Dynamics of nonlinear systems: The heavy damping limit

R. A. Guyer
Laboratory for Low Temperature Physics, University of Massachusetts, Amherst, Massachusetts 01003
(Received 5 November 1979)

The Smoluchowski equation for diffusion through phase space is solved in terms of the eigenstates of the relaxation operator equation. Formally exact expressions for single-particle averages, two-particle averages, the linear response, etc., are found. An Einstein relation is established between the diffusion constant and the mobility that describes a displacement current. This formal apparatus is able to be implemented if the eigenvalues and eigenstates of the relaxation operator equation are available. The many-particle wave functions that solve the relaxation operator equation are found by employing a variational ansatz. The low-lying excited states of the relaxation operator problem are able to be built up from the many-particle ground state and from the single-particle states that describe the equilibrium statistical mechanics. A number of problems are examined to illustrate the content of the formal solution to the Smoluchowski equation and to provide a test of the adequacy of the variational ansatz. These problems are (a) two single-particle problems (a particle in a harmonic potential and a particle in a sinusoidal potential), (b) two exactly soluble problems, i.e., problems for which the relaxation operator equation can be solved exactly (a linear chain of harmonically coupled particles and this chain with each particle in a harmonic external potential), and (c) the ϕ^4 chain and the sine-Gordon chain. Comparison of the exact solution and the variational solution to (b) shows the variational solution to give a good description of the low-lying excited states. For the latter two problems the linear response, diffusion constant, dynamic structure factor, etc., are calculated. Particular attention is given to the role of kinks in the dynamics of the ϕ^4 chain and the sine-Gordon chain.

I. INTRODUCTION

Over the past few years there has been considerable interest in physical systems that have properties which exist because of essential nonlinearities in the fields with which they are described.[1,2] Often those systems are mapped onto one of a small number of nonlinear models, e.g., the sine-Gordon chain, the ϕ^4 chain, etc. As a consequence these models have recently been the subject of intense investigation and a great deal has been learned about their properties; e.g., the Newtonian dynamics of the models has been extensively explored[3-5] (i.e., the $F = ma$ properties of the system) as has the equilibrium statistical mechanics.[6-12] However, relatively little is known about the statistical dynamics of nonlinear systems except in a weak coupling limit in which the statistical dynamics is approximated by the Newtonian dynamics.[5,7,13-16] The purpose of this paper is to describe a general treatment of the statistical dynamics of nonlinear systems in the heavy damping limit. In this limit, the opposite of the weak coupling limit, the Smoluchowski equation can be used to describe the motion of the distribution function of the system through configuration space.

In Sec. II the Smoluchowski equation is introduced and solved formally in terms of the many-particle eigenstates and eigenvalues of the relaxation operator. Formally correct expressions for the time evolution of single-particle averages and of two-particle averages are worked out. The linear response of a system to an external field is related to the time evolution of the displacement fluctuations; an Einstein relation between the diffusion constant D and the mobility μ that measures the displacement response is established. Then, since displacement current is related to the probability current, a remarkably simple and useful expression for D results. The usefulness of this formal apparatus is predicated on the belief that solutions of the relaxation operator equation are available. In Sec. III we solve the relaxation operator equation, a many-particle Schrödinger equation, for the low-lying excited states using the variational principle and an ansatz similar to the "Feynman phonon" ansatz.[17] In the circumstance in which the equilibrium statistical mechanics is described by a single-particle Schrödinger equation we find that the many-particle excited states of the relaxation operator are built up from the many-particle ground state and the solutions of a single-particle Schrödinger equation. We specialize further discussion to this circumstance (although it is not necessary) and exhibit a variety of useful formulas for calculating matrix elements between many-particle wave functions, etc. In Sec. IV we describe the solution to two single-particle problems; a particle in a harmonic potential and a particle in a sinusoidal potential. (The relaxation operator equations for these prob-

lems are single-particle equations that can be solved exactly; the variational ansatz is unnecessary.) We show that the existence of an Einstein relation and the probability current ↔displacement current relationship permits one to achieve a result for D for the latter problem that is identical to that found by Festa and d'Agliano[18,19] by careful examination of the formally correct expression for D. In Sec. V we examine two many-particle problems for which the relaxation operator equation can be solved exactly. These are a conventional harmonically coupled linear chain and a harmonically coupled linear chain with each particle in a harmonic external potential. We solve the relaxation operator equation exactly and we solve it using the variational ansatz. We compare the exact eigenvalue spectrum of the relaxation operator with that found using the variational ansatz and we also calculate the diffusion constant using the exact eigenstates and eigenvalues and the variational eigenstates and eigenvalues. The results are identical. This latter calculation serves two purposes; it illustrates the delicacy of calculations of long-time behavior and it shows that the variational ansatz yields behavior for the low-lying excited states that is quite satisfactory. In Sec. VI we make application of the formal apparatus for solving the Smoluchowski equation to two nonlinear systems; the ϕ^4 chain and the sine-Gordon chain. For the ϕ^4 chain we calculate the displacement response to an external field and the dynamic structure factor. In certain limits the results are the same as those of Imada.[20] For the sine-Gordon chain we calculate the dynamic structure factor and two related structure factors introduced by Schneider *et al.*[21] These structure factors probe the chain for the presence of kinks (solitons), phonons, and breathers. We also calculate the diffusion constant by appeal to the argument in Sec. II. We do not find the peculiar long-time behavior found by Stoll *et al.*[22] For both the ϕ^4 chain and the sine-Gordon chain we find the kinks to play a dominant role in the $\omega \to 0$ dynamics. Certain details that are used in the body of the paper are briefly described in several Appendices.

II. SOLUTION TO THE SMOLUCHOWSKI EQUATION

In this section we solve the Smoluchowski equation (SE) and we exhibit the formal expressions for the quantities that we are interested in calculating, e.g., two-point correlation functions, linear response to an external field, etc. We consider a system of N classical particles having coordinates $u_1 \cdots u_N \equiv \vec{u}$, that interact with one another and external fields through the potential energy $V(u_1 \cdots u_N) = V(\vec{u})$ and that are acted upon by viscous forces of suitable strength that the evolution of the system through configuration space is described by the Smoluchowski equation. The Smoluchowski equation for the configuration space distribution function $\sigma(\vec{u})$ is

$$\frac{\partial \sigma(\vec{u})}{\partial t} = D \sum_{i=1}^{N} \frac{\partial}{\partial u_i} \left[e^{-\beta V(\vec{u})} \frac{\partial}{\partial u_i} [e^{\beta V(\vec{u})} \sigma(\vec{u})] \right] , \tag{1}$$

where D is a diffusion constant. Equation (1) is solved subject to the specification of the coordinates $u_1 \cdots u_N$ at some initial time t_0 ($u_1^0 \cdots u_N^0 \equiv \vec{u}_0$), and any constraints that exists among the u_i [e.g., periodicity like $\delta(u_N - u_1)$]. The solution to this equation is employed to calculate the average value of $A(u_1 \cdots u_N) \equiv A(\vec{u})$ at time t; i.e.,

$$\langle A_t \rangle = \int d\vec{u} \int d\vec{u}_0 A(\vec{u}) \sigma(\vec{u}t | \vec{u}_0 t_0) P(\vec{u}_0) , \tag{2}$$

where $P(\vec{u}_0)$ is the probability that the configuration of the system at t_0 is $\vec{u}_0$. In Eq. (2) and sometimes elsewhere we use a notation that denotes the initial conditions that are involved in determining σ.

To solve Eq. (1) we replace the equation for σ by one for $\tilde{\sigma}$ defined by[18,23]

$$\sigma = e^{-\beta V/2} \tilde{\sigma} , \tag{3}$$

i.e., by

$$\frac{\partial \tilde{\sigma}}{\partial t} = -\mathcal{S}(\vec{u}) \tilde{\sigma} , \tag{4}$$

where

$$\mathcal{S}(\vec{u}) = D \sum_{i=1}^{N} \left[-\frac{\partial^2}{\partial u_i^2} + U_i(\vec{u}) \right] \tag{5}$$

and

$$U_i(\vec{u}) = \left[\tfrac{1}{2} \beta \frac{\partial V}{\partial u_i} \right]^2 - \tfrac{1}{2} \beta \frac{\partial^2 V}{\partial u_i^2} . \tag{6}$$

The operator $\mathcal{S}(\vec{u})$ in Eq. (5), the "relaxation" operator, is Hermitian. It is convenient to seek solution to Eq. (4) in terms of the solution to the auxiliary, relaxation operator problem

$$\mathcal{S}(\vec{u}) \Psi_\nu(\vec{u}) = s_\nu \Psi_\nu(\vec{u}) . \tag{7}$$

For this problem the ground state is $s_0 = 0$, $\Psi_0(\vec{u}) = \exp[-\frac{1}{2}\beta V(\vec{u})]$, $\langle \Phi_\mu / \Psi_\nu \rangle = \delta_{\mu\nu}$ [here we use $\Phi_\mu(\vec{u})$ to denote $\Psi_\nu^*(\vec{u})$][24] and the equilibrium distribution function is $\Phi_0(\vec{u})\Psi_0(\vec{u})$. Upon expanding $\tilde{\sigma}(\vec{u})$ in terms of the $\Psi_\nu(\vec{u})$ in Eq. (7), i.e.,

$$\tilde{\sigma}(\vec{u}t | \vec{u}_0) = \sum_\nu \bar{\sigma}_\nu(\vec{u}_0 t) \Psi_\nu(\vec{u}) , \tag{8}$$

we find $\bar{\sigma}_\nu(\vec{u}_0 t) = \bar{\sigma}_\nu(\vec{u}_0) \exp(-s_\nu t)$, (here we use a notation that shows that the amplitudes $\bar{\sigma}_\nu$ depend on the initial conditions $\vec{u}_0$; from this point onward

we take the fiducial time t_0 to be zero). At $t=t_0=0$ we have $\sigma(\vec{u}0|\vec{u}_0 0)=\Phi_0(\vec{u})\tilde{\sigma}(\vec{u}0|\vec{u}_0 0)=\delta(\vec{u}-\vec{u}_0)$ and $\tilde{\sigma}(\vec{u}0|\vec{u}_0 0)=\sum_\nu \tilde{\sigma}_\nu(\vec{u}_0 0)\Psi_\nu(\vec{u})$ or $\tilde{\sigma}_\nu(\vec{u}_0 0)=\Phi_\nu(\vec{u}_0)\Phi_0(\vec{u}_0)$. Thus, we have

$$\tilde{\sigma}(\vec{u}t|u_0 0)=\sum_\nu \frac{\Phi_0(\vec{u})}{\Phi_0(\vec{u}_0)}\Phi_\nu(\vec{u}_0)\Psi_\nu(\vec{u})e^{-s_\nu t} \quad . \tag{9}$$

Averages: Upon using Eq. (9) in Eq. (2) we find

$$\langle A_t\rangle=\sum_\nu \langle\Phi_0|A|\Psi_\nu\rangle\langle\Phi_\nu|\Phi_0^{-1}P\rangle e^{-s_\nu t} \quad , \tag{10}$$

where $\langle\Phi_\nu|A|\Psi_\nu\rangle\equiv\int d\vec{u}\,\Phi_\mu(\vec{u})A(\vec{u})\Psi_\nu(\vec{u})$ is a many-particle matrix element. If we set $P(\vec{u}_0)$ equal to the equilibrium distribution function $\Phi_0(\vec{u}_0)\Psi_0(\vec{u}_0)$, then $\langle A_t\rangle=\langle\Phi_0|A|\Psi_0\rangle$ and is independent of time.

