Nonlinear response theory: Transport coefficients for driving fields of arbitrary magnitude

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A theory of nonlinear response is developed for driving fields of arbitrary magnitude. Exact and usable expressions are provided for electrical and thermal mobility, and related transport coefficients, in terms of correlation functions of the system. A generalization into the nonlinear domain is provided of the Wiedemann-Franz law connecting electrical and thermal response and of the Einstein relation relating the diffusion constant and the mobility. [S1063-651X(97)08511-5]

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I. INTRODUCTION AND THE PRIMARY RESULT

Until the middle of this century, the standard manner of calculating the response of a system to externally imposed fields consisted of attempting the solution of the full dynamical equations of motion, such as the Liouville equation or the Boltzmann equation, incorporating the external field into the system Hamiltonian or evolution matrix. One of the great simplifications introduced by Kubo [1] and others [2–4] lies in the possibility of the description of the effect of external fields in terms of a system's own correlation functions. Thus, if mobility is the property under investigation, one now calculates merely the velocity autocorrelation function of the system, *without* including the field in the Hamiltonian, and expresses the mobility in the linear response limit as the time integral of the autocorrelation function. This simplification, conceptual as well as practical, is unfortunately present only in the *linear* limit, i.e., for cases in which the external field is weak. The purpose of the present paper is to show that such a highly desirable feature can be obtained in nonlinear response theory as well, in a well-defined and practical situation.

The system we first consider is a charged particle of charge q and mass m moving in a one-dimensional space and subjected to a system potential $U(x)$ and an external electric field E. Our result for the nonlinear mobility μ, defined as the ratio of the particle velocity to the field E, is

$$\mu(\epsilon)=\frac{\mu_{\infty}}{\epsilon\int_{0}^{\infty}dy\ e^{-\epsilon y}c(y)}. \tag{1}$$

Here ϵ is the ratio qE/kT of the electric force on the particle to its thermal energy kT and has the dimensions of a reciprocal length, y is the distance coordinate along the electric field, and $c(y)$ is the system correlation function given by an ensemble average (denoted by an overbar)

$$c(y)=\overline{\exp[U(y)/kT]\exp[-U(0)/kT]} \tag{2}$$

over the random potential U. An equivalent expression for the ensemble average is

$$c(y)=\lim_{L\to\infty}(1/L)\int_{0}^{L}dx\ e^{-[U(x)-U(x+y)]/kT}, \tag{3}$$

where L is the spatial extent of the system, taken to be infinite in the limit.

Equation (1) is our primary result. It shows that the mobility at arbitrary strength of the applied field is expressed in terms of a Laplace transform of the system correlation function. The correlation function itself is to be calculated from the system parameters in the absence of the external field, just as in linear-response theory. We will also derive related results, specifically, expressions for the diffusion constant and for thermal transport coefficients. We introduce in Sec. II the Langevin equation for the particle as our starting point and indicate how Eq. (1) may be obtained. Our derivation follows closely along the lines of previous Brownian motion analyses by Risken [5] and is similar to a study of a discrete master equation by Derrida [6]. Our emphasis in the present paper is on the form of the result (1) and on exploiting that form as discussed above. In Sec. III we show a number of consequences of the mobility result for various realizations of the correlation $c(y)$ corresponding to stochastic as well as deterministic systems. In Sec. IV we extend our formalism to include thermal transport coefficients and comment on an interesting generalization of the Wiedemann-Franz law in the nonlinear regime. In Sec. V we analyze the diffusion constant, present a generalization of the Einstein relation connecting the diffusion constant to mobility, and examine the diffusion constant for the examples considered in Sec. III. In Sec. VI we present concluding remarks, including a discussion of applications such as to charge transport in molecularly doped polymers [7,8] and microwave interactions with ceramics [9,10].

II. DERIVATION OF THE NONLINEAR RESPONSE FORMULA FOR THE MOBILITY

Our starting point is the Langevin equation governing the Brownian motion of the charged particle under the simultaneous action of the applied electric field, the force due to a

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spatially varying potential in the system, and the temporally random force $R(t)$, which represents the bath at temperature T,

$$m\frac{d^2x}{dt^2}+m\gamma\frac{dx}{dt}+\frac{dU}{dx}=qE+R(t). \tag{4}$$

Here γ is the damping constant and the random force $R(t)$ is a Gaussian, stationary, δ-correlated stochastic process with zero mean:

$$\langle R(t)\rangle=0,\quad \langle R(t)R(t')\rangle=\Gamma\,\delta(t-t'). \tag{5}$$

The strength of the correlation Γ and the damping constant γ are related via the fluctuation-dissipation theorem

$$\Gamma=2m\gamma kT. \tag{6}$$

If the motion is highly damped to the extent that we can neglect the inertial term md^2x/dt^2, we obtain

$$\frac{dx}{dt}+\frac{1}{m\gamma}\frac{dU}{dx}-\frac{qE}{m\gamma}=\xi(t), \tag{7}$$

with

$$\langle\xi(t)\rangle=0,\quad \langle\xi(t)\xi(t')\rangle=\frac{2kT}{m\gamma}\delta(t-t'). \tag{8}$$

The corresponding Fokker-Planck equation for the probability distribution $P(x,t)$ of the position of the particle, more commonly called the Smoluchowski equation, reads

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial x}\left[\left(\frac{1}{m\gamma}\right)\left(\frac{dU}{dx}-qE\right)P+\left(\frac{kT}{m\gamma}\right)\frac{\partial P}{\partial x}\right]. \tag{9}$$

The average velocity of the particle, given as $\langle v(t)\rangle=\int dx(dx/dt)P(x,t)$, is obtained from Eq. (7):

$$\langle v(t)\rangle=-\frac{1}{m\gamma}\int dx\; P(x,t)\frac{dU(x)}{dx}+\frac{qE}{m\gamma}. \tag{10}$$

In the stationary situation, $P(x,t)$ loses its time dependence and the Smoluchowski equation (9) reduces to

$$0=\frac{d}{dx}\left[\left(\frac{dU}{dx}-qE\right)P+kT\frac{dP}{dx}\right]. \tag{11}$$

For calculational convenience, we will initially consider a finite system of length L with periodic boundary conditions, reserving the limit $L\to\infty$ for systems where it is appropriate. The linear equation (11) can then be solved by evaluating the constants of integration from the normalization condition and the periodicity of $P(x)$:

$$\int_0^L P(x)dx=1,\quad P(x+L)=P(x). \tag{12}$$

Substitution of the solution to Eq. (11) into Eq. (10) gives, for the velocity of the particle,

$$\langle v\rangle=(1-e^{-qEL/kT})\,\frac{kT/m\gamma}{\int_0^L dy\;\exp\left(-\frac{qEy}{kT}\right)C(L,y)}, \tag{13}$$

where the finite-space correlation function $C(L,y)$ is given by

$$C(L,y)=\frac{1}{L}\int_0^L dx\;\exp\left(-\frac{U(x)-U(x+y)}{kT}\right). \tag{14}$$

