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Quantum-mechanical harmonic chain attached to heat baths. I. Equilibrium properties

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Starting from quantum Langevin equations for operators we study thermal properties of a one-dimensional harmonic chain to whose ends independent heat baths are attached. In this paper, we mainly discuss the thermal equilibrium state that the chain eventually approaches if the heat baths are at equal temperatures. In the classical limit, this state is determined by the Gibbs ensemble of the free chain, whereas in the quantal case, this is only true if the strength of coupling between chain and heat baths is made infinitely small. We find that corrections for finite coupling strength are appreciable only in boundary layers near both ends of the chain. The thickness of the boundary layers depends only on the temperature and not on the damping constant. Outside these boundary layers we find an analogy between thermal properties of the chain and a discrete random walk.

I. INTRODUCTION

Quantum mechanics of macroscopically large systems has attracted much interest during the past ten years both with respect to fundamental problems[1] and practical applications.[2] For example, the apparent differences in the behavior of classical and quantum systems have raised the question whether within a quantum-mechanical treatment the empirically observed classical aspects of large systems can be deduced. For a class of problems where a single quantum-mechanical degree of freedom couples to a heat bath, this question has been answered in the affirmative in many cases.[3,4] In the present paper we investigate this problem for a macroscopically large system which is coupled to two heat baths. Because both the interactions within the system and the couplings of the heat baths to the system are of short range, we expect that the bulk behavior of the system is described by the Gibbs state of the free system. Deviations of the behavior are to be expected in boundary layers near the heat baths where the coupling strength of the adjacent heat baths enters the state of the system.

We choose as a model a linear harmonic chain with nearest-neighbor interactions to whose ends independent heat baths are attached. Both heat baths introduce energy via fluctuating forces and dissipate energy via damping forces that are proportional to the instantaneous momenta of the particles at the ends of the chain, i.e., we consider Ohmic dissipation. Fluctuations and dissipation are not independent but are connected by a fluctuations-dissipation theorem.[5] In general, long-living correlations of the fluctuating forces exist and therefore a Markovian description is not adequate.[6] The influence of heat baths may most conveniently be described within the framework of quantum Langevin equations which can exactly be derived from a microscopic Hamiltonian model of heat baths.[7,8] The simplicity of this system allows an exact treatment of its equilibrium and nonequilibrium properties. By an appropriate choice of the system parameters we may obtain the classical limit in which we recover the Markovian model studied by Rieder, Lebowitz, and Lieb.[9] To make cross referencing easy we adopt their notation as far as possible.

The outline of the paper is as follows. The model of a damped harmonic chain is discussed in more detail in Sec. II. In Sec. III, we derive the equations of motion for the second moments of the coordinates and momenta of the particles of the chain. In the Ohmic case, the second moments relax towards unique stationary values as time goes to infinity. Because of the linearity of both the chain and the heat baths, the stationary states are Gaussian, and hence completely determined by the stationary second moments. Rather than having to perform the limit of infinite time, these second moments may be obtained as solutions of algebraic equations. In Sec. IV, these equations are solved for the particular case in which the bath temperatures are equal. Finally, in Sec. V, we draw some conclusions.

II. MODEL

A. Harmonic chain

We consider a one-dimensional chain of particles of equal mass m with harmonic nearest-neighbor interactions characterized by a force constant c. The displacement and conjugate momentum of the nth particle are denoted by $x_n(t)$ and $p_n(t)$, respectively. The center of mass movement of a finite chain with length N can be removed by imposing additional harmonic forces to the first and last particles. Dimensionless quantities are introduced by measuring time in units of the inverse of the half Debye frequency $2\omega_D^{-1}=\sqrt{m/c}$ and lengths in units of the lattice constant a. The Hamilton operator for the free chain is then given by

$$H=\frac{1}{2}\sum_{n=1}^{N}p_n^2+\frac{1}{2}\sum_{n=1}^{N-1}(x_n-x_{n+1})^2+\frac{1}{2}x_1^2+\frac{1}{2}x_N^2 \ . \tag{2.1}$$

