi q \Delta t)^{1/2}} \exp\left(-\frac{|B(\Delta t)|^2}{2q\Delta t}\right), \tag{2.3}$$

where

$$q = 2\beta k T/m^2$$

and k is Boltzman's constant. This choice of $\rho_B(B(\Delta t))$ ensures that the distribution of impurity-atom position and velocity will, after a sufficiently long period, assume the characteristics of thermal equilibrium at temperature T.

For computational convenience, the potential $V(x)$ is taken as piece-wise quadratic as follows:

$$\begin{aligned} V(x) &= \tfrac{1}{2}\kappa_w x^2, \quad |x| \leq \tfrac{1}{4}b \\ V(x) &= \tfrac{1}{16}\kappa_w b^2 - \tfrac{1}{2}\kappa_w(\tfrac{1}{2}b - x)^2, \quad \tfrac{1}{4}b \leq |x| \leq \tfrac{1}{2}b, \end{aligned} \tag{2.4}$$

and is defined for all other values of x by the requirement that $V(x)$ is periodic with period equal to the lattice parameter b. The barrier height E_b is then seen to be

$$E_b = \tfrac{1}{16}\kappa_w b^2 .$$

Since it is difficult to solve the Langevin equation analytically for this potential, a computer formulation is developed. In devising a procedure for computer simulation of the model described by Eqs. (2.1)–(2.4), it is clear that we are not seeking a numerical procedure for computing an approximation to the solution $x(t)$ of Eq. (2.1), which will converge to the true solution as the numerical time step $\delta t \to 0$, since the velocity $v(t)$ has the property of being everywhere nondifferentiable.[15] Rather, the time interval Δt, described prior to Eq. (2.2), is regarded as the smallest of physical interest and the computer simulation calculates only statistical information about the behavior of impurity atom position and velocity for time periods long with respect to Δt.

In order to produce a random fluctuating force with the characteristics given by Eqs. (2.2) and (2.3), the following procedure has been found convenient. Let the finite-difference time step used in the computation, δt, be taken as a small fraction of Δt; $F(t)$ is taken as constant in each successive time interval δt with the value

$$F = (-1)^R (q/\delta t)^{1/2}, \tag{2.5}$$

where R is an odd or even integer with equal probability. Then it follows from the central-limit theorem that the probability distribution function for $B(\Delta t)$ will approach the required Gaussian form of Eq. (2.3) as $\delta t/\Delta t \to 0$.

Because of the procedure used to simulate the statistical characteristics of $F(t)$, the numerical finite-difference time step δt employed will be small compared to the time interval Δt in which the change in x and v is small. A consequence of this small size of δt is that a simple Euler scheme may be used for the numerical integration aspect of the computer simulation.[16] The finite-difference equations used to determine $x(n+1)$ and $v(n+1)$, the impurity position and velocity at time $t(n+1) = t(n) + \delta t$, in terms of the values of $x(n)$, $x(n-1)$ and $v(n)$, are then simply

$$x(n+1) = x(n) + v(n)\delta t, \tag{2.6}$$

$$v(n+1) = v(n) + m^{-1}[-V'(n) - \beta v(n) + (-1)^{R(n)}(q/\delta t)]^{1/2}]\delta t, \tag{2.7}$$

where $V'(n) = dV/dx$ evaluated at $x(n)$ and $R(n)$ is the nth randomly generated even or odd number.

In addition, the computer program contains sorting routines to determine the phase-space distribution of the particle. For this purpose, prescribed large ranges of x and v are subdivided into n equal intervals of width Δx and Δv, respectively, with the ith coordinate interval, whose central value is x_i, denoted by $\Delta_i x$. Similarly, the ith velocity interval, with central value v_i, is denoted by $\Delta_i v$. Associated with each interval $\Delta_i x$(or $\Delta_i v$), the program contains a counter $n_i(x,r)$ [or $n_i(v,r)$] which records the total number of times that the position (or velocity) falls in the interval $\Delta_i x$ (or $\Delta_i v$) in the period of computation up to $t(r) = r\delta t$. Then

$$\rho_x(x_i; t(r))\Delta x = n_i(x,r)/r ;$$

$$\rho_v(v_j; t(r))\Delta v = n_j(v,r)/r ,$$

and, when x and v are independent random variables,

$$\rho_{x,v}(x_i, v_j; t(r)) = \rho_x(x_i; t(r))\rho_v(v_j; t(r)). \tag{2.8}$$

The lattice parameter b was used to nondimensionalize distance and the frequency $\omega = (\kappa_w/m)^{1/2}$ was used to nondimensionalize time, i.e., units of length and time were chosen in which $b = \omega = 1$. Temperature levels are expressed in terms of the ratio kT/E_b and the friction constant in terms of the dimensionless group $\beta/m\omega$. Most of the computations reported on used a numerical time step $\delta t = 0.1$; check computations performed with $\delta t = 0.05$ showed that the former value was sufficient.