The mobility is thus given by

$$\mu=\frac{\langle v\rangle}{E}=(1-e^{-qEL/kT})\times\frac{q/m\gamma}{\left(\frac{qE}{kT}\right)\int_0^L dy\;\exp\left(-\frac{qEy}{kT}\right)C(L,y)}. \tag{15}$$

Equating L with the (macroscopic) length of the sample through which the particle moves, we can take formally the limit that L becomes infinitely large and obtain our expression (1), where $c(y)$ in Eq. (2) is given by $\lim_{L\to\infty}C(L,y)$ and $\mu_\infty=q/m\gamma$ is the well-known Drude expression obtained in the absence of a potential U. In the presence of disorder, i.e., when the system potential U is random, the limiting procedure involving $L\to\infty$ is obviously the same as the ensemble average [see the right-hand sides of Eqs. (2) and (3)].

III. CONSEQUENCES OF THE MOBILITY FORMULA

Several general conclusions follow immediately from Eq. (1) with the help of Tauberian theorems. At high electric fields, the mobility saturates to the value μ_∞ since $\lim_{\epsilon\to\infty}\epsilon\int_0^\infty dy\; e^{-\epsilon y}c(y)=\lim_{y\to 0}c(y)=1$. This is clear directly from Eq. (3). The field addition qEx to the potential dominates, in this extreme, over the effects of the random potential $U(x)$ and thus leads to the Drude result with no $U(x)$. Graphically, the tilt produced in the potential by the field overwhelms the relatively small corrugations that the random potential contributes. At low fields, the linear-response limit of the mobility is obtained as $\mu_\infty/c(\infty)$ since $\lim_{\epsilon\to 0}\epsilon\int_0^\infty dy\; e^{-\epsilon y}c(y)=\lim_{y\to\infty}c(y)=c(\infty)$. Typically, the correlation function $c(y)$ rises from the value 1 to a saturation value higher than 1 as y increases. We now consider a simple deterministic example of the potential $U(x)$ as well as several stochastic examples involving dichotomous noise and examine, in their context, consequences of our mobility formula (1).

A. Deterministic example: Sinusoidal potential

If the potential in which the particle moves is sinusoidal with period l, i.e., $U(x)=\Delta\;\cos(2\pi x/l)$, the evaluation of the correlation function (14) is straightforward whenever L is a multiple of l. We expand the exponentials in terms of modified Bessel functions and write

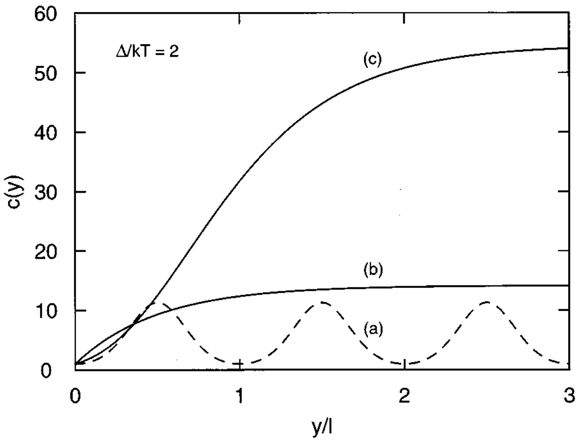

FIG. 1. Correlation function $c(y)$ as a function of the dimensionless position variable y/l for (a) the sinusoidal potential, (b) the dichotomous potential, and (c) the Ornstein-Uhlenbeck potential. For each curve, the amplitude of the potential is adjusted so that $\Delta = 2kT$. See the text for definitions of Δ and l for each potential.

$$C(L,y) = \sum_{m,n} (-1)^m I_m\left(\frac{\Delta}{kT}\right) I_n\left(\frac{\Delta}{kT}\right) \times (1/l)\int_0^l dx\,\cos\frac{2\pi m x}{l}\cos\frac{2\pi n(x+y)}{l}, \tag{16}$$

where the m,n summation is from $-\infty$ to ∞. We expand the trigonometric product, employ standard summation formulas involving cylindrical functions, and obtain the correlation function

$$C(L,y) = I_0\left(\frac{2\Delta}{kT}\sin\frac{\pi y}{l}\right) = C(l,y). \tag{17}$$

This correlation function is plotted in Fig. 1 as a function of the dimensionless parameter y/l for several periods of the potential. In Fig. 2 the corresponding mobility expression

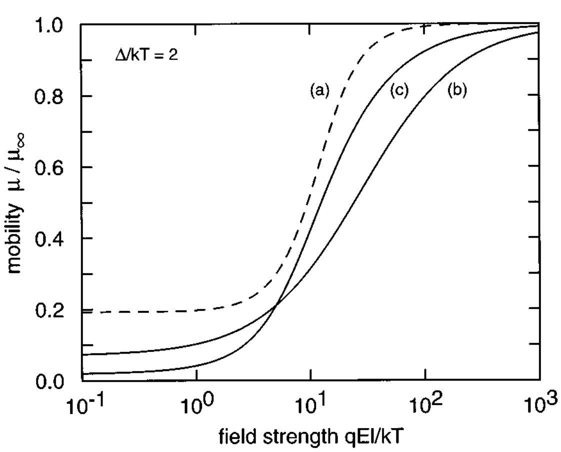

FIG. 2. Mobility, normalized to the infinite-field value, as a function of the dimensionless field strength qEl/kT for (a) the sinusoidal potential, (b) the dichotomous potential, and (c) the Ornstein-Uhlenbeck potential. For each curve, the amplitude of the potential is adjusted so that $\Delta = 2kT$, as in Fig. 1. See the text for definitions of Δ and l for each potential.

$$\mu = (1 - e^{-qEl/kT})\,\frac{kT/m\gamma E}{\int_0^l dy\,\exp(-qEy/kT)\,I_0\left(\frac{2\Delta}{kT}\sin\frac{\pi y}{l}\right)} \tag{18}$$

is plotted as a function of the dimensionless field strength qEl/kT. In both figures we have set the amplitude of the potential such that $\Delta = 2kT$.