We define the AB correlation function to be

$$\langle A_t B_0\rangle\equiv\int d\vec{u}\int d\vec{u}_0\,A(\vec{u})\sigma(\vec{u}t|\vec{u}_0 0)B(\vec{u}_0)P_0(\vec{u}_0) \quad , \tag{11}$$

where $P_0(\vec{u}_0)=\exp[-\beta V(\vec{u}_0)]=\Phi_0(\vec{u}_0)\Psi_0(\vec{u}_0)$ is the equilibrium function. Using Eq. (9) we have

$$\langle A_t B_0\rangle=\sum_\nu \langle\Phi_0|A|\Psi_\nu\rangle\langle\Phi_\nu|B|\Psi_0\rangle e^{-s_\nu t} \quad . \tag{12}$$

This equation involves the calculation of quantities typical of those we will discuss in succeeding sections. For example we will discuss the diffusion constant $D\propto(d/dt)\langle u_t u_0\rangle$. From Eq. (12) we see that to learn the behavior of the AB correlation function we need to learn *both the eigenvalues and the eigenfunctions of* S, Eq. (7). We also see that the long-time behavior of the AB correlation function depends on the qualitative nature of the eigenvalue spectrum of S. If s_ν has a gap as $\nu\to 0$, then[25]

$$\langle A_t B_0\rangle\sim\langle\Phi_0|A|\Psi_0\rangle\langle\Phi_0|B|\Psi_0\rangle=\langle\langle A\rangle\rangle\langle\langle B\rangle\rangle \quad , \tag{13}$$

where $\langle\langle F\rangle\rangle$ is the equilibrium average of $F(\vec{u})$,

$$\langle\langle F\rangle\rangle\equiv\int d\vec{u}\,e^{-\beta V}F(\vec{u})/\int e^{-\beta V}d\vec{u}=\langle\Phi_0|F|\Psi_0\rangle \quad . \tag{14}$$

(Let us pause briefly to call attention to notation; we use $\langle\cdots\rangle$ to denote averages calculated with σ and we use $\langle\langle\cdots\rangle\rangle$ to denote equilibrium averages.) If s_ν is dense as $\nu\to 0$ the long-time behavior of the AB correlation function can be quite complex. See, for example, Sec. V or Ref. 18.

Linear response: Suppose we disturb the system of particles discussed above by adding the external potential

$$\Delta V=+\sum_{i=1}^{N}u_i F(t) \tag{15}$$

to $V(1\cdots N)$. Then, returning to Eqs. (1) and (3) we find to linear order in F,

$$\frac{\partial\tilde{\sigma}}{\partial t}=-S\tilde{\sigma}-\frac{\beta D}{\Phi_0}\sum_{i=1}^{N}\frac{\partial}{\partial u_i}[\Phi_0\Psi_0 F(t)] \quad . \tag{16}$$

Upon expanding $\tilde{\sigma}$ in the complete set of states generated by S we have

$$\tilde{\sigma}(\vec{u}t|u_0 0)=\sum_\nu\frac{\Phi_0(\vec{u})}{\Phi_0(\vec{u}_0)}\Phi_\nu(\vec{u}_0)\Psi_\nu(\vec{u})e^{-s_\nu t}+\beta^2 D\sum_{\nu\neq 0}\Psi_\nu(\vec{u})\sum_i\langle\Phi_\nu|\frac{\partial V}{\partial u_i}|\Psi_0\rangle F_\nu(t) \quad , \tag{17}$$

where

$$F_\nu(t)=\int_0^t dt'\,e^{-s_\nu(t-t')}F(t') \quad . \tag{18}$$

Here we have used $\sigma(\vec{u}t|\vec{u}_0 0)=\delta(\vec{u}-\vec{u}_0)$; the restriction $\nu\neq 0$ in the second term is not really necessary since $\langle\Phi_0|\partial V/\partial u_i|\Psi_0\rangle$, the average force on particle i in equilibrium, is zero. The response of $A(\vec{u})$ to the perturbation in Eq. (15) is

$$\langle A_t\rangle=\int d\vec{u}\int d\vec{u}_0\,A(\vec{u})\sigma(\vec{u}t|\vec{u}_0 0)P_0(\vec{u}_0) \quad , \tag{19}$$

where $P_0(\vec{u}_0)$ is the equilibrium distribution function. For $A(\vec{u})$ such that $\langle\Phi_0|A|\Psi_0\rangle=0$, we have

$$\langle A_t\rangle=+\beta^2 D\sum_\nu\langle\Phi_0|A|\Psi_\nu\rangle\langle\Phi_\nu|\sum_i\frac{\partial V}{\partial u_i}|\Psi_0\rangle F_\nu(t) \quad . \tag{20}$$

Consider the special case $F(t)=F_0\Theta(t)$. Then, $F_\nu(t)=F_0(1-e^{-s_\nu t})/s_\nu$ and as $t\to+\infty$ we have (we assume we need not worry about $s_\nu t$ as $\nu\to 0$)

$$\langle A_t\rangle\sim+\beta^2 D F_0\sum_\nu\langle\Phi_0|A|\Psi_\nu\rangle\frac{1}{s_\nu}\langle\Phi_\nu|\sum_i\frac{\partial V}{\partial u_i}|\Psi_0\rangle \quad . \tag{21}$$

On the other hand for the perturbation in Eq. (15) as $t\to+\infty$ the system approaches a new equilibrium appropriate to $V(1\cdots N)+\sum_{i=1}^{N}u_i F_0$. (We deal here with systems for which the perturbation does not lead to a current, e.g., the ϕ^4 system.) Thus we expect

$$\lim_{t\to+\infty}\langle A_t\rangle\sim\langle\langle A\rangle\rangle=\int d\vec{u}\exp(-\beta V)\exp\left[-\beta F_0\sum_i u_i\right]A\Big/\int d\vec{u}\exp(-\beta V) \quad . \tag{22}$$

Linearizing the right-hand side in F_0 and using $\Phi_0(\vec{u}) = \Psi_0(\vec{u}) = \exp[-\frac{1}{2}\beta V(\vec{u})]$ leads to

$$\lim_{t\to+\infty} \langle A_t \rangle \sim \langle\langle A \rangle\rangle = \beta F_0 \sum_\nu \langle \Phi_0 | A | \Psi_\nu \rangle \langle \Phi_\nu | \sum_i u_i | \Psi_0 \rangle \quad . \quad (23)$$

Comparison of Eqs. (21) and (23) leads to the identity

$$\mathcal{S}_\nu \langle \Phi_0 | u_i | \Psi_\nu \rangle = \beta D \langle \Phi_0 | \frac{\partial V}{\partial u_i} | \Psi_\nu \rangle \quad . \quad (24)$$

This identity can be proved directly from manipulation of the Smoluchowski equation; it is independent of the special conditions that led to Eqs. (21) and (23).

Einstein relation: We take the definition of the diffusion constant to be[18]

$$D = \lim_{t\to+\infty} \frac{d}{dt} \frac{1}{2} \langle (X_t - X_0)^2 \rangle = - \lim_{t\to+\infty} \frac{d}{dt} \langle X_t X_0 \rangle \quad , \quad (25)$$

where $X = N^{-1} \sum_i u_i$, the center of mass. Upon using Eq. (12), we have

$$D = - \lim_{t\to+\infty} \sum_\nu \langle \Phi_0 | X | \Psi_\nu \rangle \langle \Phi_\nu | X | \Psi_0 \rangle \mathcal{S}_\nu e^{-\mathcal{S}_\nu t} \quad . \quad (26)$$

We take the definition of the mobility to be

$$\mu = \lim_{t\to+\infty} \frac{d}{dt} \frac{\langle X_t \rangle}{F_0} \quad , \quad (27)$$

where $\langle X_t \rangle$ is calculated as the linear displacement response to the external field $+\sum_i u_i F_0 \Theta(t)$. Using Eq. (20) we have

$$\langle X_t \rangle = \beta^2 D F_0 \sum_\nu \langle \Phi_0 | X | \Psi_\nu \rangle \frac{1}{\mathcal{S}_\nu} \times \langle \Phi_\nu | \sum_i \frac{\partial V}{\partial u_i} | \Psi_0 \rangle (1 - e^{-\mathcal{S}_\nu t}) \quad . \quad (28)$$

Thus

$$\mu = \lim_{t\to+\infty} \beta^2 D F_0 \sum_\nu \langle \Phi_0 | X | \Psi_\nu \rangle \langle \Phi_\nu | \sum_i \frac{\partial V}{\partial u_i} | \Psi_0 \rangle e^{-\mathcal{S}_\nu t} \quad . \quad (29)$$

Employing the identity in Eq. (24) we can write

$$\mu = \beta \lim_{t\to+\infty} \sum_\nu \langle \Phi_0 | X | \Psi_\nu \rangle \langle \Phi_\nu | X | \Psi_0 \rangle \mathcal{S}_\nu e^{-\mathcal{S}_\nu t}$$

or

$$\mu = \beta D \quad , \quad (30)$$

the Einstein relation.

The current we have used to define the mobility in Eq. (27) is the displacement current μF_0, $\langle u_t \rangle \sim \mu F_0 t$. This definition is unconventional but necessary. In the Smoluchowski equation picture a current related to a property of the velocity would not make sense.

The displacement current defined by Eq. (27) can be related to the probability current associated with the Smoluchowski equation. Upon integrating Eq. (1) over $u_2 \cdots u_N$ we have

$$\frac{\partial \sigma(u_1)}{\partial t} = D \frac{\partial}{\partial u_1} J(u_1) \quad ,$$

where

$$J(u_1) = \int d2 \cdots dN \left[e^{-\beta U} \frac{\partial}{\partial u_1} (e^{\beta U} \sigma) \right] \quad (31)$$

is the probability current and $U(1 \cdots N) = V(1 \cdots N) + \sum_i u_i F_0$. In steady state the probability current is a constant, $J(u_1) \equiv W$, that can be found by very simple means.[8,26] We expect the steady-state displacement current μF_0 to be directly proportional to the steady-state probability current. Then, from the Einstein relation in Eq. (30), we can relate the diffusion constant to the steady-state probability current. This relationship is of great computational utility. The diffusion constant can be very hard to calculate directly,[18] whereas, the probability current is easily calculated directly; $W \to \mu \to D$.

III. SOLUTION TO THE RELAXATION OPERATOR PROBLEM

It is clear from the formal manipulation in Sec. III that a premium is placed on solution to the relaxation operator equation, Eq. (7). Here we describe an approximate treatment of the relaxation operator equation; we find the eigenvalues, the eigenfunctions, and we exhibit formulas for the matrix elements that are useful in carrying out calculations. An essential feature of our method of solution of the $\mathcal{S}$ equation, Eq. (7), is the use of the complete set of single-particle states generated by the transfer integral solution to the equilibrium statistical mechanics (this method of treating the equilibrium statistical mechanics is outlined in Appendix A).