III. CHECK COMPUTATIONS

In order to check the computer-simulation procedure described in Sec. II, two computations were performed for which analytical solutions are available. These check computations were performed by appropriate specialization of the general computer program for the periodic potential described in Sec. II. Therefore, the same dimensionless groups as listed at the end of that section were employed as well to describe the conditions of the check calculation, although some of the parameters such as b and E_b become irrelevant for the check computations. These irrelevant parameters could, of course, be eliminated from the presentation of the numerical results of the check computations, but they have been retained here to simplify comparison with the results for the periodic-potential case.

The first case is the Brownian motion of a particle trapped in a harmonic potential well, that is, one for which the potential $V(x)$ is

$$V(x) = \tfrac{1}{2}\kappa_w x^2 . \tag{3.1}$$

The aim of this calculation is to verify that the computed phase-space distribution at time $t(r)$, $\rho_{x,v}(x_i, v_j; t(r))$, as given by Eq. (2.8), approaches for sufficiently large $t(r)$ the theoretical distribution for thermal equilibrium,

$$\rho_{x,v}(x, v) = \left(\frac{m\omega}{2\pi kT}\right)\exp\left(-\frac{mv^2 + \kappa_w x^2}{2kT}\right). \tag{3.2}$$

The harmonic-oscillator computation is performed for the case $\beta/m\omega = 0.1$ and $kT/E_b = 0.5$. The results are shown in Fig. 2 and the agreement between theory and numerical results is seen to be quite satisfactory.

The second case is the Brownian motion of a free particle, that is, one for which the potential $V(x) = 0$. The procedure used to determine the diffusion coefficient from the computer-simulation results is based on the following theory[14]: Consider an ensemble of free Brownian particles which at time $t = 0$ all start from $x = x_0$ with the same velocity v_0. Then the probability distribution of the particle displacement $u = x(t) - x_0$ at time t, $\rho_u(u, t; v_0)$, is given by Chandrasekhar[14] as

$$\rho_u(u, t; v_0) = \frac{1}{(\pi/R)^{1/2}} \exp\left[-R(t)\left(u - \frac{v_0(1 - e^{-\bar{\beta}t})}{\bar{\beta}}\right)^2\right], \tag{3.3}$$

where $\bar{\beta} = \beta/m$ and

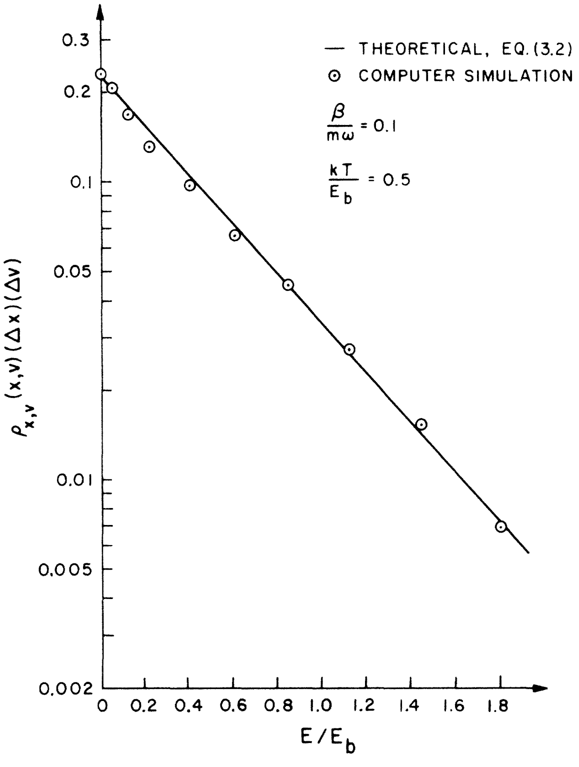


FIG. 2. Computer-simulation test of Brownian motion trapped in a harmonic potential well. $\rho_{x,v}(x,v)\Delta x \Delta v$ is fraction of computed values of $x(r)$ and $v(r)$ found in intervals of width $\Delta x, \Delta v$, respectively, with central values x, v; the results are plotted as a function of $E(x, v) = \frac{1}{2}(mv^2 + \kappa_w x^2)$. Values of $\Delta x = 0.05$, $\Delta v = 0.05$, in units in which $b = \omega = 1$, were employed. This calculation, as well as all others reported in these figures, utilized a numerical time step $\delta t = 0.1$.

$$R(t) = m\bar{\beta}^2[2kT(2\bar{\beta}t - 3 + 4e^{-\bar{\beta}t} - e^{-2\bar{\beta}t})]^{-1}. \tag{3.4}$$

We next consider an ensemble of such ensembles of particles in which the initial velocity v_0 distribution corresponds to thermal equilibrium at temperature T, that is, for which

$$\rho_{v_0}(v_0) = (m/2\pi kT)^{1/2}\, e^{-mv_0^2/2kT} .$$

Then the over-all ensemble distribution function for the particle displacement at time t, $\bar{\rho}_u(u, t)$, is given by

$$\bar{\rho}_u(u, t) = \int_{-\infty}^{\infty} \rho_{v_0}(v_0)\rho_u(u, t; v_0)\, dv_0 = \frac{1}{(2\pi\langle u^2\rangle)^{1/2}}\, e^{-u^2/2\langle u^2\rangle}, \tag{3.5}$$

where

$$\langle u^2\rangle(t) = (2kT/m\bar{\beta}^2)(\bar{\beta}t - 1 + e^{-\bar{\beta}t}) . \tag{3.6}$$