B. Stochastic example: Single dichotomous potential

Let us assume that the potential $U(x)$ takes only two values separated by 2Δ, making discontinuous jumps at random points along the one-dimensional space. With U_0 a constant, we have

$$U(x) = U_0 + \eta(x), \quad \eta(x) = \Delta(-1)^{n(x,0)}, \tag{19}$$

where the randomness of the function $\eta(x)$ has been expressed in terms of the random function $n(x_2,x_1)$, which counts the number of jumps the potential makes between the values $U_0+\Delta$ and $U_0-\Delta$ in the interval between $x=x_1$ and $x=x_2$. We assume that the points of jump are distributed randomly and uniformly. It follows that

$$\overline{n(x_2,x_1)} = |x_2 - x_1|/l, \tag{20}$$

where the ''correlation length'' l is the mean distance between jumps. Furthermore, $\overline{\eta(x)} = 0$ and the probability distribution of $n(x,0)$ is Poissonian. Explicitly, denoting $n(x,0)$ by n,

$$p(n) = \exp(-\overline{n})\overline{n}^n/n!. \tag{21}$$

The above-stated properties of $n(x_2,x_1)$ allow a straightforward calculation of the spatial correlation function for the dichotomous potential [11]:

$$K(x_1,x_2) = \overline{\eta(x_1)\,\eta(x_2)} = \Delta^2 \exp(-2|x_1 - x_2|/l). \tag{22}$$

Equation (22) describes the correlation function of the potential $U(x)$. Our interest lies in the correlation function of the *exponential* of the potential. The two-state nature of the potential facilitates the calculation since $[\eta(x)]^{2n} = \Delta^{2n}$ and $[\eta(x)]^{2n+1} = \Delta^{2n}\eta(x)$. We notice that

$$\exp\left(-\frac{U(x)}{kT}\right) = e^{-U_0/kT}\sum_n^{\infty} (-1)^n \frac{1}{n!}\left(\frac{1}{kT}\right)^n [\eta(x)]^n = e^{-U_0/kT}\left\{\cosh(\Delta/kT) - \frac{\eta(x)}{\Delta}\sinh(\Delta/kT)\right\}. \tag{23}$$

It is now straightforward to write the system correlation function

$$c(y) = \overline{\exp\left(-\frac{U(x)}{kT}\right)\exp\left(\frac{U(x+y)}{kT}\right)} = \cosh^2(\Delta/kT) - e^{-2y/l}\sinh^2(\Delta/kT) \tag{24}$$

and the final expression for the mobility

$$\mu = \frac{\mu_\infty}{\cosh^2(\Delta/kT) - \left(1+\frac{2kT}{qEl}\right)^{-1}\sinh^2(\Delta/kT)}. \quad (25)$$

We see that the mobility equals $\mu_\infty/\cosh^2(\Delta/kT)$ for low fields (linear response), rises algebraically from this value for moderate fields, and saturates to μ_∞ for high fields. A plot of the correlation function for the dichotomous potential appears in Fig. 1 as a function of the dimensionless distance y/l for $\Delta = 2kT$. The mobility corresponding to this appears in Fig. 2 as a function of the dimensionless field parameter qEl/kT.

C. Stochastic example: Sum of dichotomous potentials

Generalization of the above case to a potential with many differing Δ's and l's can be carried out as follows. The total potential is now a finite sum of N independent dichotomous potentials

$$U(x) = \eta_1(x) + \eta_2(x) + \cdots + \eta_N(x), \quad (26)$$

where the $\eta_i(x)$ obey

$$\langle \eta_i(x)\rangle = 0, \quad \langle \eta_i(x_1)\eta_j(x_2)\rangle = \delta_{ij}\Delta_i^2 \exp\left(-2\frac{|x_1-x_2|}{l_i}\right). \quad (27)$$

We can use, as previously, the fact that for a single system

$$\eta_i^{2n}(x) = \Delta_i^{2n}, \quad \eta_i^{2n+1}(x) = \Delta_i^{2n}\eta_i(x) \quad (28)$$

and obtain

$$e^{-U(x)/kT} = e^{-U_0/kT}\prod_{i=1}^{N}\exp\left(-\frac{\eta_i(x)}{kT}\right) = e^{-U_0/kT}\prod_{i=1}^{N}\left(\cosh\delta_i - \frac{\eta_i(x)}{\delta_i}\sinh\delta_i\right), \quad (29)$$

with $\delta_i = \Delta_i/kT$. Furthermore,

$$e^{-U(x)/kT}e^{U(x+y)/kT} = \prod_{i=1}^{N}\left\{\cosh^2\delta_i - \eta_i(x)\eta_i(x+y)\frac{1}{\delta_i^2}\sinh^2\delta_i + \frac{1}{\delta_i}\sinh\delta_i\cosh\delta_i(\eta_i(x+y)-\eta_i(x))\right\}. \quad (30)$$

Since the η_i are independent with zero mean, we obtain the correlation function as given by

$$c(y) = \langle e^{-U(x)/kT}e^{U(x+y)/kT}\rangle = \prod_{i=1}^{N}\left[1+(1-e^{-2y/l_i})\sinh^2\left(\frac{\Delta_i}{kT}\right)\right]. \quad (31)$$

The field dependence of the mobility is given as

$$\mu = \mu_\infty\left[\prod_{j=1}^{N}\cosh^2\left(\frac{\Delta_j}{kT}\right)\right]^{-1}\left(1+\sum_{k=1}^{N}(-1)^k \times \sum_{i_1<i_2<\cdots<i_k}\frac{\prod_{n=1}^{k}\tanh^2\left(\frac{\Delta_{i_n}}{kT}\right)}{1+(2kT/qE)\sum_{n=1}^{k}1/l_{i_n}}\right)^{-1}. \quad (32)$$

It is clear that Eq. (32) reduces to Eq. (25) for $N=1$. If we consider the sum of many dichotomous potentials all with the same Δ_i (each equal to $\Delta/\sqrt{N}$) and the same l_i (each equal to l), we get, in the limit $N\to\infty$, an Ornstein-Uhlenbeck process. The expression for the correlation function $c(y)$ for finite N is

$$c(y) = \left[\cosh^2\left(\frac{\Delta}{kT\sqrt{N}}\right) - e^{-2y/l}\sinh^2\left(\frac{\Delta}{kT\sqrt{N}}\right)\right]^N. \quad (33)$$

In the limit $N\to\infty$ we obtain the result for the Ornstein-Uhlenbeck potential

$$c(y) = \exp[(\Delta/kT)^2(1-e^{-2y/l})]. \quad (34)$$

This form (34) for the correlation function may also be obtained directly from the fact that the Ornstein-Uhlenbeck process is Gaussian.