We rewrite Eq. (7) in the form that suggests a many particle Schrödinger equation; i.e.,

$$\sum_{i=1}^{N} \left[-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mu_i^2} + \tilde{U}_i(1 \cdots N) \right] \Psi_\nu(1 \cdots N) = E_\nu \Psi_\nu(1 \cdots N) \quad , \quad (32)$$

where $\tilde{U}_i = \hbar^2 U_i / 2m$ and $E_\nu = \hbar^2 \mathcal{S}_\nu / 2mD$. We seek to solve this equation. Certainly depending upon the details of a particular problem a wide variety of methods may have application to solution to Eq. (32). In this paper we are primarily concerned with

systems in which the particles are strongly coupled so that particle-particle interactions cannot be treated as a perturbation. Further we are interested in phenomena like diffusion in which the long-time behavior of the system is examined. From Eq. (26) we see that this means that the low-lying excited states of Eq. (32) are important. Thus we want to focus on methods of solving Eq. (32) that give reliable information on the low-lying excited states of a strongly coupled system. Since, we are fortunate to have the ground-state solution to Eq. (32) and all of the n-particle correlation functions for the ground state available from the transfer integral solution to the equilibrium statistical mechanics, Appendix A, it is natural to seek the low-lying excited states in the form

$$\Psi(1 \cdots N) = C \sum_{i=1}^{N} F_i(u_i)\Psi_0(1 \cdots N) \quad , \tag{33}$$

where C is a constant to be adjusted to normalize Ψ and $F_i(u_i) = F_i(i)$ is a single-particle function that depends upon u_i and possibly upon the index i that locates a particle along the chain.[25] This latter dependence is present in principle because the particles are not free to move in any way relative to one another but rather are ordered along the chain. We denote the Hamiltonian in Eq. (32) by H, $H\Psi_0 = E_0\Psi_0$, $E_0 = 0$. The procedure is to calculate the expectation value of H using Ψ_ν from Eq. (33) and to vary the result with respect to the functional form of $F_i(u_i)$. For the expectation value of H, we have $(E = \langle\Psi|H|\Psi\rangle/\langle\Psi/\Psi\rangle)$,

$$E = E_0 = \frac{\hbar^2}{2m} \frac{\sum_i \int \rho^{(1)}(i)\nabla F_i^*(u_i)\nabla F_i(u_i)\, di}{\left[\sum_{i,j} \int \rho^{(2)}(i,j) F_i^*(u_i) F_j(u_j)\, di\, dj\right]^{-1}} \quad , \tag{34}$$

where $\rho^{(1)}(u_i)$ and $\rho^{(2)}(u_i u_j)$ are the single-particle and pair densities for the ground state (see Appendix A). Varying E with respect to $F_i(u_i)$ leads to the equation of motion

$$-\frac{\hbar^2}{2m}\nabla_i[\rho^{(1)}(i)\nabla F_i(i)] - \lambda \sum_j \int \rho^{(2)}(ij) F_j(j)\, dj = 0 \quad . \tag{35}$$

This equation is simplified upon making the substitution

$$G_i(u_i) = [\rho^{(1)}(i)]^{1/2} F_i(u_i) \quad ; \tag{36}$$

Eq. (35) becomes

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial u_i^2} G_i(u_i) + \frac{\hbar^2}{2m}\frac{G_i(u_i)}{[\rho^{(1)}(u_i)]^{1/2}}\frac{\partial^2}{\partial u_i^2}[\rho^{(1)}(u_i)]^{1/2} = \lambda \sum_j \int dj \frac{\rho^{(2)}(ij)}{[\rho^{(1)}(i)\rho^{(1)}(j)]^{1/2}} G_j(u_j) \quad . \tag{37}$$

Let us assume that the single-particle density $\rho^{(1)}$ can be derived from a Schrödinger equation; i.e.,

$$h\psi_0(u_i) \equiv -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial u_i^2}\psi_0(u_i) + W(u_i)\psi_0(u_i) = e_0\psi_0(u_i) \quad , \tag{38}$$

where $[\rho^{(1)}(i)]^{1/2} = \psi_0(u_i)$. Then, Eq. (37) becomes

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial u_i^2} + W(u_i)\right] G_i(u_i) = e_0 G_i(u_i) - \lambda \sum_j \int dj\, K_0(ij) G_j(j) \quad , \tag{39}$$

where $K_0(ij) = \rho^{(2)}(ij)/[\rho^{(1)}(i)\rho^{(1)}(j)]^{1/2}$, a known function. We can solve this equation analytically if the transfer integral problem associated with determination of the equilibrium statistical mechanics can be reduced to a Schrödinger equation. To head in this direction we expand $G_i(u_i)$ in terms of the complete set of states generated by the transfer integral problem

$$G_i(u_i) = e^{i\theta_i} \sum_\nu g_\nu \psi_\nu(u_i) \quad , \tag{40}$$

where θ_i is a phase that depends upon the location of particle i along the chain. We have

$$\sum_\nu \langle\mu|h|\nu\rangle g_\nu = e_0 g_\nu - \lambda \sum_j e^{i(\theta_j - \theta_i)} \langle\mu|K_0(ij)|\nu\rangle g_\nu \quad . \tag{41}$$

The right-hand side of this equation is greatly simplified upon using the expressions for $\rho^{(1)}$ and $\rho^{(2)}$ given in Appendix A:

$$[\rho^{(1)}(u)]^{1/2} = \psi_0(u) \quad , \qquad \rho^{(2)}(u_i u_j) = \sum_\nu \phi_0(u_i)\psi_\nu(u_i)\phi_\nu(u_j)\psi_0(u_j) \times \exp[-|l_{ij}|\beta(\epsilon_\nu - \epsilon_0)] \quad , \tag{42}$$

where $l_{ij} = n_i - n_j$ (n_i, n_j locate particles i,j along the chain). We have

$$\langle\mu|K_0(ij)|\nu\rangle = \sum_{\nu'} \int di\, dj\, \phi_\mu(i)\psi_{\nu'}(i)\phi_{\nu'}(j)\psi_\nu(j) \times \exp[-|\bar{l}_{ij}|\beta(\epsilon_{\nu'} - \epsilon_0)] = \delta_{\mu,\nu} \sum_\nu \exp[-|\bar{l}_{ij}|\beta(\epsilon_\nu - \epsilon_0)] \quad ; \tag{43}$$

i.e., the right-hand side of Eq. (41) is diagonal in ν. We have

$$\sum_\nu \langle\mu|h|\nu\rangle g_\nu = [e_0 - \lambda T_\nu(\theta)] g_\mu \quad , \tag{44}$$

where

$$T_\nu(\theta) = \sum_l e^{il\theta} e^{-|l|\beta(\epsilon_\nu - \epsilon_0)} = \frac{\sinh x_\nu}{\cosh x_\nu - \cos\theta} \quad , \tag{45}$$

$x_\nu=\beta(\epsilon_\nu-\epsilon_0)$ and we have assumed the phase θ_i to be of the form $\phi_i=n_i\theta$. It is very common in the treatment of transfer integral problems to work in the limit that the transfer integral can be reduced to a Schrödinger equation, i.e., the complete set of states that gives the equilibrium statistical mechanics is generated from $h\psi_\nu=\epsilon_\nu\psi_\nu$, Eq. (38). From this point onward we specialize our treatment to this case. When the transfer integral equation is reduced to an equation like Eq. (38) we refer to this reduction as the Schrödinger equation approximation (SEA). Using SEA, Eq. (44) becomes diagonal and we have

$$E_\nu(q)=\lambda_\nu(q)=(e_\nu-e_0)/T_\nu(q) \quad . \tag{46}$$

These energy eigenvalues depend upon the phase factor $\theta=qa$ (a is a length that describes positions along the chain) and the index ν which specifies the single-particle excitation level. The many-body wave function appropriate to $E_\nu(q)$ is

$$\Psi_{q,\nu}(1\cdots N)=C_{q\nu}\sum_i e^{iqan_i}\psi_\nu(u_i)\psi_0(u_i)^{-1}\times\Psi_0(1\cdots N) \quad , \tag{47}$$

where $C_{q\nu}\{[NZT_\nu(q)]^{1/2}\}^{-1}$ and Z is the partition function for the equilibrium problem (see Appendix B where the normalization and other properties of the many-particle wave functions are worked out). The constant $C_{q\nu}$ in this equation is chosen such that

$$\langle\Phi_{q'\mu}(1\cdots N)|\Psi_{q\nu}(1\cdots N)\rangle=\delta_{qq'}\delta_{\nu\mu} \quad . \tag{48}$$

From Sec. II we see that the quantities of interest typically involve matrix elements between the many-particle ground state and the excited states, e.g., $\langle A_t B\rangle$ involves $\langle\Phi_0|A|\Psi_\nu\rangle$. For $A(\vec{u})=\sum_{i=1}^N A(u_i)$, we have

$$\langle\Phi_0|A(\vec{u})|\Psi_{q\nu}\rangle=\delta_{q,0}C_{q,\nu}NZT_\nu(q)A_{0\nu} \quad , \tag{49}$$

where

$$A_{0\nu}=\int du\,\phi_0(u)A\,\psi_\nu(u) \tag{50}$$

is a single-particle matrix element involving the single-particle states of the transfer integral (TI) problem. It is the enormous simplification offered by the reduction of many-particle matrix elements to single-particle matrix elements, illustrated by Eq. (49), that makes the ansatz of Eq. (33) particularly useful. We note that matrix elements of $A(\vec{u})$ that involve the ground state, like the matrix element in Eq. (49), do not require the phase factor in the specification of the excited state; i.e., they always involve $\delta_{q,0}$. For the matrix elements of a quantity that depends upon phase, e.g., $\sum_i\exp(-iq'an_i)A(u_i)\equiv A_{q'}(\vec{u})$ or $A_{q'}$, we have

$$\langle\Phi_0|A_{q'}(\vec{u})|\Psi_{q,0}\rangle=\delta_{q',q}C_{q,\nu}NZT_\nu(q)A_{0\nu} \quad . \tag{51}$$

Finally, using the results above for many-particle matrix elements we are able to write the AB correlation function in a way which involves knowing only the properties of the single-particle transfer integral problem

$$\langle A_{q,t}B_{-q',0}\rangle=\delta_{q,q'}\sum_\nu T_\nu(q)A_{0\nu}B_{\nu 0}e^{-s_{q,\nu}t} \quad , \tag{52}$$

where $s_{q,\nu}=2mDE_\nu(q)/\hbar^2$.

Below when we discuss the $S(q,\omega)$, the diffusion constant, we will make use of many of the results displayed here.

IV. SINGLE-PARTICLE PROBLEMS

Here we describe the solution to two single-particle problems using the formalism developed in Secs. II and III. The purpose of this section is to illustrate with simple examples some of the manipulations that are helpful in calculations of the type under discussion.