The form assumed by $\bar{\rho}_u(u, t)$ for $t \gg 1/\bar{\beta} = m/\beta$ is

$$\bar{\rho}_{uL}(u, t) = (\beta/4\pi kTt)^{1/2}\, e^{-\beta u^2/4kTt} . \tag{3.7}$$

If the latter distribution is regarded as a solution to the one-dimensional diffusion equation, then it is seen that the diffusion coefficient D_F for the free particle is given by

$$D_F = kT/\beta . \tag{3.8}$$

It is convenient to define a time-dependent diffusion coefficient $D_F(t)$ in an analogous fashion based on the mean-square deviation of the Gaussian distribution of Eq. (3.5), namely,

$$D_F(t) = (kT/m\bar{\beta}^2 t)(\bar{\beta}t - 1 + e^{-\bar{\beta}t}) . \tag{3.9}$$

It should be noted, however, that Eq. (3.5) does not represent a solution to the diffusion equation with diffusion coefficient $D_F(t)$.

The distribution $\bar{\rho}_u(u, t)$ provides the basis for the determination of the function $D_F(t)$ by the computer simulation of the Langevin equation for the free Brownian particle. By the numerical procedure described in Sec. II, we determine the particle position $x(r)$ at time $t = r\delta t$. Let

$$u(N, r) = x(r) - x(r - N) \tag{3.10}$$

be the displacement the particle has undergone in the N time steps previous to time $t = r\delta t$. After an induction period $t_{\text{in}} \gg m/\beta$, the particle velocity distribution corresponds to thermal equilibrium. Therefore, if we discard the data for $0 < t < t_{\text{in}}$, we may expect that the distribution of $u(N, r)$ with N fixed will correspond to that given by Eqs. (3.5) and (3.6) with $t = N\delta t$. The computer-simulation distribution of these displacements is determined by a sorting routine based on $u(N, r)$ similar to that described for x and v in Sec. II. For each value of N, a Gaussian is fitted to the numerically determined distribution by a least-square procedure. An example of the numerically determined distribution of $\bar{\rho}_u(u, t)$ for the case $\beta/m\omega = 0.5$ is shown in Fig. 3. The increased scatter of the data for larger values of $N\delta t$ is due to the fewer values of $u(N, r)$ [Eq. (3.10)] which are obtained for larger N. As the next step in the calculation, $D_F(N, t)$ is determined from the mean-square deviation of the fitted Gaussian.[17] Each computer simulation for a given set of parameters and a particular β, concurrently determines five values of $D_F(N, t)$ corresponding to five different fixed time intervals $N\delta t$. A comparison between the computed and theoretical values of $D_F(Nt)$ [Eq. (3.9)] for $\beta/m\omega = 0.5$ and $kT/E_b = 0.5$ is shown in Fig. 4. The agreement is seen to be good. It is observed that as $N\delta t$ increased, the computer results asymptotically approach the value predicted by Eq. (3.8) in the manner described by Eq. (3.9). The error bars in this figure represent the measure of the uncertainty in the slope of the straight line which is fitted by a least-square procedure to the natural log of the distribution $\bar{\rho}_u(u, t)$. The uncertainty of the computed diffusion coefficient is seen to be greater for larger $N\delta t$ because of the smaller number of values of $u(N, r)$ for large N.

IV. BROWNIAN MOTION IN PERIODIC POTENTIAL

Having verified by the check computations of Sec. III that the computer-simulation procedure is capable of accurate results, we turn in this section to its use in the computer simulation of our one-dimensional model of impurity-atom diffusion in a crystal lattice. As described in Sec. I, this model corresponds to the Brownian motion of a particle in a periodic potential, $V(x)$.

A. Jump rate

We are confining attention here, as noted previously, to sufficiently weak coupling so that it has negligible effect on the jump rate from a given well. This will be the case, as derived by Kramers,[11] if the friction constant $\beta \ll 4\pi\omega m$, where ω is the circular frequency of oscillation in the harmonic region. Under these conditions the average rate f of passage over a single barrier is given by the usual Arrhenius expression as

$$f = (\omega/2\pi)e^{-E_b/kT} . \tag{4.1}$$

This theoretical jump-rate expression provides a check of the computer-simulation procedure as applied to the periodic potential in which the computer program keeps track of the number J of barriers jumped in the total time t of the computer simulation and yields a computed jump rate $f_C = J/t$.

A comparison of the time-averaged jump rate from the computer-simulation with the theoretical average jump rate, Eq. (4.1), for several values of friction constant β and temperature T is shown in Fig. 5. The agreement between computer simulation and theory is seen to be good and, as predicted by the Kramers analysis, shows little dependence on the friction constant β.