Performing the Laplace transform of Eq. (34), we obtain the mobility expression

$$\mu = \mu_\infty\frac{2kT/qEl}{(\Delta/kT)^{-(qEl/kT)}e^{(\Delta/kT)^2}\gamma(qEl/2kT,(\Delta/kT)^2)}, \quad (35)$$

where $\gamma(\alpha,x)$ is the incomplete gamma function [not to be confused with the damping constant γ in Eq. (4)]

$$\gamma(\alpha,x) = \int_0^x e^{-t}t^{\alpha-1}dt. \quad (36)$$

Equation (35) can also be expressed simply in terms of ${}_1F_1$, the confluent hypergeometric function [14]:

$$\mu = \frac{\mu_\infty}{{}_1F_1(1,1+(qEl/2kT),(\Delta/kT)^2)}.$$

A plot of the correlation function for the Ornstein-Uhlenbeck potential appears in Fig. 1 as a function of the dimensionless distance y/l for $\Delta = 2kT$. The mobility corresponding to this appears in Fig. 2 as a function of the dimensionless field parameter qEl/kT. Intermediate results corresponding to a continuous manifold of possible correlation lengths l lead to interesting consequences, which will be reported elsewhere [12].

IV. EXTENSION OF THE FORMALISM FOR THERMAL RESPONSE

It is straightforward to extend this formalism of nonlinear response to treat thermal stimuli. Let us consider the case of a constant applied thermal gradient T', the response under investigation being the thermal current. Equation (9) is now

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial x}\left[\left(\frac{1}{m\gamma}\right)\left(\frac{dU}{dx}\right)P+\frac{k}{m\gamma}(T_0+xT')\,\frac{\partial P}{\partial x}\right], \quad (37)$$

where T_0 is the temperature at one end of the sample. We rewrite this as

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial x}\left[\left(\frac{1}{m\gamma}\right)\left(\frac{dU}{dx}+kT'\right)P\right]+\left(\frac{kT}{m\gamma}\right)\,\frac{\partial^2 P}{\partial x^2}, \quad (38)$$

T being the temperature T_0+xT', and compare it to the alternative form

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial x}\left[\left(\frac{1}{m\gamma}\right)\left(\frac{dU}{dx}-qE\right)P\right]+\left(\frac{kT}{m\gamma}\right)\,\frac{\partial^2 P}{\partial x^2} \quad (39)$$

of Eq. (9). We see that Eq. (38) differs from Eq. (39) only in the substitution of the electric force qE by the ''thermal force'' $-kT'$. If we consider the sample length to be taken small enough to ensure that the variation of T is negligible, we can immediately write an expression for the thermal mobility μ_{th} defined as the ratio of the velocity of the carrier carrying the thermal current to the temperature gradient T':

$$\mu_{th}(\tau)=\frac{k/\gamma m}{\tau\int_0^\infty dy\ e^{-\tau y}c(y)}. \quad (40)$$

As expected, the expression (40) for the thermal mobility is nearly identical to the expression (1) for the electrical mobility. The differences are the appearance of the Boltzmann constant k in place of the carrier charge q and the replacement of $\epsilon=qE/kT$ by $\tau=T'/T$ as the Laplace variable in the transform expressions.

Being valid in the nonlinear domain, our theory allows an interesting generalization of the well-known Wiedemann-Franz law valid for electric fields and temperature gradients of arbitrary magnitude. The Wiedemann-Franz law states [13] that the ratio of the thermal conductivity $\kappa=nkT\mu_{th}$ to the product of the temperature T and the electrical conductivity $\sigma=nq\mu$ is a universal constant (known as the Lorenz ratio) provided that the electric current and the thermal current are carried by the same particles. That law is normally stated only in the limit of a linear response. Our theory allows us to extend it to the entire nonlinear domain. We see that it is obeyed not only for small fields and gradients since $(1/T)(\lim_{\tau\to 0}\kappa/\lim_{\epsilon\to 0}\sigma)$ equals a universal constant $(k/q)^2$, but also at very high fields and gradients since $(1/T)(\lim_{\tau\to\infty}\kappa/\lim_{\epsilon\to\infty}\sigma)$ also equals $(k/q)^2$. The law, in the form known in linear-response theory, is, however, not obeyed at intermediate values of fields and gradients. Generally, the Lorenz ratio is found to be

$$\frac{\kappa}{\sigma T}=\left(\frac{qE}{kT'}\right)\,\frac{\tilde{c}(T'/T)}{\tilde{c}(qE/kT)}L_0, \quad (41)$$

where by L_0 we mean the linear-response Lorenz ratio $(k/q)^2$. The multiplicative correction factor that our theory produces for nonlinear response involves the Laplace transform of the correlation function $c(y)$ at two different values of the Laplace variable: T'/T and qE/kT. A powerful scaling statement can be made, in addition, for a nonlinear response: The thermal mobility for arbitrary values of temperature gradient plotted as a function of T'/T and the electrical mobility for arbitrary values of electric field plotted as a function of qE/kT are identical to each other except for a multiplicative factor that is a universal constant k/q.

In the general case in which thermal and electrical stimuli are simultaneously present, the Fokker-Planck equation takes the form

$$\frac{\partial P}{\partial t}=\frac{\partial}{\partial x}\left[\left(\frac{1}{m\gamma}\right)\left(\frac{dU}{dx}-qE+kT'\right)P\right]+\left(\frac{kT}{m\gamma}\right)\,\frac{\partial^2 P}{\partial x^2}. \quad (42)$$

The counterpart of Eq. (13) for this case in the limit $L\to\infty$ is then

$$\langle v\rangle=\frac{kT/m\gamma}{\int_0^\infty dy\ \exp\left[-y\left(\frac{qE}{kT}-\frac{T'}{T}\right)\right]c(y)}, \quad (43)$$

which results in the well-known general transport relations connecting electrical and thermal transport (see, e.g., Ref. [13]):

$$j_{el}=q^2K_0E-\frac{q}{T}K_1T', \quad (44)$$

$$j_{th}=qK_1E-\frac{1}{T}K_2T', \quad (45)$$

where the K's are given by

$$K_0=\frac{n_0}{m\gamma\varphi\tilde{c}(\varphi)},\quad K_1=\frac{n_0kT}{m\gamma\varphi\tilde{c}(\varphi)},\quad K_2=\frac{n_0(kT)^2}{m\gamma\varphi\tilde{c}(\varphi)}. \quad (46)$$

Here the Laplace variable is $\varphi=qE/kT-T'/T$. In Eqs. (44) and (45) we have fully nonlinear expressions for the electric and thermal currents. However, simple proportionality relations exist between the nonlinear transport coefficients K_0, K_1, and K_2. In the so-called Seebeck effect, open current circuit conditions are maintained ($j_{el}=0$), which means that φ vanishes. The K's then have their linear limiting values and the thermoelectric power, the ratio of the electric field to the temperature gradient, is simply k/q. In the Peltier effect, the temperature gradient is maintained zero. The K's do not have their linear limiting values, but the ratio of the thermal current to the electric current, known as the Peltier coefficient, is kT/q and thus the Kelvin relation of thermoelectricity [13], viz., that the Peltier coefficient equals the absolute temperature times the thermoelectric power, holds in this nonlinear domain we treat. We have given here a simple classical analysis that does not introduce factors such as $\pi^2/3$ that arise from a treatment that includes Fermi-Dirac statistics for the carriers.