Example 1: a single-particle in the external potential $\frac{1}{2}\Gamma u^2$. The equilibrium statistical mechanics is simple and does not require the use of TI methods. Equation (7) or (32) takes the form

$$-(\hbar^2/2m)\psi_\nu''+\tfrac{1}{2}V_0u^2\psi_\nu=E_\nu\psi_\nu \quad , \tag{53}$$

where $V_0=(\frac{1}{2}\beta\Gamma)^2\hbar^2/m$, $E_\nu=\epsilon_\nu+(\beta\Gamma\hbar^2)/2m)$, and $s_\nu=2m\epsilon_\nu D/\hbar^2$. The eigenstates of Eq. (53) are the harmonic oscillator states, $E_\nu=(\nu+\frac{1}{2})\hbar\omega_0$, $\omega_0^2=V_0/m$ so that

$$s_\nu=\nu\beta\Gamma, \quad \nu=0,1,2,\ldots \quad . \tag{54}$$

The relaxation operator spectrum is discrete, $s_0=0$, $s_1=\beta\Gamma D$, $s_2=2\beta\Gamma D$, ... For the displacement-displacement correlation function we have

$$\langle u_t u_0\rangle=\sum_\nu\langle 0|u|\nu\rangle\langle\nu|u|0\rangle e^{-s_\nu t}=|\langle 0|u|1\rangle|^2\exp(-\beta\Gamma Dt) \quad , \tag{55}$$

where the second line follows upon using the properties of harmonic oscillator matrix elements. Using the ground state and first excited state from Eq. (53) leads to

$$\langle u_t u_0\rangle=(k_BT/\Gamma)\exp(-\beta\Gamma Dt) \quad . \tag{56}$$

As $t\to+\infty$, $\langle u_t u_0\rangle\to 0$, since the excitation spectrum in Eq. (49) has a gap above the ground state, $s_1-s_0=\beta\Gamma D$.

Example 2: a single particle in the external potential $-V_0\cos\theta$. Equation (7) or (32) takes the form

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_\nu}{d\theta^2}+\tilde{U}(\theta)\psi_\nu=E_\nu\psi \quad , \tag{57}$$

with

$$\tilde{U}(\theta) = (\hbar^2/2m)[(\tfrac{1}{2}\beta V_0)^2 \sin^2\theta - \tfrac{1}{2}\beta V_0 \cos\theta] \quad (58)$$

and $E_\nu = (\hbar^2/2m)\mathcal{E}_\nu$. The quantum-mechanical problem set by Eqs. (57) and (58) is difficult. However, at low temperature $\tilde{U}(\theta)$ may be approximated by the first term in Eq. (58) and Eq. (57) becomes

$$-\frac{d^2\psi_\nu}{d\theta^2} + \tfrac{1}{2}(\tfrac{1}{2}\beta V_0)^2(1-\cos 2\theta)\psi_\nu = \frac{\lambda_\nu}{D}\psi_\nu \ , \quad (59)$$

a form of the Mathieu equation. The solutions to the Mathieu equation are in Floquet form and a band-structure results. As $T \to 0$ the lowest band has a width related to tunneling through the barrier,[6,8,9] $(\frac{1}{2}\beta V_0)^2$, between the potential minima at $0, \pi, 2\pi, \ldots$, the eigenfunctions are tight-binding wave functions, $E_0 \to 0$ and a continuum of states occurs above E_0.

For the displacement-displacement correlation function involved in calculation of the diffusion constant we have

$$\langle \theta_t \theta_0 \rangle = \sum_{\nu n} \langle 0|\theta|\nu n\rangle \langle \nu n|\theta|0\rangle e^{-\mathcal{E}_{n\nu} t} \ , \quad (60)$$

where n is a band index and ν is a wave vector. Certainly as $t \to +\infty$ the n sum in Eq.(60) is dominated by the lowest band, $n=0$. As $\nu \to 0$ $\mathcal{E}_{0,\nu} \propto \nu^2$. It is clear that a very delicate balance in the assessment of the ν dependence in Eq. (60) is involved in determination of the $t \to +\infty$ behavior of $\langle u_t u_0 \rangle$ and in calculating the diffusion constant. Festa and d'Angliano have carefully examined this problem and have calculated the diffusion constant. They find

$$\frac{1}{\tau} = \frac{1}{\tau_0}(2\pi)^2 \Big/ \int_0^{2\pi} \frac{d\theta}{\rho(\theta)} \ , \quad (61)$$

where $\rho(\theta) = \phi_0(\theta)\psi_0(\theta)$ is normed to 1 over 2π and we have written $D_0 = 1/\tau_0$ for the case of diffusion through angle. On the other hand employing the procedure for calculating the steady-state probability current, illustrated in the treatment of the sine-Gordon chain,[8,26] one finds the probability current to be

$$\mu F_0 = 2\pi W = (2\pi)^2 \beta F_0/\tau_0 \int_0^{2\pi} \frac{d\theta}{\rho(\theta)} = \beta D F_0 \ . \quad (62)$$

Thus by direct computation the relation between the diffusion constant D, and the steady-state probability current W described at the end of Sec. III is confirmed.

V. EXACTLY SOLUBLE MANY-PARTICLE PROBLEMS

A. Linear chain

The linear chain of harmonically coupled particles is described by

$$V(1 \cdots N) = \sum_{i=1}^{N} \tfrac{1}{2}\Gamma_2 (u_{i+1} - u_i)^2 \ . \quad (63)$$

From Eq. (32) the relaxation operator equation appropriate to this system is

$$\sum_{i=1}^{N} = \left[-\frac{\partial^2}{\partial u_i^2} - \beta\Gamma_2 + \tfrac{1}{4}\beta^2\Gamma_2^2 (2u_i - u_{i+1} - u_{i-1})^2 \right] \Psi_\nu = \frac{\mathcal{E}_\nu}{D}\Psi_\nu \ . \quad (64)$$

The eigenstates to this equation are the phonon states that are built up from the ground state

$$\Psi_\nu(1 \cdots N) = |n_1 \cdots n_N\rangle = (a_{q_1}^\dagger)^{n_1} \cdots (a_{q_N}^\dagger)^{n_N} |\Psi_0\rangle \ , \quad (65)$$

where Ψ_0 is the well-known correlated Gaussian ground state and at least one of the n_i must be nonzero; the eigenvalues are

$$\mathcal{E}_0 = 0 \ , \quad (66)$$

$$\mathcal{E}_\nu = 2\beta\Gamma D \sum_q \sin^2 \frac{qa}{2} n_q \ , \quad (67)$$

where ν denotes the set of occupation numbers $\{n_1 \cdots n_N\}$. Let us use these states to calculate $S(k;t)$. We have

$$S(k,t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} \langle (e^{iku_i})_t (e^{-iku_j})_0 \rangle \ , \quad (68)$$

which upon using Eq. (52) becomes

$$S(k,t) = \frac{1}{N}\sum_{ij} \langle \Phi_0|e^{iku_i}|\Psi_\nu\rangle \langle \Phi_\nu|e^{-iku_j}|\Psi_0\rangle e^{-\mathcal{E}_\nu t} \ . \quad (69)$$

Instead of proceeding to evaluate this expression as it stands we use the well-known operator identity[27] for combining the exponentials to write

$$\langle (e^{iku_i})_t (e^{-iku_j})_0 \rangle = \langle e^{ik(u_{i,t} - u_{j,0})} \rangle e^{k^2[u_{i,t}, u_{j,0}]/2} \ . \quad (70)$$

Then, using standard methods we find

$$\langle (e^{iku_i})_t (e^{-iku_j})_0 \rangle = \exp\left[-\frac{k^2}{2}\frac{D}{N} \right] \times \sum_q \frac{1 - e^{-\mathcal{E}_q^{(1)} t} e^{iq(R_i - R_j)}}{\mathcal{E}_q^{(1)}} \ , \quad (71)$$

where $\mathcal{E}_q^{(1)}$ is the value of $\mathcal{E}$ for a one-phonon excitation into state q; $\mathcal{E}_q^{(1)} = 2\beta\Gamma_2 D \sin^2(\frac{1}{2}qa)$ and $R_i = n_i a$ locates particle i at site n_i along the chain. Interestingly, we find that we need only the one-phonon states to carry through the calculation exactly. Equations (69) and (71) may be manipulated to yield the following result:

$$S(k,t) = \sum_n S_n(k,t) \ ,$$

where

$$S_n(k,t)=\exp\left[-\frac{k^2}{2\beta\Gamma_2}\right]\left[W_n+\int_0^{t/t_D}e^{-x}I_n(x)\,dx\right] , \tag{72}$$

with

$$W_n=\frac{1}{\pi}\int_o^{\pi}\left[\frac{1-\cos n\nu}{1-\cos\nu}\right]d\nu \ ; \tag{73}$$

I_n is the modified Bessel function, W_n is the Debye-Waller factor for particles separated by n, $n=|n_i-n_j|$ and $t_D^{-1}=\beta\Gamma_2 D$. As $t\to+\infty$ the integrand in large parentheses approaches $x^{-1/2}$ and $\to+\infty$, $S_n(k,t)\to 0$.

Let us use the phonon states to calculate the rate of diffusion of the center of mass

$$X(\vec{u})=\frac{1}{N}\sum_{i=1}^{N}u_i \ .$$

We have

$$D_X=\tfrac{1}{2}\lim_{t\to+\infty}\frac{d}{dt}\langle[X(\vec{u})-X(\vec{u})_0]_t^2\rangle$$

$$=\lim_{t\to+\infty}\frac{d}{dt}[\langle X(\vec{u})_0^2\rangle-\langle X(\vec{u})_t X(\vec{u})_0\rangle] \ . \tag{74}$$

Using the phonon states from above and the results in Sec. III we have

$$D_X=\lim_{t\to+\infty}\frac{d}{dt}\frac{D}{N^3}\sum_i\sum_j\sum_q e^{iq(R_i-R_j)}\frac{1-e^{-s_q^{(1)}t}}{s_q^{(1)}} \ . \tag{75}$$

(As above we find that only the one-phonon states are involved.) The sum on i and j yields $N^2\sum_G \times\delta_{q,G}$, where G is a reciprocal-lattice vector. Thus, since q is confined to the first Brillouin zone, then

$$D_X=\lim_{t\to+\infty}\frac{d}{dt}\frac{Dt}{N}$$

or

$$D_X=D/N \ . \tag{76}$$

In this expression for D, and that for $S(k,t)$ above, we have two exact results because we are able to exactly solve the Smoluchowski equation. It will be useful to compare these exact results to those obtained using the product ansatz for the many-particle wave function. To this end let us calculate D_X using Ψ_ν and s_ν from Sec. III.

The equilibrium statistical mechanics of the linear harmonically coupled chain involves plane wave eigenstate, $\psi_K(u)\propto\exp(iKu)$ and free-particle eigenvalues, $\beta\epsilon_K=K^2/2\beta\Gamma_2$; see Appendix C. Thus, for the many-body wave functions we have

$$\Psi_{q,K}(1\cdots N)=C_{qK}\sum_i e^{iqan_i}\psi_K(u_i)\Psi_0(1\cdots N) \ , \tag{77}$$

where $\Psi_0(1\cdots N)$ is the correlated Gaussian ground-state wave function and $C_{qK}=[NZT_K(q)]^{1/2}$.