B. Diffusion coefficient

If it is assumed that successive particle jumps are completely uncorrelated, then the diffusion coefficient for the periodic potential may be determined directly from the jump rate f [Eq. (4.1)] by the relation for a one-dimensional random walk with step size b, namely,

$$D_{PR} = \tfrac{1}{2} f b^2 , \tag{4.2}$$

where the subscripts indicate that the diffusion coefficient corresponds to a particle in a periodic potential computed on the basis of an uncorrelated random-walk assumption. We turn next to a direct

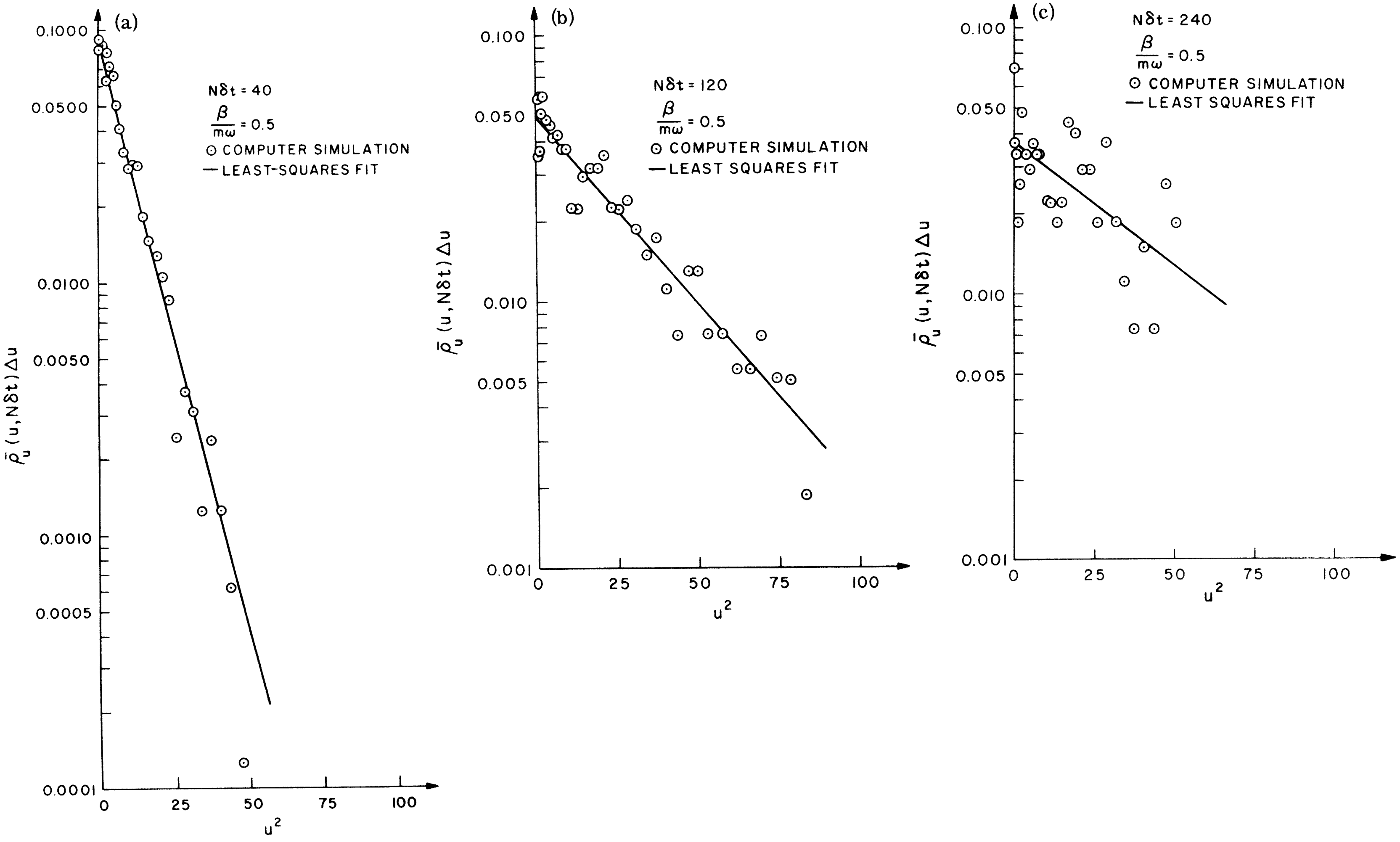


FIG. 3. Computer-simulation test of Brownian motion of free particle. $\bar{\rho}_u\,(u, N\delta t)$ is fraction of computed values of $u\,(N, r)$ [Eq. (3.10)] found in interval of width Δu centered on u; the results are plotted as a function of u^2. The value $\Delta u = 0.25$ in units in which $b = 1$ was employed. (a) $N\delta t = 40$. (b) $N\delta t = 120$. (c) $N\delta t = 240$.