V. DERIVATION OF THE NONLINEAR RESPONSE FORMULA FOR THE DIFFUSION CONSTANT

In Sec. II the Fokker-Planck equation for the probability distribution $P(x,t)$ was obtained and used to determine the velocity and mobility of a particle moving in response to a driving force of arbitrary magnitude. In this section we are interested in obtaining an expression for the diffusion constant that is valid under the same conditions. To this end, we adapt a calculation given by Derrida [6] for a discrete chain of hopping sites to that of a particle moving in a continuous random potential.

Thus we now consider our system potential $U(x)$, originally defined on a section of length L, to be periodically repeated throughout all space. The result of this construction is an infinite sample with a periodic system potential $U(x) = U(x+L)$, but a constant driving force qE of arbitrary magnitude. The probability density $P(x,t)$ for the system is now normalized over the entire real line, but still obeys the Fokker-Planck equation (9), which we can write compactly in the form $\partial P/\partial t = \mathcal{L}_x P$, thereby implicitly defining the differential operator $\mathcal{L}_x$.

For this system it is then possible to express the particle's velocity

$$\frac{d}{dt}\langle x(t)\rangle = \frac{d}{dt}\int_{-\infty}^{\infty} xP(x,t)dx \tag{47}$$

$$= \frac{d}{dt}\int_0^L \sum_{k=-\infty}^{\infty}(x+kL)P(x+kL,t)dx = \int_0^L \frac{\partial\sigma}{\partial t}dx \tag{48}$$

in terms of a spatially periodic function

$$\sigma(x,t) = \sum_{k=-\infty}^{\infty}(x+kL)P(x+kL,t) \tag{49}$$

of period L. Note that at long times, Eq. (47) must approach the steady-state drift velocity $\langle v\rangle$, implying that

$$\sigma(x,t) \to \rho_0(x)\langle v\rangle t + \tau(x), \tag{50}$$

where $\rho_0(x)$ and $\tau(x)$ are time-independent but spatially periodic functions, with the integral of ρ_0 over one period being equal to unity. By writing an equation similar to Eq. (47) for $\langle x^2(t)\rangle$, using the Fokker-Planck equation (9), integrating it by parts, and performing a manipulation similar to that in Eq. (48), it is straightforward to relate $\sigma(x,t)$ to the time rate of change of the second moment as well. We find that

$$\frac{d}{dt}\langle x^2(t)\rangle = \frac{2}{\beta m\gamma} - \frac{2}{\beta m\gamma}\int_0^L \beta(U' - qE)\sigma(x,t)dx, \tag{51}$$

where the prime denotes differentiation with respect to x.

Combining Eqs. (47)–(51), the diffusion constant D is then simply expressible in terms of the periodic function $\tau(x)$ introduced in Eq. (50):

$$D = \lim_{t\to\infty}\frac{1}{2}\frac{d}{dt}[\langle x^2(t)\rangle - \langle x(t)\rangle^2] \tag{52}$$

$$= \frac{1}{\beta m\gamma}\left[1 - \int_0^L \beta(U' - qE)\tau\, dx - \beta m\gamma\langle v\rangle\int_0^L \tau\, dx\right]. \tag{53}$$

To determine the function $\tau(x)$, we first take the time derivative of Eq. (49), and use Eq. (9) to obtain

$$\frac{d\sigma}{dt} = \mathcal{L}_x\sigma - \frac{1}{\beta m\gamma}\left[\beta(U' - qE)\rho(x,t) + 2\frac{\partial\rho(x,t)}{\partial x}\right], \tag{54}$$

where $\rho(x,t) = \Sigma_{k=-\infty}^{\infty}P(x+kL,t)$ is another spatially periodic function whose integral over one period is equal to unity and whose equation of motion is easily shown to be the same Fokker-Planck equation as $P(x,t)$. In fact, for equivalent initial conditions, the periodic function $\rho(x,t)$ and the periodic probability density $P(x,t)$ of Sec. II must be identical insofar as they obey the same normalization and the same equations of motion. Thus, at long times, $\rho(x,t)$ approaches a stationary limit which just turns out to be the function $\rho_0(x)$ introduced in Eq. (50). To see this, substitute Eq. (50) into Eq. (54) and equate powers of t, obtaining two independent relations. The first relation confirms that ρ_0 obeys the same stationarity condition $\partial\rho_0/\partial t = \mathcal{L}_x\rho_0 = 0$ as the function $\rho(x,t)$ at long times. This latter equation is equivalent to the steady-state continuity equation for the constant current density

$$j = \frac{\langle v\rangle}{L} = -\frac{1}{\beta m\gamma}\left[\beta(U' - qE)\rho_0(x,t) + \frac{\partial\rho_0(x,t)}{\partial x}\right]. \tag{55}$$

The second relation stemming from the aforementioned procedure yields the differential equation

$$\mathcal{L}_x\tau = \frac{1}{\beta m\gamma}[\beta(U' - qE)\rho_0 + 2\rho_0'] + \langle v\rangle\rho_0 \equiv \psi' \tag{56}$$

obeyed by the function $\tau(x)$. In Eq. (56) we have expressed the right-hand side as the derivative of a new periodic function $\psi(x)$. Using Eq. (55) to integrate Eq. (56) and invoking the periodicity of ψ and ρ_0, we find that

$$\psi(x) = \frac{\rho_0(x)}{\beta m\gamma} + \frac{\langle v\rangle}{L}\int_0^L dy\; y\rho_0(x+y) + \lambda, \tag{57}$$

where λ is independent of x. With $\psi(x)$ determined, Eq. (56) gives an inhomogeneous equation for $\tau(x)$, the periodic solution to which is

$$\tau(x) = \frac{-\beta m\gamma}{1 - e^{-\beta qEL}}\int_0^L e^{-\beta qEy}\psi(x+y)e^{-\beta[U(x)-U(x+y)]}dy. \tag{58}$$

Moreover, from Eq. (56) we find that $\beta(U'-qE)\tau=\beta m\gamma\psi-\tau'$, which allows Eq. (53) to be written as

$$D=\frac{1}{\beta m\gamma}\left[1-\beta m\gamma\int_0^L\psi(x)dx-\beta m\gamma\langle v\rangle\int_0^L\tau(x)dx\right]. \tag{59}$$