The relaxation operator eigenvalue appropriate to the many-body wave function is, Eq. (46)

$$s_{q,K}=\beta\Gamma_2 D\frac{\cosh x_K-\cos qa}{\sinh x_K/x_K} \ , \tag{78}$$

where $x_K=K^2/2\beta\Gamma_2$. We note that as $K\to 0$, $s_{q,K}$ approaches $s_q^{(1)}$, the exact one-phonon relaxation operator eigenvalue, from above as the variational principle requires. To calculate the diffusion constant for the center of mass we use Eq. (74) [see also Eq. (25)] for D_X and we use the formulas in Sec. III for the many-particle matrix elements, e.g.,

$$\sum_i\langle\Phi_0|u_i|\Psi_{qK}\rangle=\delta_{q,0}C_{0,K}NZT_K(0)\langle 0|u|K\rangle \ , \tag{79}$$

and we find

$$D_X=\lim_{t\to+\infty}\frac{d}{dt}\frac{1}{N}\sum_K T_K(0)\langle 0|u|K\rangle\langle K|u|0\rangle(1-e^{-s_{0,K}t}) , \tag{80}$$

where $s_{0,K}=2\beta\Gamma_2 D x_K\tanh(\frac{1}{2}x_K)$ and $T_K(0)^{-1}=\tanh(\frac{1}{2}x_K)$. This equation can be rearranged to yield

$$D_X=D\lim_{t\to\infty}\frac{d}{dt}\sum_K K^2\langle 0|u|K\rangle\langle K|u|0\rangle\frac{(1-e^{-s_{0,K}t})}{s_{0,K}} \ . \tag{81}$$

To perform the K sum we use

$$K\langle 0|u|K\rangle=-i\int du\,\phi_0(u)u\frac{d}{du}\psi_K(u)$$

$$=i\langle 0|K\rangle=i\delta_{K,0}=K\langle K|u|0\rangle^* \tag{82}$$

to obtain

$$D_X=D/N \ . \tag{83}$$

This result for D is the same as that found above, Eq. (76), using the exact eigenstates. We see that this is in part due to the fact that D involves the $q\to 0$ and $K\to 0$ limit of $s_{q,K}$. The variational ansatz seems to give this limit correctly. On the other hand the manipulations displayed above expose the delicacy of the limit that yields the correct large t behavior [see in particular Eq. (82)]. It is concern for handling these manipulations (and for the consequences of an approximate s_ν) that leads us to prefer to get at D from the probability current –Einstein relation route described in Sec. II.

B. Linear chain in an external field

The linear chain of harmonically coupled particles in an external field is described by

$$V(1\cdots N)=\sum_{i=1}^{N}[\tfrac{1}{2}\Gamma_2(u_{i+1}-u_i)^2+\tfrac{1}{2}\Gamma_1 u_i^2] \ . \tag{84}$$

Because of the harmonic single-particle potential $\frac{1}{2}\Gamma_1 u^2$ the relaxation operator eigenvalue problem has a gap between the ground state and the first excited state. Thus $\langle X_t X_0\rangle$ decays to zero as $t\to+\infty$ and there is no diffusion constant, $S(k,t)\to S(k,+\infty)$, a nonzero value, as $t\to+\infty$, etc.

VI. NONLINEAR SYSTEMS

Here we describe the results of application of the formalism developed in Secs. II and III to two nonlinear systems: (A) the ϕ^4 chain and (B) the sine-Gordon chain.

A. The ϕ^4 chain

The ϕ^4 system is described by the potential energy[7]

$$V(1\cdots N)=\sum_{i=1}^{N}V_4(u_i)+\sum_{i=1}^{N}\tfrac{1}{2}\Gamma_2(u_{i+1}-u_i)^2 \ , \tag{85}$$

with

$$V_4(u_i)=-\tfrac{1}{2}|A|u_i^2+\tfrac{1}{4}Bu_i^4 \ . \tag{86}$$

Both the statistical mechanics and the dynamics of this sytem have been extensively studied. In the SEA [see the remark above Eq. (46)] the statistical mechanics is described in terms of the solutions to

$$\left(-\frac{1}{2\beta^2\Gamma}\frac{d^2}{du^2}-V_4(u)\right)\psi_\nu=\epsilon_\nu\psi_\nu \ . \tag{87}$$

At low temperatures the statistical mechanics is dominated by the first few low-lying states from Eq. (87). These are the tunnel-split ground state (ψ_{0+}, ψ_{0-}, $0<E_{0-}-E_{0+}\ll E_{1+}-E_{0+}$) and the low-lying tunnel-split excited states (ψ_{n+}, ψ_{n-}, $0<E_{n-}-E_{n+}\ll E_{n+1,+}-E_{n+}$); see Appendix C.

The displacement response of the ϕ^4 system to a perturbing field

$$-\sum_i u_i F_0\Theta(t) \ , \tag{88}$$

is given by Eq. (20),

$$\langle u_t\rangle=\beta^2 D\frac{F_0}{N}\sum_\nu\langle\Phi_0|\sum_i u_i|\Psi_\nu\rangle \times\langle\Phi_\nu|\sum_j\frac{\partial V}{\partial u_j}|\Psi_0\rangle\frac{1-e^{-s_\nu t}}{s_\nu} \ . \tag{89}$$

Using Eq. (24) this becomes

$$\langle u_t\rangle=\beta\frac{F_0}{N}\sum_{ij}\sum_\nu\langle\Phi_0|u_i|\Psi_\nu\rangle \times\langle\Phi_\nu|u_j|\Psi_0\rangle(1-e^{-s_\nu t}) \ . \tag{90}$$

Then, using the results from Sec. III for many-body particle matrix elements we have

$$\langle u_t\rangle=\beta F_0\sum_\nu T_\nu(0)\langle 0|u|\nu\rangle\langle\nu|u|0\rangle(1-e^{-s_\nu t}) \ . \tag{91}$$

At low temperature we expect this response to be dominated by the matrix elements to the first few excited states.

For this system $S(k,t)$ is given by Eqs. (68), (69), and (49);

$$S(k,t)=N\sum_\nu T_\nu(0)\langle 0|e^{iku}|\nu\rangle\langle\nu|e^{-iku}|0\rangle e^{-s_\nu t} \ . \tag{92}$$

The ground state and first excited state, $\psi_0\equiv\psi_+$ and $\psi_1\equiv\psi_-$, are $\psi_\pm=[\theta_R(u)\pm\theta_L(u)]/\sqrt{2}$ and $\langle 0|e^{iku}|1\rangle=i\langle 0|\sin ku|1\rangle\simeq i\sin ku_0$. Thus,

$$S(k,t)\simeq N\sin^2 ku_0 T_1(0)e^{-s_1 t} \ , \tag{93}$$

with $s_1=2\beta\Gamma_2 D(\epsilon_1-\epsilon_0)/T_1(0)$ and $T_1(0)^{-1}=\tanh[\frac{1}{2}\beta(\epsilon_1-\epsilon_0)]$. The energy difference $\beta(\epsilon_1-\epsilon_2)$ is related to the tunnel splitting in the equilibrium problem which we take to give the number of thermally activated kinks. We define

$$n_K=\beta(\epsilon_1-\epsilon_0) \ . \tag{94}$$

Then,

$$S(k,t)\simeq N\sin^2 ku_0\frac{1}{\tanh(\frac{1}{2}n_K)} \times\exp(-2\Gamma_2 D n_K)[\tanh(\tfrac{1}{2}n_K)]t \ . \tag{95}$$

As $T\to 0$, $n_K\to 0$ and we have

$$S(k,t)\simeq 2N\sin^2 ku_0 e^{-\Gamma_2 D n_K^2 t}/n_K \ . \tag{96}$$

The behavior of $S(k,t)$ is dominated by kinks; $S(kt)$ decays very slowly in time and its amplitude increases as n_K^{-1}. Results similar to these have been achieved by Imada.[20] The static structure factor is

$$S(k)=N\sum_\nu T_\nu(0)\langle 0|e^{iku}|\nu\rangle\langle\nu|e^{-iku}|0\rangle \ . \tag{97}$$

We note that $S(k,t)$ and $S(k)$ defined here have spatial structure that depends only upon the behavior of a single particle; the matrix elements that give the k dependence in Eq. (92) are between single-particle states. Certainly these single-particle states contain information about the coupling and the correlated motion of particles along the chain.

Consider the response of the ϕ^4 system to an alternating external field that couples with a different phase to each particle, i.e.,

$$-\sum_i e^{iqan_i}u_i F_0 e^{-i\omega t} \ , \tag{98}$$

where n_i locates a particle along the chain. Then, for the $q-\omega$ Fourier component of the displacment response, we have

$$\langle u(q,\omega)_t\rangle = \beta F_0 \sum_{ij}\sum_{\nu} e^{iqa(n_i-n_j)}\langle\Phi_0|u_i|\Psi_\nu\rangle\langle\Phi_\nu|u_j|\Psi_0\rangle \times \frac{e^{-i\omega t}-e^{-\mathcal{S}_\nu t}}{\mathcal{S}_\nu - i\omega}\mathcal{S}_\nu \ . \quad (99)$$

[Once again we have made use of Eq. (24).] Using the matrix elements from Sec. III we have

$$\langle u(q,\omega)_t\rangle = \beta F_0 \sum_n T_n(q)\langle 0|u|n\rangle\langle n|u|0\rangle \times \frac{e^{-i\omega t}-e^{-\mathcal{S}_{qn} t}}{\mathcal{S}_{qn}-i\omega}\mathcal{S}_{qn} \ . \quad (100)$$

At long times we may write this expression as

$$\frac{\langle u(q,\omega)_t\rangle}{\beta F_0 u_0^2} = \sum_n [A_n(q,\omega)+iB_n(q,\omega)] \ , \quad (101)$$

where the *in-phase* component of the response is

$$A_n(q,\omega) = \frac{\langle 0|u|n\rangle\langle n|u|0\rangle}{u_0^2}\frac{T_n(q)\mathcal{S}_{qn}^2}{\mathcal{S}_{qn}^2+\omega^2} \ , \quad (102)$$

and the *out-of-phase* component of the response is

$$B_n(q,\omega) = \frac{\langle 0|u|n\rangle\langle n|u|0\rangle}{u_0^2}\frac{T_n(q)\mathcal{S}_{qn}\omega}{\mathcal{S}_{qn}^2+\omega^2} \ . \quad (103)$$

At low temperature $A(q,\omega)$ and $B(q,\omega)$ are dominated by the $n=1$ contribution; we have $\langle 0|u|1\rangle \simeq u_0$,

$$A(q,\omega) \simeq n_K f_1/(f_1^2+y^2) \quad (104)$$

and

$$B(q,\omega)_1 \simeq n_K y/(f_1^2+y^2) \ , \quad (105)$$

where $y=\omega/\omega_D$, $\omega_D \equiv 2\Gamma_2 D$, and

$$f_1(q,n_K) = \frac{\cosh n_K - \cos qa}{\sinh n_K/n_K} \ . \quad (106)$$

In Fig. 1 we plot f_1, the halfwidth or inverse height of $A(q\omega)$, as a function of qa. Both A and B are very narrow as $T\to 0$ and $n_K\to 0$. Of course the response implied by Eqs. (104) and (105) is the Lorentzian response of a damped system.

In writing Eqs. (104) and (105) we have neglected excitation to the higher excited states. Again, at low temperatures excitation to the third excited state ψ_1– involves matrix elements of order u_0 but in this case the energy difference is of order 1. The resulting contribution to $\langle u(q\omega)_t\rangle$ has almost no structure as a function of qa. The amplitude $A_2(q,0)$ is of order 1 compared to $A_1(q,0)\simeq n_K^{-1}$.