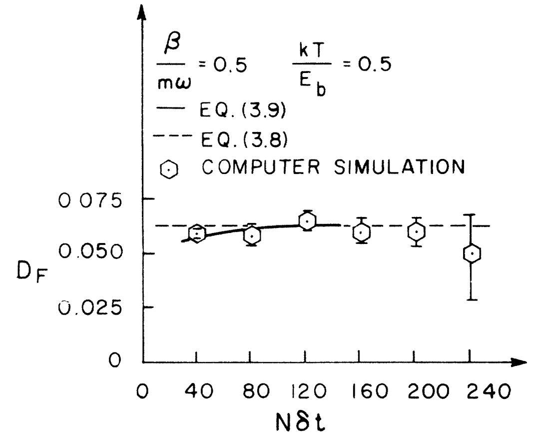


FIG. 4. Diffusion coefficient $D_F(t)$ for free particle as determined by computer simulation. Units in which $\omega = b = 1$ are employed. The error bars denote the root-mean-square deviation of the computed $D_F(t)$.

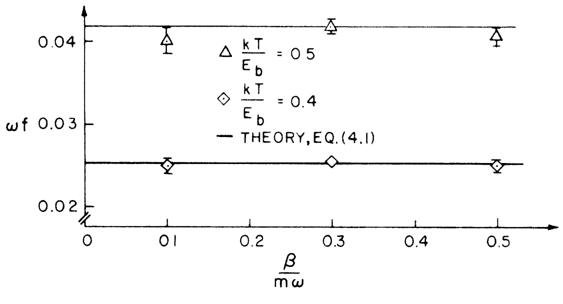


FIG. 5. Jump frequency f for particle in periodic potential as determined by computer simulation. The error bars denote the root-mean-square deviation of the computed jump frequency.

determination of the diffusion coefficient for a Brownian particle in a periodic potential using the same computer-simulation procedure based on the distribution function $\bar{\rho}_u(u, t)$ followed for the free Brownian particle in the check computation of Sec. III. That is, although this function is, of course, no longer given by the analytical expression of Eq. (3.5), it is still possible to determine its form by computer simulation, by numerically determining a sample path $x(r)$ and using the computer sorting routine to determine $\bar{\rho}_u(u, t)$. It is found that this distribution function is Gaussian, as for the free Brownian particle; typical plots of the numerical results are shown in Fig. 6. From the mean-square deviation at time t of these Gaussian distributions[17], may be calculated an effective diffusion constant $D_P(t)$, analogous to the effective diffusion constant $D_F(t)$ for the free particle discussed after Eq. (3.9). The limiting value, at large time of $D_P(t)$, denoted by D_P, with the limit determined simply by graphical means (Fig. 7), then corresponds to the macroscopic diffusion constant for the periodic potential. It is interesting to note that whereas in the free-particle case $D_F(t)$ approaches its limiting value from below (Fig. 4), in the case of a periodic potential (Fig. 7), the limiting value D_P is approached from above.

It may seem surprising that the distribution $\bar{\rho}_u(u, t)$ for the periodic potential is Gaussian (Fig. 6) with no perturbations due to the potential wells. This is a consequence of the definition of $u(N, r)$, Eq. (3.10), in which only information regarding the relative particle displacement is retained. In order to fix the particle displacement relative to the potential, the program also considered a subset A of the set of all of the computed displacements for fixed $N, \{u(N, r)\}$, where a displacement

$$u(N, r) = x(r) - x(r-N)$$

is assigned to the subset A if $x(r-N)/b$ differs from an integer by a prescribed tolerance α, that is, if the displacement $u(N, r)$ is one starting from the bottom of a well (to within a prescribed tolerance). The result of sorting the displacements u in the subset for a tolerance $\alpha = 0.025$ is shown in Fig. 8 for several values of $N\delta t$ and shows clearly the effects of the potential wells.

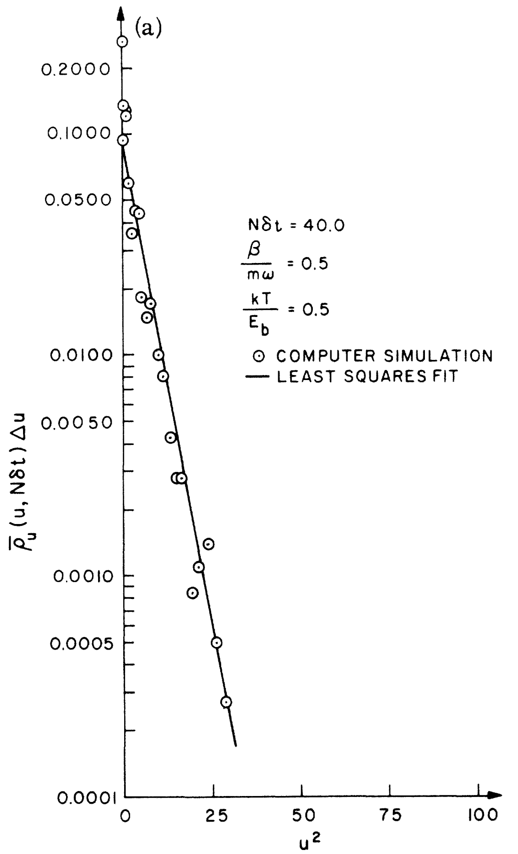
C. Dependence of diffusion coefficient on friction constant