Using Eq. (58), the last integral of Eq. (59) can be rewritten in the form

$$\int_0^L\tau dx=-\frac{\beta m\gamma}{1-e^{-\beta qEL}}\int_0^L dx\int_0^L dy\ e^{-\beta qEy}\psi(x+y)\times e^{-\beta[U(x)-U(x+y)]}=-\frac{\beta m\gamma}{1-e^{-\beta qEL}}\int_0^L dx\ \mu(x)\psi(x). \tag{60}$$

Here we have introduced the periodic function

$$\mu(x)=\int_0^L dy\ e^{-\beta qEy}e^{-\beta[U(x-y)-U(x)]}, \tag{61}$$

whose integral

$$\int_0^L\mu(x)dx=\frac{L}{\beta m\gamma\langle v\rangle}[1-e^{-\beta qEL}] \tag{62}$$

follows from Eqs. (61) and (13). To obtain Eq. (60) we have broken the original integral over x up into two parts, one from 0 to $L-y$ and the other from $L-y$ to L; changed variables (to $z=x+y$ in the first, $z=x+y-L$ in the second); used periodicity; and recombined the resulting integrals.

With Eqs. (57), (60), (61), and (62), Eq. (59) finally reduces to a relatively simple expression of the form

$$D=D_0-\Delta D, \tag{63}$$

where

$$D_0=\frac{\langle v\rangle}{(1-e^{-\beta qEL})}\int_0^L\mu(x)\rho_0(x)dx \tag{64}$$

and

$$\Delta D=\frac{\langle v\rangle L}{2}-\frac{\beta m\gamma\langle v\rangle^2}{1-e^{-\beta qEL}}\frac{1}{L}\int_0^L dx\int_0^L dy\ \mu(x)\rho_0(x+y)y. \tag{65}$$

These expressions require the definition of $\mu(x)$ from Eq. (61) and the stationary probability density

$$\rho_0(x)=\frac{\beta m\gamma}{1-e^{-\beta qEL}}\frac{\langle v\rangle}{L}\int_0^L e^{-\beta[U(z)-U(z+x)]}dz, \tag{66}$$

which follows from a straightforward integration of the continuity equation $\partial\rho_0/\partial t=\mathcal{L}_x\rho_0=\partial j/\partial x=0$, with $j=\langle v\rangle/L$. Equations (63)–(65) can be used to obtain the diffusion constant for an arbitrary periodic potential $U(x)$. In the limit of an infinitely long sample, these expressions simplify and can be expressed in terms of correlation functions similar to those that appear in the mobility. To see this, we substitute Eqs. (66) and (61) into Eqs. (64) and (65) and take the limit $L\to\infty$. For D_0, this leads to the relation

$$D_0=\langle v\rangle\int_0^\infty\mu(x)\rho_0(x)dx=\beta m\gamma\langle v\rangle^2\int_0^\infty dz\int_0^\infty dz'\,e^{-\beta qE(z+z')}c(z+z'), \tag{67}$$

where $c(y)=\lim_{L\to\infty}C(L,y)$ is the same function that appears in the mobility [see Eq. (1)]. Since the integrand of Eq. (67) depends only on the combination $z+z'$, we can change variables on the double integral to $y=z+z'$ and $x=(z-z')/2$, with y going from 0 to ∞ and x ranging from $-y$ to $+y$. After performing the x integration, we obtain

$$D_0=\beta m\gamma\langle v\rangle^2\int_0^\infty dy\ e^{-\beta qEy}yc(y)=-\frac{\langle v\rangle^2}{\beta q}\frac{\partial}{\partial E}\left[\beta m\gamma\int_0^\infty dy\ e^{-\beta qEy}c(y)\right], \tag{68}$$

where the term in square brackets can be identified from Eq. (13) as the corresponding $L\to\infty$ limit of $1/\langle v\rangle$. Thus we find that, in this limit, we can write

$$D_0=\frac{1}{\beta q}\frac{\partial\langle v\rangle}{\partial E}. \tag{69}$$

Equation (69) constitutes a generalization of the standard Einstein relation $D=\langle v\rangle/\beta qE$ appropriate to linear-response theory.

Before inserting Eqs. (66) and (61) into Eq. (65) to obtain a similar expression for ΔD, it is convenient to first rewrite that expression using an identity

$$\int_0^L dz\int_0^L dx\int_0^L dy\ y\rho_0(x+y)\mu(z)=\frac{L}{2}\frac{L^2}{\beta m\gamma\langle v\rangle}[1-e^{-\beta qEL}] \tag{70}$$

that follows from Eq. (62). A little manipulation allows us to use this relation to combine the two terms on the right-hand side of Eq. (65) into the form

$$\Delta D=\frac{\beta m\gamma\langle v\rangle^2}{1-e^{-\beta qEL}}\frac{1}{L^2}\int_0^L dz\int_0^L dx\int_0^L dy\ y\ \rho_0(x+y)\times[\mu(z)-\mu(x)]. \tag{71}$$

Substituting Eqs. (61) and (66) into this last expression and taking $L\to\infty$, we obtain

$$\Delta D=(\beta m\gamma)^2\langle v\rangle^3\int_0^\infty dw\int_0^\infty dz\ e^{-\beta qEw}e^{-\beta qEz}G(w,z), \tag{72}$$

where

$$G(w,z)=\lim_{L\to\infty}\frac{1}{L}\int_0^L dy\ y[c(w)c(z)-c_4(z,w,y)], \tag{73}$$

in which $c(y)$ is given by Eq. (2) and the four-point correlation function $c_4(z,w,y)$ is defined through the relation

$$c_4(z,w,y)=\lim_{L\to\infty}\frac{1}{L}\int_0^L dx e^{\beta[U(x+y+w)-U(x+y)+U(x)-U(x-z)]}$$
$$=\overline{e^{\beta[U(y+w)-U(y)+U(0)-U(-z)]}}. \tag{74}$$

Just as the electrical mobility, the thermal mobility, and the cross-transport coefficients K can be found respectively from Eqs. (15), (40), and (46) in terms of the correlation $c(y)$ given in Eq. (2), the diffusion constant can now be calculated explictly through Eqs. (63), (69), and (72) in terms of the correlation functions $c(y)$ and $c_4(y)$ in Eq. (74). We now apply these expressions to study the diffusion constant for the deterministic sinusoidal potential and the stochastic models treated in Sec. III. In each of these systems we can take $L\to\infty$ but keep the period l, in the case of the sinusoidal potential, and the correlation length, in the case of a stochastic potential, finite. In this limit the contribution to the diffusion constant arising from D_0 is given by Eq. (69) and reduces at low fields to the standard Einstein relation. In what follows we consider deviations from this generalized Einstein relation as represented by Eqs. (72) and (73).