Just as we defined the response to an external field that has different phase at each site we can define a

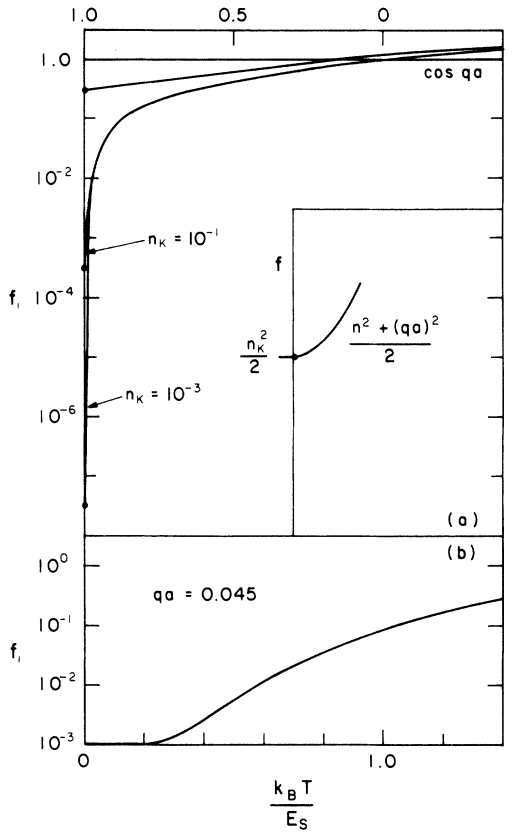

FIG. 1. Linewidth as a function of qa and T. The width of $S(q,\omega)$, f_1 given by Eq. (106), depends upon temperature through $n_K=\exp(-\beta E_S)$ and wave vector qa. As $T\to 0$, $n_K\to 0$, and $f_1\to 0$ for $qa \lesssim n_K$: the linewidth is a strong function of qa as shown in the inset. For $qa >> n_K$ the line shape is only a mild function of qa. At fixed but small qa the linewidth is a strong function of T as shown in (b).

dynamic structure factor with a similar phase dependence

$$S(qk;t) = \frac{1}{N}\sum_{i=1}^{N}\sum_{j=1}^{N} e^{iqa(n_i-n_j)}\langle (e^{iku_i})_t (e^{-iku_j})\rangle \ ; \quad (107)$$

we have

$$S(qk;t) = N\sum_n T_n(q)\langle 0|e^{iku}|n\rangle\langle n|e^{-iku}|0\rangle e^{-\mathcal{S}_{qn}t} \quad (108)$$

and

$$S(qk;\omega) = \sum_n \langle 0|e^{iku}|n\rangle\langle n|e^{-iku}|0\rangle T_n(q)\frac{\mathcal{S}_{qn}}{\omega^2+\mathcal{S}_{qn}^2} \ . \quad (109)$$

We write Eq. (109) in the form

$$\frac{S(qk,\omega)}{N} = \sum_n S_n(qk;\omega) \ . \quad (110)$$

Then for S_1 we have

$$S_1(kq;\omega) = |\langle 0|e^{iku}|1\rangle|^2 (n_K/\omega_D)(f_1^2+y^2)^{-1} \quad , \quad (111)$$

where

$$f_1 = \frac{\cosh n_K - \cos qa}{\sinh n_K / n_K} \quad ,$$

Eq. (106). The form factor $|\langle 0|e^{iku}|1\rangle|^2$ measures the structure of the single-particle state at wave vector k. At low temperature $|\langle 0|e^{iku}|1\rangle|^2 \simeq \sin^2 ku_0$ and[20]

$$S_1(qk,\omega) \simeq \sin^2(ku_0)(n_K/\omega_D)(f_1^2+y^2)^{-1}$$
$$= \sin^2(ku_0) B_1(q,\omega)/\omega \quad . \quad (112)$$

B. The sine-Gordon chain

The sine-Gordon (SG) chain is described by the potential energy

$$V(1 \cdots N) = \sum_{i=1}^{N} V_{SG}(\theta_i) + \sum_{i=1}^{N} \tfrac{1}{2} E_2 (\theta_{i+1} - \theta_i)^2 \quad (113)$$

with

$$V_{SG}(\theta) = -E_1 \cos\theta \quad . \quad (114)$$

Both the statistical mechanics and the dynamics of this sytem have been extensively studied.[8,9] In the SEA the statistical mechanics is described in terms of the solution to the Mathieu equation; i.e.,

$$\left(-\frac{1}{2\beta^2 E_2} \frac{d^2}{d\theta^2} - E_1 \cos\theta \right) \psi_\nu = \epsilon_\nu \psi_\nu \quad . \quad (115)$$

At low temperatures the statistical mechanics is dominated by the states in the first few bands of Eq. (115); the width of the first band goes to zero as $\exp(-\beta E_\phi)$ as $T \to 0$ and the spacing between bands goes to zero as T, see Appendix C. Unlike the ϕ^4 system, the response of the SG system to an external field like that in Eq. (88) is the flow of current. This current response has been extensively studied. [See Refs. 8(c) and 26.] We return to it below. Let us begin by looking at the dynamic structure factor. Proceeding as above, we find

$$S(qk;\omega) = N \sum_\nu \langle 0|e^{ik\theta}|\nu\rangle \langle \nu|e^{ik\theta}|0\rangle \times \frac{\beta(\epsilon_\nu - \epsilon_0)}{\omega_D} \frac{1}{f_\nu^2 + y^2} \quad , \quad (116)$$

where $f_\nu = (\cosh x_\nu - \cos qa)/(\sinh x_\nu / x_\nu)$, $\omega_D = 2\Gamma_2 D$, and $x_\nu = \beta(\epsilon_\nu - \epsilon_0)$. Let us at the same time consider two other probes of the behavior of the system, the sine and cosine dynamics structure factors defined by Schneider, Stoll, and Bishop[21,22]

$$S_{CC}(q;t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{iqa(n_i - n_j)} \langle (\cos\theta_i)_t (\cos\theta_j)_0 \rangle \quad (117)$$

and

$$S_{SS}(q;t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j=1}^{N} e^{iqa(n_i - n_j)} \langle (\sin\theta_i)_t (\sin\theta_j)_0 \rangle \quad . \quad (118)$$

For these dynamic structure factors we have

$$S_{CC}(q,\omega) = N \sum_\nu \langle 0|\cos\theta|\nu\rangle \langle \nu|\cos\theta|0\rangle \times \frac{\beta(\epsilon_\nu - \epsilon_0)}{\omega_D} \frac{1}{f_\nu^2 + y^2} \quad (119)$$

and

$$S_{SS}(q,\omega) = N \sum_\nu \langle 0|\sin\theta|\nu\rangle \langle \nu|\sin\theta|0\rangle \times \frac{\beta(\epsilon_\nu - \epsilon_0)}{\omega_D} \frac{1}{f_\nu^2 + y^2} \quad . \quad (120)$$

The three dynamic structure factors above have striking similarity. They differ only because of differences that occur in the matrix elements which determine the modes to which the probe couples. At low temperatures tight-binding wave functions can be used and we find (here n denotes the band index and ν is the wave vector)

$$\langle 0|e^{ik\theta}|n\nu\rangle = \delta_{k,\nu}\delta_{n,0} \quad , \quad (121a)$$

$$\langle 0|\sin\theta|n\nu\rangle = \delta_{n,1}\delta_{\nu,0}^2 (k_B T/E_\phi)^{1/2} \quad , \quad (121b)$$

and

$$\langle 0|\cos\theta|n\nu\rangle = \delta_{n,2}\delta_{\nu,0} 2\sqrt{2} k_B T/E_\phi \quad . \quad (121c)$$

Thus

$$\frac{S(qk;\omega)}{N} = \frac{\beta(\epsilon_{0k} - \epsilon_{00})}{\omega_D} \frac{1}{f_{0k}^2 + y^2} \quad , \quad (122)$$

$$\frac{S_{SS}(q;\omega)}{N} = 4 \frac{k_B T}{E_\phi} \frac{\beta(\epsilon_{10} - \epsilon_{00})}{\omega_D} \frac{1}{f_{10}^2 + y^2} \quad , \quad (123)$$

and

$$\frac{S_{CC}(q;\omega)}{N} = 8 \left(\frac{k_B T}{E_\phi} \right)^2 \frac{\beta(\epsilon_{20} - \epsilon_{00})}{\omega_D} \frac{1}{f_{20}^2 + y^2} \quad . \quad (124)$$

For the energy differences we have $\beta(\epsilon_{n0} - \epsilon_{00}) = n/\xi$, $\xi^2 = E_2/E_1$, and

$$\beta(\epsilon_{0k} - \epsilon_{00}) = 2 n_K \sin^2(\tfrac{1}{2}k) \quad ,$$

where n_K is the number of thermally activated kinks (Appendix C). The integrated amplitudes under the $S(qk;\omega)$, $S_{SS}(q;\omega)$, and $S_{CC}(q,\omega)$ curves are

$$\frac{\omega_D S(q,k)}{N} = \frac{\sinh x_k}{\cosh x_k - \cosh qa} \quad , \quad (125)$$

$$\frac{\omega_D S_{SS}(q)}{N} = 4 \frac{k_B T}{E_\phi} \frac{\sinh(1/\xi)}{\cosh(1/\xi) - \cos qa} \quad , \quad (126)$$

and

$$\frac{\omega_D S_{CC}(q)}{N} = 8\left(\frac{k_B T}{E_\phi}\right)^2 \frac{\sinh(2/\xi)}{\cosh(2/\xi) - \cos qa} \quad . \quad (127)$$

These amplitudes are shown in Fig. 2 as a function of qa [for simplicity we take $\xi = 10$ and $n_K = \exp \times (-\beta E_\phi)$]. Both S_{SS} and S_{CC} are mild functions of qa whereas $S(q,k)$ becomes a sensitive function of qa as n_K, the number of kinks, approaches zero.

The three probes $S(q,k)$, $S_{SS}(q)$, and $S_{CC}(q)$ detect three qualitatively different features of the system; $S(q,k)$ is sensitive to the presence of kinks, $S_{SS}(q)$ is sensitive to displacement fluctuations (phonons); and $S_{CC}(q)$ is sensitive to width fluctuations

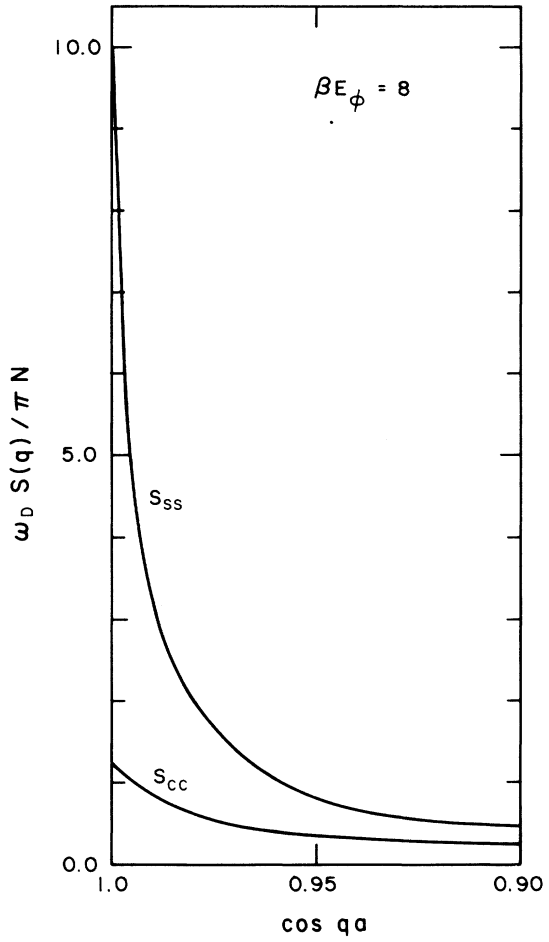

FIG. 2. Sine and cosine amplitudes as a function of qa. The amplitudes of the sine and cosine scattering factors, Eqs. (126) and (127), are shown as a function of qa for $\beta E_\phi = 8$. Changes in temperature produce a mild change in the amplitude of these functions. The amplitude, $S(qk,0)$, Eq. (125), is of order 10^{-3} for $k = q$ at $\beta E_\phi = 8$ and is not shown. Although the scattering from kinks is not strong enough to appear in the static structure factors, it dominates the $\omega \to 0$ dynamic structure factor.