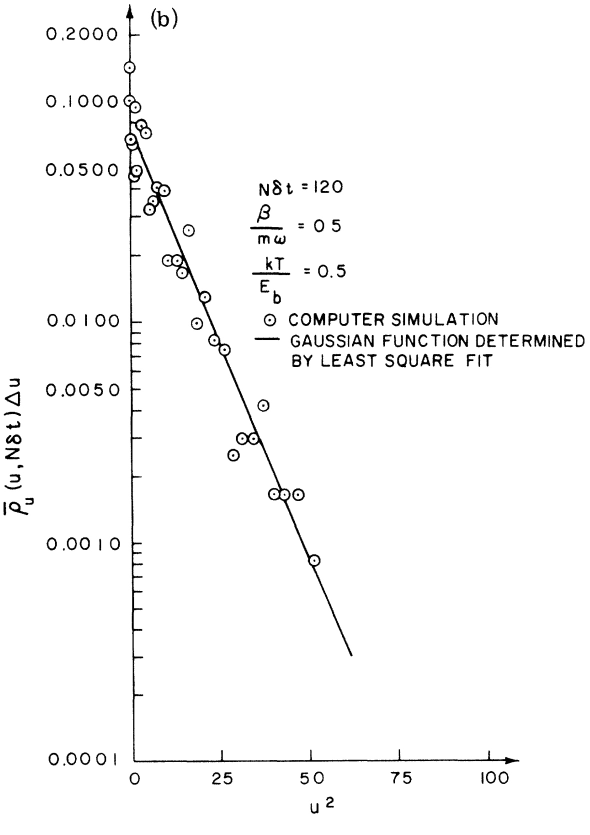
By use of the computer-simulation procedure described above, the diffusion coefficient D_P of a Brownian particle in a periodic potential has been determined for three different values of the friction constant β. The results are shown in Fig. 9. It is seen that only for sufficiently large $\beta(\beta/m\omega \geq 0.5)$ is the diffusion constant D_P as determined by computer simulation equal to the value D_{PR} [Eq. (4.2)] based on uncorrelated jumps. Since it has been previously verified for this range of β that the computer-simulated jump rate agrees with the theoretical value of Eq. (4.1), it appears that the uncorrelated jump assumption is invalid for $\beta/m\omega < 0.5$.

To examine this question further we have employed a measure for persistence of jump direction for the diffusion process used by Bennet and Alder[12] in their computer study of diffusion in a crystal of hard spheres. It is defined as the average $\langle \mu \rangle$ of the cosine of the angle between successive impurity jumps and given by

$$\langle \mu \rangle = \frac{1}{J} \sum_{i=1}^{J} \mu_i , \tag{4.3}$$

where J is the number of jumps and μ_i is the co-





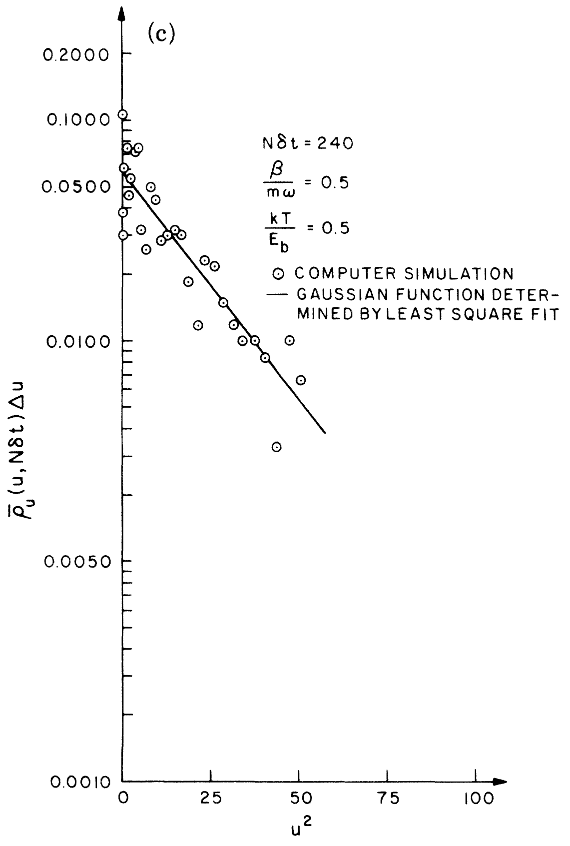


FIG. 6. Computer simulation of Brownian motion of particle in periodic potential $V(x)$ defined in Eq. (2.4). $\bar{\rho}_u(u, N\delta t)\Delta u$ is fraction of computed values of $u(N, r)$ [Eq. (3.10)] found in interval of width Δu centered on u; the results are plotted as a function of u^2. The value $\Delta u = 0.25$ in units in which $b = 1$ was employed. (a) $N\delta t = 40$. (b) $N\delta t = 120$. (c) $N\delta t = 240$.

sine of the angle between the $(i-1)$st and ith jump. For the one-dimensional case, the form of μ_i is simply

$$\mu_i = a_i a_{i-1},$$

where a_i $(i = 1, \ldots, J)$ has a value of $+1$ or -1 if the ith jump was in the positive or negative x direction, respectively. The value of $\langle \mu \rangle$ approaches its limit of $+1$ when there is complete persistence of jump direction.