For the sinusoidal potential of Sec. III A, it is possible to break the integral in Eq. (73) into intervals of length equal to the period l of the potential, change variables in each to a single fundamental period, and show that, for this case,

$$G(w,z)=\frac{1}{l}\int_0^l dy\ y[C(w)C(z)-C_4(z,w,y)]$$

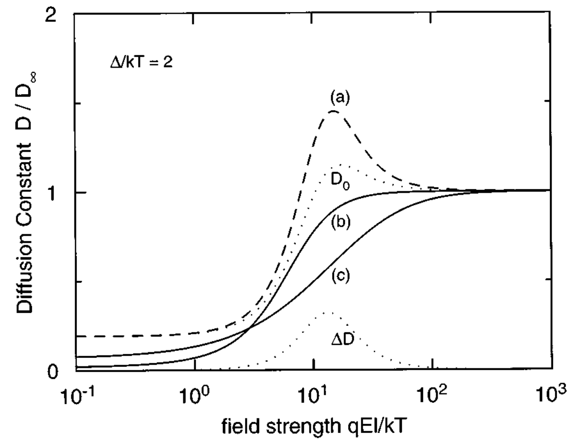

FIG. 3. Diffusion constant, normalized to the infinite-field value, as a function of the dimensionless field strength qEl/kT for (a) the sinusoidal potential, (b) the dichotomous potential, and (c) the Ornstein-Uhlenbeck potential. For each curve, the amplitude of the potential is adjusted so that $\Delta=2kT$, as in Fig. 1. See the text for definitions of Δ and l for each potential. The two contributions D_0 and ΔD to the diffusion constant for the sinusoidal potential are included as dotted lines.

$$=\frac{l}{2}[C(w)C(z)-I(z,w)], \tag{75}$$

where $C(y)=I_0(2\delta\sin\pi y/l)$ and

$$I(z,w)=\frac{2}{l^2}\int_0^l y\ C_4(z,w,y)dy$$
$$=\frac{2}{(2\pi)^2}\int_0^{2\pi}\hat{y}\ C_4(z,w,y)d\hat{y}. \tag{76}$$

In this last expression we have introduced the reduced notation $\hat{y}=2\pi y/l$, with similar definitions for the quantities $\hat{x}$, $\hat{w}$, and $\hat{z}$, to appear below. Also, in Eq. (76), $C_4(y)$ is the finite length $(L=l)$ version of the correlation function (74). With $\delta=\Delta/kT$ we have

$$C_4(z,w,y)=\frac{1}{2\pi}\int_0^{2\pi}d\hat{x}\ e^{\delta\cos(\hat{x}+\hat{y}+\hat{w})}e^{-\delta\cos(\hat{x}+\hat{y})}e^{\delta\cos(\hat{x})}e^{\delta\cos(\hat{x}-\hat{z})}$$
$$=\frac{1}{2\pi}\int_0^{2\pi}d\hat{x}\ e^{-2\delta\sin(\hat{w}/2)\sin(\hat{x}+\hat{y}+\hat{w}/2)}e^{-2\delta\sin(\hat{z}/2)\sin(\hat{x}-\hat{z}/2)}$$
$$=\frac{1}{2\pi}\int_0^{2\pi}d\hat{x}\ e^{-2\delta\sin(\hat{w}/2)\cos(\hat{x}+\hat{y}+\hat{w}/2)}e^{-2\delta\sin(\hat{z}/2)\cos(\hat{x}-\hat{z}/2)}$$
$$=\sum_{n,m}(-1)^{n-m}I_n(2\delta\sin\hat{w}/2)I_m(2\delta\sin\hat{z}/2)\frac{1}{2\pi}\int_0^{2\pi}d\hat{x}\ h(\hat{x}), \tag{77}$$

where the m,n sums are between $\pm\infty$ and $h(\hat{x})=\exp\{i[n(\hat{x}+\hat{y}+\hat{w}/2)-m(\hat{x}-\hat{z}/2)]\}$. The last integral

$$\frac{1}{2\pi}\int_0^{2\pi}d\hat{x}\ h(\hat{x})=\delta_{m,n}e^{in[\hat{y}+(\hat{w}+\hat{z})/2]} \tag{78}$$

is easily evaluated, giving

$$C_4(z,w,y)=\sum_n C_n(\hat{w})C_n(\hat{z})e^{in[\hat{y}+(\hat{w}+\hat{z})/2]}, \tag{79}$$

where $C_n(\hat{w})\equiv I_n(2\delta\sin\hat{w}/2)$. With Eq. (79), we can perform the integral in Eq. (76) to obtain

$$I(z,w)=\sum_{n=-\infty}^{\infty}\frac{C_n(\hat{w})C_n(\hat{z})}{2\pi^2}\exp\{in[(\hat{w}+\hat{z})/2]\}\int_0^{2\pi}\hat{y}e^{in\hat{y}}d\hat{y} \tag{80}$$

$$=C_0(\hat{w})C_0(\hat{z})+\frac{2}{\pi}\sum_{n=1}^{\infty}n^{-1}C_n(\hat{w})C_n(\hat{z})\sin[n(\hat{w}+\hat{z})/2], \tag{81}$$

where we have expanded the exponential into its real and imaginary parts and noted that the imaginary parts for positive and negative $n>0$ cancel. Thus we find that

$$G(w,z)=\frac{l}{2}[C_0(w)C_0(z)-I(z,w)]$$
$$=-\frac{l}{\pi}\sum_{n=1}^{\infty}n^{-1}C_n(\hat{w})C_n(\hat{z})\sin[n(\hat{w}+\hat{z})/2]. \tag{82}$$

This allows us to write

$$\Delta D=(\beta m\gamma)^2\langle v\rangle^3\int_0^{\infty}dw\int_0^{\infty}dz\ e^{-\beta qEw}e^{-\beta qEz}G(w,z)$$
$$=-\frac{(\beta m\gamma)^2\langle v\rangle^3 l}{\pi}\sum_{n=1}^{\infty}n^{-1}\int_0^{\infty}dw\int_0^{\infty}dz\ e^{-\beta qEw}e^{-\beta qEz}C_n(\hat{w})C_n(\hat{z})\sin[n(\hat{w}+\hat{z})/2]. \tag{83}$$