(breathers). (Of course, in the heavy damping limit the dynamics of all of these is seen as an $\omega \to 0$ mode.) From this observation we learn that the breathers make themselves known in the equilibrium statistical mechanics through renormalization of the $n = 0$ band width and in the $n = 2$ band. For example, $\cos\theta_i$ correlations on the equilibrium chain obey

$$\langle\langle \cos\theta_i \cos\theta_j \rangle\rangle = \sum_\nu \langle 0|\cos\theta|\nu\rangle \langle \nu|\cos\theta|0\rangle \times e^{-|n_i - n_j|\beta(\epsilon_\nu - \epsilon_0)} \quad . \quad (128)$$

From Eqs. (121) this reduces to

$$\langle\langle \cos\theta_i \cos\theta_j \rangle\rangle = 8(k_B T/E_\phi)^2 \exp(-2|n_i - n_j|/\xi) \quad . \quad (129)$$

Width fluctuations or cosine correlations decay over length $l_{CC} = \frac{1}{2}\xi$. Similarly the displacement fluctuations or sine correlations $\langle\langle \sin\theta_i \sin\theta_j \rangle\rangle$ decay over length $l_{SS} = \xi$. Both l_{CC} and l_{SS} are independent of temperature. On the other hand the correlations involved in $S(qk;\omega)$ decay over length $l = \exp(+\beta E\phi)$, $l \to +\infty$ as $T \to 0$.

Now let us turn to a discussion of the diffusion constant for the sine-Gordon chain. From above, Sec. V we consider the diffusion of the center of mass Θ,

$$\Theta = \frac{1}{N}\sum_{i=1}^{N} \theta_i \quad . \quad (130)$$

We define

$$D = \tfrac{1}{2}\lim_{t\to 0} \frac{d}{dt}\langle(\Theta - \Theta_0)_t^2\rangle \quad . \quad (131)$$

If we proceed directly to evaluate this expression we are led to an equation much like Eq. (81). Instead of proceeding in this way we use the result of the discussions in Sec. II (see also remarks in Sec. IV). The diffusion constant is related to the mobility by an Einstein relation; the mobility can be calculated directly in terms of the probability current for which a very simple expression obtains. Then we have

$$D = k_B T D_0 (2\pi)^2 \Big/ \int_0^{2\pi} \frac{d\theta}{\rho_0(\theta)} \quad . \quad (132)$$

where $\rho_0(\theta)$ is the single-particle density for the equilibrium problem; see Appendix B. A substantial amount of discussion about this formulation of a calculation of the current is already in the literature, the role of kinks as current carrying entities has been discussed, etc. We refer the reader to this literature for details.[8,26]

The principal point we wish to make here is that the probability current, displacement current, and diffusion constant are well defined and exist for the sine-Gordon chain. Thus averages like $\langle(\Theta - \Theta_0)_t^2\rangle$

have well-defined known behavior for large t. This should be compared to the result reported by Schneider and Stoll,[22] $\langle(\Theta-\Theta_0)_t^2\rangle \sim t^{4/3}$, who do their calculations in the weak damping limit.

VIII. CONCLUSION

In this paper we have described an approximate solution to the Smoluchowski equation.[28] *Formal* solution to the Smoluchowski equation and *formal* expressions for single-particle averages, two-particle averages, the linear response, etc., can be written using the complete set of many-particle states generated by the relaxation operator equation. This equation is a many-particle Schrödinger equation. The task of finding a practical method of solution of the relaxation operator equation, is tackled in Sec. III using a variational ansatz. We find that the many-particle excited states of the relaxation operator for a system can be built up from the many-particle ground state (which is known) using the single-particle states appropriate to the description of the equilibrium statistical mechanics of the system. As a consequence the many-particle quantities, e.g., matrix elements, called for in the formal expressions for averages, etc., are expressed in terms of single-particle quantities, e.g.,single-particle matrix elements, etc. Since, the single-particle problem is well known and easily solved for the systems of interest the variational ansatz yields a remarkably useful solution to the relaxation-operator equation.

We make application of the Smoluchowski equation to two exactly soluble problems (problems for which the relaxation-operator equation can be solved exactly) and we compare an exact calculation of the diffusion constant with a calculation that uses the approximate solution to the relaxation-operator equation found with the variational ansatz. The value of D is the same for both calculations. We take this agreement to support the position that the variational ansatz reliably describes the low-lying excited states of the relaxation operator. This position is given further support when we make application of the variational ansatz to the solution of the relaxation operator equation for the ϕ^4 chain and the sine-Gordon chain. We find that the many particle eigenvalues of the relaxation operator for the ϕ^4 chain agree with a result for these quantities found by Imada (using perturbation theory) for a particular circumstance.

As an illustration of the application of the variational ansatz to a nontrivial problem we examine the behavior of the dynamic structure factors and the linear response of the ϕ^4 chain and the sine-Gordon chain. We also argue that the diffusion constant is well defined for the sine-Gordon chain and that there is no reason to expect exotic long time behavior for this system.

ACKNOWLEDGMENTS

It is a pleasure to thank F. X. Canning and M. D. Miller for helpful discussions. This work was supported in part by the National Science Foundation and by the Army Research Office (Durham).

APPENDIX A: EQUILIBRIUM STATISTICAL MECHANICS

Here we have assembled most of the results that are necessary for carrying out calculations of the equilibrium properties of a system. The equilibrium statistical mechanics of a classical system described by

$$V(1\ \cdots\ N)=\sum_{i=1}^{N}[V_1(u_i)+\tfrac{1}{2}\Gamma_2(u_{i+1}-u_i)^2]\ , \quad \text{(A1)}$$

and subject to the constraint $\delta(u_{N+1}-u_1)$ (this constraint ties the system to itself but leaves it free to move as a whole, e.g., to have a diffusion constant) is given in terms of

$$Z=\int d1\ \cdots\ dN+1\,\delta(u_{N+1}-u_1)e^{-\beta V(1\ \cdots\ N)}\ . \quad \text{(A2)}$$

The partition function Z is calculated exactly using the complete set of states given by the transfer integral equation[6-8]

$$\int du\, e^{-\beta V_1(u)}e^{-\beta\Gamma_2(v-u)^2/2}\psi_\nu(v)=e^{-\beta\epsilon_\nu}\psi_\nu(u)\ . \quad \text{(A3)}$$

We denote the corresponding left-hand function by $\phi_\nu(u)$. Then,

$$Z=\sum_\nu e^{-N\beta\epsilon_\nu} \quad \text{(A4)}$$

and

$$F=-k_BT\ln Z\ . \quad \text{(A5)}$$

For single-particle averages we have

$$\langle\langle A(u_i)\rangle\rangle=\frac{1}{Z}\sum_\nu e^{-N\beta\epsilon_\nu}\langle\nu|A|\nu\rangle=\langle 0|A|0\rangle\ , \quad \text{(A6)}$$

where

$$\langle\nu|A|\mu\rangle=\int du\,\phi_\nu(u)A(u)\psi_\mu(u)$$

and the reduction of $\langle\langle A\rangle\rangle$ to $\langle 0|A|0\rangle$ occurs in the thermodynamic limit, $N\to+\infty$. For a two-particle average we have

$$\langle\langle A(u_i)B(u_j)\rangle\rangle=\sum_\nu\langle 0|A|\nu\rangle\langle\nu|B|0\rangle \times e^{-|n_{ij}|\beta(\epsilon_\nu-\epsilon_0)}\ , \quad \text{(A7)}$$

where $|n_{ij}|=|i-j|$ measures the separation of i and

j on the chain. (Once again we have taken $N \to +\infty$.) (See Ref. 6 or 8 for a slightly more-general form of these averages and for remarks on circumstances that force one to be careful in taking the thermodynamic limit.) Of particular interest are the *single-particle* density

$$\rho^{(1)}(u) = \langle\langle \delta(u_i - u) \rangle\rangle = \phi_0(u)\psi_0(u) \tag{A8}$$

and the two-particle density

$$\rho^{(2)}(u_i u_j) = \langle\langle \delta(u_i - u)\delta(u_j - v) \rangle\rangle = \sum_\nu \phi_0(u)\psi_\nu(u)\phi_\nu(v)\psi_0(v) e^{-|n_{ij}|\beta(\epsilon_\nu - \epsilon_0)} . \tag{A9}$$

It is these latter two equations that are used extensively in the body of the paper, e.g., Sec. III.

The transfer integral equation, Eq. (A2) is reduced to a Schrödinger equation in a variety of circumstances (see, e.g., Ref. 8). Then, Eq. (A2) is replaced by

$$\left(-\frac{1}{2\beta^2\Gamma_2}\frac{d^2}{du^2} + V_1(u)\right)\psi_\nu(u) = \tilde{\epsilon}_\nu \psi_\nu(u) \tag{A10}$$

and $\tilde{\epsilon}_\nu$ differs from ϵ_ν in Eq. (A2) by an unimportant ν-independent additative quantity.[8] Equation (A10) is the Schrödinger-equation approximation (SEA) used extensively above. Although in SEA, $\phi = \psi^*$, we continued to use a notation that is faithful to the form of the original transfer integral problem.[24] Solutions to Eq. (A10) for particular systems of interest are described in Appendix C.