The value of $\langle \mu \rangle$ was computed as part of the same program used to compute D_p, and the resulting values of $\langle \mu \rangle$ are shown in Fig. 10. It is seen that the dependence of $\langle \mu \rangle$ upon β is similar to the corresponding dependence of D_p. We may therefore conclude that the larger values of the diffusion coefficient D_p which are observed at smaller values of the friction constant β are due to the greater persistence of motion which occurs then, so that the average value of the particle

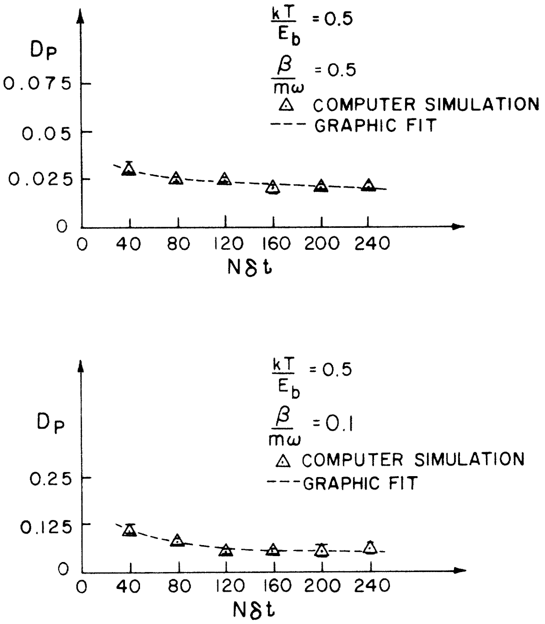


FIG. 7. Diffusion coefficient $D_P(t)$ for particle in periodic potential as determined by computer simulation. The error bars denote the root-mean-square deviation of the computer $D_P(t)$. Units in which $\omega = b = 1$ are employed.

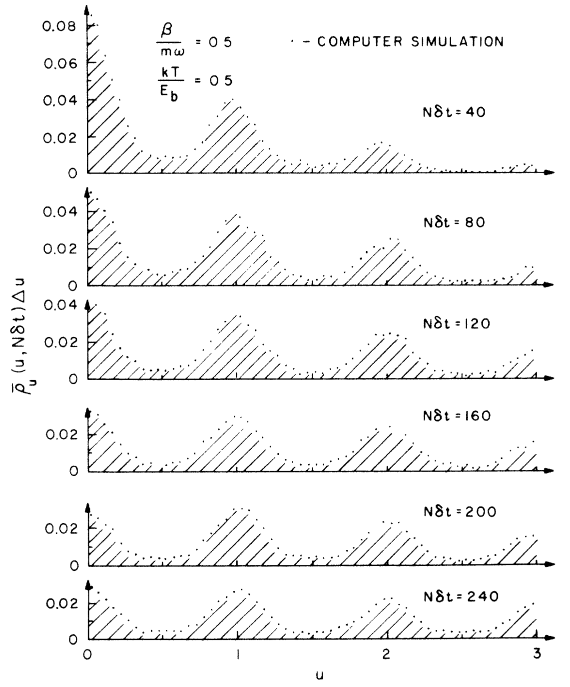


FIG. 8. Distribution function $\bar{\rho}_u(u, N\delta t)$ of particle displacements in periodic potential as determined by computer simulation with sorting restricted to those displacements $u(N, r)$ [Eq. (3.10)] which begin from a potential minimum with a tolerance of 0.025; $\Delta u = 0.05$. Units in which $\omega = b = 1$ are employed.

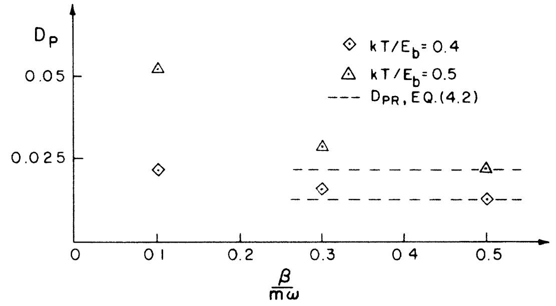


FIG. 9. Diffusion coefficient D_P for particle in periodic potential, determined by computer simulation, for several values of $\beta/m\omega$ as compared with the value of D_{PR} [Eq. (4.2)] which is based on the assumption of uncorrelated jumps.

jump for small β is greater than b, the distance between adjacent wells.