Breaking the trigonometric function up, the resulting double integral factors to give

$$\Delta D=-\frac{2(\beta m\gamma)^2\langle v\rangle^3 l^3}{\pi}\sum_{n=1}^{\infty}n^{-1}A_nB_n, \tag{84}$$

where

$$A_n=\frac{1}{l}\int_0^{\infty}dwe^{-\beta qEw}C_n(\hat{w})\cos[n\hat{w}/2]$$
$$=\frac{1}{1-e^{-2\beta qEl}}\frac{1}{\pi}\int_0^{2\pi}d\theta\ e^{-\beta qEl\theta/\pi}I_n\left(\frac{2\Delta}{kT}\sin\theta\right)\cos(n\theta) \tag{85}$$

and

$$B_n=\frac{1}{l}\int_0^{\infty}dwe^{-\beta qEw}C_n(\hat{w})\sin[n\hat{w}/2]$$
$$=\frac{1}{1-e^{-2\beta qEl}}\frac{1}{\pi}\int_0^{2\pi}d\theta\ e^{-\beta qEl\theta/\pi}I_n\left(\frac{2\Delta}{kT}\sin\theta\right)\sin(n\theta). \tag{86}$$

Thus, for the sinusoidal potential the diffusion constant deviates from the generalized Einstein relation (69) by a nonzero amount that may be evaluated as a function of the field using Eqs. (84)–(86). In Fig. 3, D_0, $|\Delta D|$, and $D=D_0-\Delta D$ are plotted as functions of the dimensionless field strength qEl/kT for the sinusoidal potential with $\Delta=2kT$.

For the stochastic models investigated in Sec. III, by contrast, we find that ΔD vanishes identically, so that the total diffusion constant D as a function of the applied field obeys the generalized Einstein relation (69). To see this, we first observe that the n-point correlation function for a single dichotomous potential has the property that

$$K_m(x_1,\ldots,x_{m-2},x_{m-1},x_m)=\overline{\eta(x_1)\cdots\eta(x_{m-2})\,\eta(x_{m-1})\,\eta(x_m)}=K_{m-2}(x_1,\ldots,x_{m-2})K(x_{m-1},x_m), \tag{87}$$

whenever $x_1<\cdots<x_{m-2}<x_{m-1}<x_m$. In particular, all odd correlation functions vanish and all even ones factorize into products of two-point correlation functions. Indeed, we have

$$K_m(x_1,\ldots,x_{m-2},x_{m-1},x_m)=\Delta^m\sum_{n_1,\ldots,n_m}(-1)^{n_1+\cdots+n_m}p(n_1,\ldots,n_m), \tag{88}$$

where $p(n_1,\ldots,n_m)$ is the joint probability distribution of having n_i jumps between 0 and x_i, $i=1,\ldots,m$. Obviously,

$$p(n_1,\ldots,n_m)=p(n_1,\ldots,n_{m-1}|n_m)p(n_m), \tag{89}$$

where $p(n_1,\ldots,n_{m-1}|n_m)$ is the conditional probability. But from the independence of the individual jumps, we can write

$$p(n_1,\ldots,n_{m-1}|n_m)=p(n_1,\ldots,n_{m-2})p(n_{m-1}|n_m), \tag{90}$$

$$p(n_{m-1}|n_m)=p(n_m-n_{m-1}). \tag{91}$$

Hence

$$\begin{aligned}K_m(x_1,\ldots,x_{m-2},x_{m-1},x_m)&=\Delta^{m-2}\sum_{n_1,\ldots,n_{m-2}}(-1)^{n_1+\cdots+n_{m-2}}p(n_1,\ldots,n_{m-2})\Delta^2\\&\quad\times\sum_{n_{m-1},n_m}(-1)^{n_{m-1}+n_m}p(n_m-n_{m-1})p(n_m)\\&=K_{m-2}(x_1,\ldots,x_{m-2})\Delta^2\sum_{n,n_m}(-1)^n p(n)p(n_m)=K_{m-2}(x_1,\ldots,x_{m-2})K(x_{m-1},x_m),\end{aligned} \tag{92}$$

where we have introduced the simplified notation $n=n_m-n_{m-1}$ and used Eq. (22).

From the definition (74) and (23) we have, for a single dichotomous potential,

$$\begin{aligned}c_4(z,w,y)&=\cosh^4(\Delta/kT)+e^{-2w/l}e^{-2z/l}\sinh^4(\Delta/kT)\\&\quad+(e^{-2(y+w)/l}-e^{-2(y+w+z)/l}-e^{-2y/l}\\&\quad+e^{-2(y+z)/l})\cosh^2(\Delta/kT)\sinh^2(\Delta/kT)\\&=c(w)c(z)+e^{-2y/l}(e^{-2w/l}-e^{-2(w+z)/l}-1\\&\quad+e^{-2z/l})\cosh^2(\Delta/kT)\sinh^2(\Delta/kT).\end{aligned} \tag{93}$$

Consequently,

$$\begin{aligned}G(w,z)&=(e^{-2w/l}-e^{-2(w+z)/l}-1\\&\quad+e^{-2z/l})\cosh^2\left(\frac{\Delta}{kT}\right)\sinh^2\left(\frac{\Delta}{kT}\right)\lim_{L\to\infty}\int_0^L y\;e^{-2y/l}dy\\&=0.\end{aligned} \tag{94}$$

It is clear from this result that $G(w,z)$ also vanishes for any potential constructed as a sum of independent dichotomous potentials and for the limiting case of the Ornstein-Uhlenbeck process. The diffusion constant is thus given in its entirety for these stochastic models by the generalized Einstein relation (69). In Fig. 3 the field-dependent diffusion constant predicted by Eq. (69) for the dichotomous and Ornstein-Uhlenbeck potentials is plotted as a function of the dimensionless field strength qEl/kT for $\Delta=2kT$, as in Figs. 1 and 2.

VI. REMARKS

We have presented a usable nonlinear-response theory valid for a one-dimensional system of independent classical carriers moving in a potential and subjected to an externally imposed driving agency that can be mechanical such as an electric field or thermal such as a temperature gradient. We have given expressions for the electrical and thermal mobility, for cross-transport coefficients that appear in Onsager relations, and for the diffusion constant, which can be evaluated explicitly for given potentials. We have generalized the Wiedemann-Franz law and shown that the Einstein relation connecting the diffusion constant and the mobility may also be generalized to give a part of the diffusion constant. For the stochastic examples considered, that part has been shown to be the entire diffusion constant. We suspect that this will also be the case for many other random potentials in which the autocorrelation function decays rapidly with distance, including most of those that arise in physical applications [15]. We have evaluated the various transport coefficients for several stated forms of the potential including one deterministic case (the sinusoidal potential) and several stochastic cases (dichotomous noise).

As stated in Sec. I, our response theory shares with the Kubo formalism [1,2] the feature that transport coefficients are obtained directly from the system correlation functions in the absence of the external fields, but goes beyond that formalism in that, while exact, our theory addresses external fields of arbitrary magnitude. The correlation functions in our theory are not time correlation functions as in the Kubo formalism but are spatial. We have found applications of our theory in the field of molecularly doped polymers [7,8] and in microwave interactions with ceramics [9,10], but the formalism has general validity.

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