APPENDIX B: MANY-PARTICLE WAVE FUNCTIONS AND MATRIX ELEMENTS

Here we work out various details of the calculations of the properties of the many-particle wave functions, etc., introduced in Sec. III. From Eq. (47) the many-particle wave functions are

$$\Psi_{q\nu}(1 \cdots N) = C_{q\nu} \sum_i e^{i\theta_i} \frac{\psi_\nu(u_i)}{\psi_0(u_i)} \Psi_0(1 \cdots N) . \tag{B1}$$

Thus, we have

$$\langle \Phi_{q'\mu} | \Psi_{q\nu} \rangle = C^*_{q'\mu} C_{q\nu} \sum_i \sum_j e^{+iqan_i} e^{-iq'an_j} \times \langle \Phi_0 | \frac{\phi_\mu(j)}{\phi_0(j)} \frac{\psi_\nu(i)}{\psi_0(i)} | \Psi_0 \rangle , \tag{B2}$$

where $\langle \Phi_0 | \cdots | \Psi_0 \rangle$ is given by

$$\langle \Phi_0 | \cdots | \Psi_0 \rangle = \int d1 \cdots dN + 1 \delta(u_{n+1} - u_1) \Phi_0 \Psi_0 = \langle\langle \cdots \rangle\rangle . \tag{B3}$$

Now, the matrix element on the right-hand side of this equation is simply a two-particle equilibrium average of the type described in Appendix A. Thus we may write

$$\langle \Phi_{q'\mu} | \Psi_{q\nu} \rangle = C^*_{q'\mu} C_{q\nu} \sum_i \sum_j e^{iqan_i} e^{-iq'an_j} M_{\mu\nu} ,$$

where we use Eq. (A7)

$$M_{\mu\nu} = \langle \Phi_0 | \frac{\phi_\mu(j)}{\phi_0(j)} \frac{\psi_\nu(i)}{\psi_0(i)} | \Phi_0 \rangle = \delta_{\mu\nu} e^{-N\beta\epsilon_0} e^{-|n_{ij}|\beta(\epsilon_\nu - \epsilon_0)}$$

The sum on ij yields $\delta_{q,q'}$ and we have

$$\langle \Phi_{q'\mu} | \Psi_{q,\nu} \rangle = \delta_{q,q'} \delta_{\mu\nu} |C_{q\nu}|^2 N T_\nu(q) e^{-N\beta\epsilon_0} . \tag{B4}$$

Here $\exp(-N\beta\epsilon_0)$ is the partition function Z for the equilibrium problem, Eq. (A3), and $T_\nu(q)$ is defined in Eq. (45). We have

$$|C_{q\nu}|^2 = 1/NZT_n(q) , \tag{B5}$$

and for the ground state, $C_0^2 = Z$. Matrix elements of the kind called for in Eqs. (12) and (20) involve the many-particle ground state and an excited state. For example,

$$\langle \Phi_0 | \sum_i A(u_i) | \Psi_{q\nu} \rangle = C_0 C_{q\nu} \sum_i \sum_j e^{iqan_j} \langle \Phi_0 | A(u_i) \frac{\psi_\nu(u_j)}{\psi_0(u_j)} | \Psi_0 \rangle . \tag{B6}$$

Once again reduction is possible using Eq. (A7). We have

$$\langle \Phi_0 | \sum_i A(u_i) | \Psi_{q\nu} \rangle = \delta_{q,0} C_0 C_{q\nu} NZT_\nu(0) \langle 0 | A | \nu \rangle , \tag{B7}$$

where $\langle 0 | A | \nu \rangle$ is a matrix element between single-particle states. For a phased quantity like $A_{q'}(\vec{u})$, Eq. (51), we have

$$\langle \Phi_0 | \sum_i e^{-iq'an_i} A(u_i) | \Psi_{q\nu} \rangle = \delta_{q,q'} C_0 C_{q\nu} NZT_\nu(q) \langle 0 | A | \nu \rangle . \tag{B8}$$

These results permit us to express the AB correlation function in simple form

$$\langle A_{-q}(\vec{u})_t B_q(\vec{u})_0 \rangle = \sum_{q,\nu} T_\nu(q) \langle 0 | A | \nu \rangle \langle \nu | B | 0 \rangle e^{-\delta_{q\nu} t} \tag{B9}$$

APPENDIX C: SINGLE-PARTICLE WAVE FUNCTIONS

In the Schrödinger equation approximation, the transfer integral equation is reduced to the solution

of the differential equation

$$\left(-\frac{1}{2\beta^2\Gamma_2}\frac{d^2}{du^2}+V_1(u)\right)\psi_\nu=\epsilon_\nu\psi_\nu \ . \qquad \text{(C1)}$$

A. The linear chain

The linear-chain problem discussed in Sec. V is described by $V_1=0$. Then, the single-particle wave functions and eigenvalues are

$$\psi_\nu(u)\propto\exp(iKu)$$

and

$$\epsilon_\nu=K^2/2\beta^2\Gamma_2 \ .$$

B. The ψ^4 chain

The ϕ^4 chain problem discussed in Sec. VI is described by

$$V_1(u)=-\tfrac{1}{2}|A|u^2+\tfrac{1}{4}Bu^4 \ . \qquad \text{(C2)}$$

This potential is characterized by a length $u_0^2=|A|/B$ and the well depth $-\frac{1}{4}|A|^2/B$; see Fig. 3(b). The solution to Eq. (C1) with $V_1(u)$ given by Eq. (C2) involves the discrete set of states of a particle in one of two wells that is split by tunneling between the wells. These states are near $-\frac{1}{4}|A|^2/B$ as $T\to 0$, they are split by $\exp(-\beta E_S)$ (E_S is the energy of the ϕ^4 soliton[7]) and separated by k_BT as $T\to 0$.

C. The sine-Gordon chain

The sine-Gordon chain problem discussed in Sec. VI is described by

$$V_1(u)=V_1(\theta)=-E_1\cos\theta \ . \qquad \text{(C3)}$$

Thus Eq. (C1) becomes the Mathieu equation

$$\left(-\frac{1}{2\beta^2E_2}\frac{d^2}{d\theta^2}-E_1\cos\theta\right)\psi_\nu=\epsilon_\nu\psi_\nu \ . \qquad \text{(C4)}$$

The solutions to this equation are in Floquet form. As $T\to 0$, the lowest energies are in the $n=0$ band just above $-E_1$. In this limit

$$\epsilon_\nu\simeq -E_1-n_K(1-\cos\nu) \ ,$$

$|\nu|\leq\frac{1}{2}$, $n_K\simeq\exp(-\beta E)_\phi$ (E_ϕ is the energy of the sine-Gordon soliton); see Fig. 3(c).

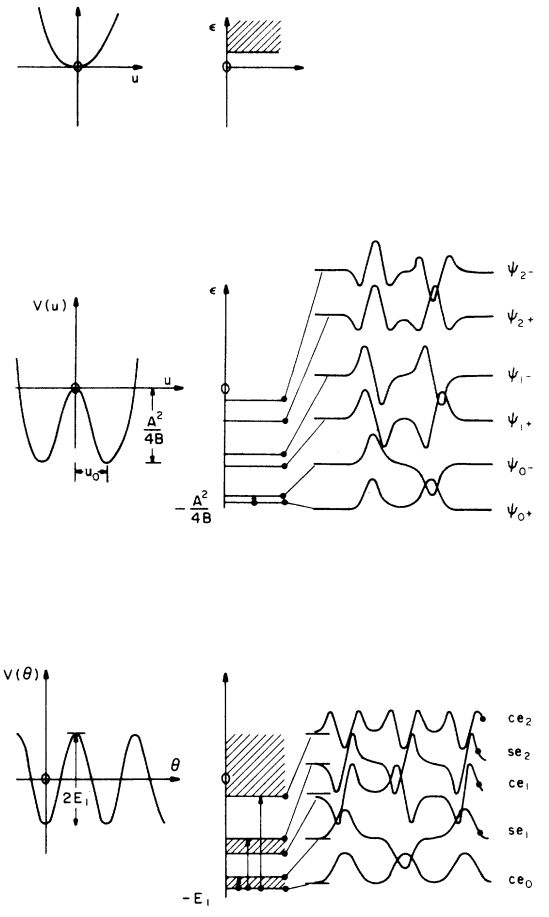

FIG. 3. Eigenvalues and eigenfunctions. The three many-particle problems studied in the text have equilibrium statistical mechanics described in terms of the complete set of states associated with a quantum-mechanical single-particle problem. Each single-particle problem is characterized by a single-particle potential and generates a complete set of eigenfunctions and eigenvalues. The relationship of the single-particle density to the wave functions permits one to understand that fluctuations in the average position of a particle are described by a linear combination of ce_0 and se_2 (or ψ_{0+},ψ_{1-}), whereas fluctuations in the average width of a particle are described by a linear combination of ce_0 and ce_2 (or ψ_{0+},ψ_{2+}). It is the observation that S_{SS} (S_{CC}) probes the transitions from ce_0 to se_2 (and ce_0 to ce_2) that lead to the identification of these states, se_2 (and ce_2), as giving information about phonons (breathers).

[1]A. C. Scott, F. V. E. Chu, and D. W. McLaughlin, Proc. IEEE 61, 1443 (1973).
[2]G. B. Whitham, *Linear and Non-Linear Waves* (Wiley-Interscience, New York, 1974).
[3]R. Jackiw, Rev. Mod. Phys. 49, 681 (1977).
[4]D. W. McLaughlin and A. C. Scott, Appl. Phys. Lett. 30, 545 (1977).
[5]M. B. Fogel, S. E. Trullinger, A. R. Bishop, and J. A. Krumhansl, Phys. Rev. Lett. 36, 411 (1976); see also, Phys. Rev. B 15, 1578 (1977).
[6]N. Gupta and B. Sutherland, Phys. Rev. A 14, 1790 (1976).
[7]J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B 11, 3535 (1974).
[8](a) R. A. Guyer and M. D. Miller, Phys. Rev. A 17, 1205

(1978); (b) 17, 1774 (1978); (c) Phys. Rev. Lett. 42, 718 (1979).
[9]J. F. Currie, M. B. Fogel, and F. L. Palmer, Phys. Rev. A 16, 796 (1977).
[10]S. Aubrey, J. Chem. Phys. 62, 3217 (1975).
[11]A. Patkos and P. Rujan, Z. Phys. B 33, 163 (1979).
[12]J. V. Jose, Phys. Rev. B 14, 2180 (1976).
[13]G. F. Mazenko and P. S. Sahni, Phys. Rev. B 18, 6139 (1978).
[14]J. V. Jose and P. S. Sahni, Phys. Rev. Lett. 43, 78 (1979).
[15]H. J. Mikeska, J.Phys. C 11, L29 (1978).
[16]D. L. Huber and K. H. Leung (unpublished).
[17]K. Huang, *Statistical Mechanics* (Wiley, New York, 1963).
[18]R. Festa and E. G. d'Agliano, Phys. Status Solidi A 90, 229 (1978).
[20]M. Imada (unpublished). Our results for the ϕ^4 chain as $n_K \to 0$ are the same as those of Imada found by generalizing the procedure described in Refs. 8 and 26.
[21]T. Schneider and E. Stoll, Phys. Rev. Lett. 41, 1429 (1978).
[22]E. Stoll, T. Schneider, and A. R. Bishop, Phys. Rev. Lett. 42, 937 (1979).
[24]We use lower case Greek letters for single-particle wave functions, $\phi, \psi \ldots$, and capital letters for many-particle wave functions, $\Phi, \Psi, \ldots$. We use a notation that regards the left-hand and right-hand single-particle and many-particle wave functions as distinct. This is in deference to a notation that is useful in dealing with transfer integrals, see Ref. 8.
[25]See, for example, E. Feenberg, *Theory of Quantum Fluids* (Academic, New York, 1969).
[26]S. E. Trullinger, M. D. Miller, R. A. Guyer, A. R. Bishop, J. A. Krumhansl, and F. Palmer, Phys. Rev. Lett. 40, 206 (1978).
[27]C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).
[28]G. Wilemski, J. Stat. Phys. 14, 153 (1976).