V. CONCLUDING REMARKS

We have presented a computer-simulation study of the classical behavior of a model for interstitial atom diffusion in which the impurity atom is regarded as a Brownian particle constrained to move in a single direction and subject to a periodic potential. As noted in Sec. I, this type of model is at the other extreme from the approach of Vineyard[4] in which the coordinates of all of the atoms, impurity and distant as well as near host atoms, are put on equal footing.

Perhaps the most valuable type of insight to be gained from this type of model is into the behavior of the system after it has surmounted a single energy barrier. In particular, we have seen that if the coupling between the interstitial impurity atom and the rest of the lattice is sufficiently weak, then enhanced values of the diffusion coefficient will arise due to the persistence of motion after one energy barrier has been surpassed.

On the other hand clearly much is lost by fo-

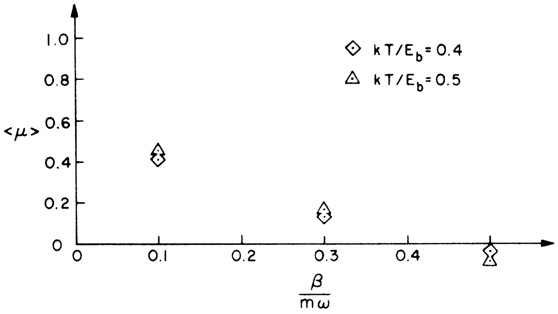


FIG. 10. Persistence of jump direction, as measured by $\langle\mu\rangle$ [Eq. (4.3)].

cusing on only a single degree of freedom. For example, correlation effects due to the interaction of the motion of host atoms and the impurity atom are included in a very natural way in the many-body formulation of Vineyard but are completely absent in the present model with only a single degree of freedom. These correlation effects will be important only for those host atoms in the immediate vicinity of the impurity. This suggests the utility of an intermediate type of model in which the coordinates and momenta of a small number of atoms are treated explicitly in a phase space of low dimensionality, with all the other atoms regarded as an interacting heat bath. Landauer and Swanson[18] have extended the work of Kramers[11] and treated the case of a system of several degrees of freedom interacting with a heat bath and their analysis is therefore relevant in this connection. They address themselves, among other questions, to that of the number of degrees of freedom which it is appropriate to treat explicitly, but like Kramers they are concerned primarily with the double-well potential and the possibility of system return, rather than to the persistence of motion possibility which exists in a periodic potential.

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†Present address: Senior Engineer, Bettis Atomic Power Laboratory, P. O. Box 79, West Mifflin, Pa. 15122. This paper is based on part of a thesis submitted by this author in partial fulfillment of the requirements for the Ph.D. in Engineering at Brown University.

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[5] The classical limit of the frequency factor of the quantum-rate theory derived in Refs. 1–3 appears to be different from the frequency factor of the classical Vineyard theory and some discussion was given in Ref. 1 attempting to explain this difference. However, a reexamination of this question has shown that the difference is only apparent. If it is assumed (in the remainder of this footnote we use the notation and equation numbers of Ref. 1) that the potential $V(x_1, \ldots, x_{3N})$ is piecewise quadratic and continuous across the hyperplane $\mathcal{P}_0$ (and this assumption is necessary for the derivation of Sec. II of Ref. 1 to be valid), then it may be shown that the matrix $C_{\alpha\beta}$ defined in the second of Eqs. (2.13) must also have the form $C_{\alpha\beta} = \lambda^U_{\underline{\alpha}} \delta_{\underline{\alpha}\beta}$ (no sum on α) for $\alpha, \beta \geq 2$. It then follows that

$$R_c^2 = 2kT \prod_{\beta=2}^{3N} \frac{\lambda^U_\beta}{|C|}$$

is equivalent to its form given in Eq. (2.18) and that ω_e as given in Eq. (2.2) agrees, in spite of its very different appearance, with the Vineyard frequency factor as exhibited in Eq. (2.24).

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[15] Cf. Sec. III of J. L. Doob, Ann. Math. 43, 351 (1942). Reprinted in *Selected Papers on Noise and Stochastic Processes*, edited by N. Wax (Dover, New York, 1953), p. 319. Since the completion of this research, the work of E. M. Simon and B. H. Zimm [J. Stat. Phys. 1, 41 (1969)] has come to our attention, in which a similar numerical procedure is used for the solution of the Langevin equation in connection with a model for the unwinding of a DNA molecule.

[16] The computations were performed on the IBM 360-67 of the Brown University Computing Laboratory. For long runs it was found necessary to use double-precision arithmetic to prevent the accumulation of round-off error.

[17] Instead of determining the mean-square deviation $\langle u^2 \rangle$ of the displacements $u(N, r)$ from the fitted Gaussian, this quantity may also be determined, of course, directly from the computed values of $u(N, r)$ themselves. Both procedures were followed for some of the tests and negligible differences in the computed values of $\langle u^2 \rangle$ were found.

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