Of course, this Hamiltonian can be considered as that of a chain consisting of $N+2$ particles with fixed boundary conditions $x_0(t)=x_{N+1}(t)=0$. The Heisenberg equations of the free motion for the operators $x_n(t)$ and $p_n(t)$ are

$$\frac{d}{dt}x_n(t)=p_n(t) \ , \tag{2.2a}$$

$$\frac{d}{dt}p_n(t)=-2x_n(t)+x_{n+1}(t)+x_{n-1}(t) \ . \tag{2.2b}$$

Acting on the mth particle by an external force $F(t)$, the equations of motion for the displacement operators become

$$\frac{d^2}{dt^2}x_n(t)=-2x_n(t)+x_{n+1}(t)+x_{n-1}(t)+\delta_{nm}F(t) \ , \tag{2.3}$$

where δ_{ij} denotes the Kronecker symbol $\delta_{ij}=1$ for $i=j$ and $\delta_{ij}=0$, otherwise. The solution of Eq. (2.3) is given by

$$x_n(t)=x_n^{\text{hom}}(t)+\int_0^t\chi_{nm}^0(t-s)F(s)ds \ , \tag{2.4}$$

where $x_n^{\text{hom}}(t)$ is the solution of Eq. (2.3) with vanishing external force fulfilling the initial conditions $x_n(0)=\hat{x}_n$ and $p_n(0)=\hat{p}_n$, where $\hat{x}_n$ and $\hat{p}_n$ are the displacement and conjugate momentum operators in the Schrödinger picture, respectively, and where $\chi_{nm}^0(t-s)$ is the classical linear response function of the harmonic chain. The linear response function $\chi_{nm}^0(t-s)$ follows from

$$\frac{d^2}{dt^2}\chi_{nm}^0(t)=-2\chi_{nm}^0(t)+\chi_{n+1,m}^0(t)+\chi_{n-1,m}^0(t)+\delta_{nm}\delta(t) \ , \tag{2.5}$$

subject to the condition of causality, $\chi_{nm}^0(t)=0$ for $t<0$. The dynamic susceptibility $\tilde{\chi}_{nm}^0(\omega)$ is related to the linear response function by

$$\chi_{nm}^0(t)=\frac{1}{2\pi}\int_{-\infty}^{+\infty}e^{i\omega t}\tilde{\chi}_{nm}^0(\omega)d\omega \ . \tag{2.6}$$

From Eq. (2.5), the dynamic susceptibility of the harmonic chain with equal mass and spring constants follows as[10]

$$\tilde{\chi}_{nm}^0(\omega)=\frac{2}{N+1}\sum_{\kappa=1}^{N}\frac{\sin(nq^\kappa)\sin(mq^\kappa)}{(\omega^\kappa)^2-\omega^2} \ , \tag{2.7}$$

where q^κ and ω^κ are the wave vector and the frequency of the κth eigenmode of the chain, respectively, given by $q^\kappa=\pi\kappa/(N+1)$ and $\omega^\kappa=2\sin(q^\kappa/2)$. Here and in the following, an upper greek index labels the eigenmode of the harmonic chain. In Eq. (2.7) it is understood that the poles are removed in the upper half of the complex ω plane for the linear response function to fulfill the condition of causality.

Finally, we mention some obvious symmetry properties of the linear response function and the dynamic susceptibility. Because the equations of motion for the operators $x_n(t)$ and $p_n(t)$ are invariant under time reversal $t\rightarrow -t$, the dynamic susceptibility is an even function of the frequency $\tilde{\chi}_{nm}^0(-\omega)=\tilde{\chi}_{nm}^0(\omega)$. Furthermore, the dynamic susceptibility is symmetrical with respect to the exchange of the particle labels n and m, $\tilde{\chi}_{nm}^0(\omega)=\tilde{\chi}_{mn}^0(\omega)$. Because the ends of the chain are on equal footing, we have the mirror symmetry about the middle of the chain, i.e., $\tilde{\chi}_{nm}^0(\omega)=\tilde{\chi}_{N+1-n,N+1-m}^0(\omega)$. Of course, the linear response function $\chi_{nm}^0(t-s)$ has the same symmetry properties in the particle labels as the dynamic susceptibility.

B. Damped harmonic chain

The influence of heat baths on quantum systems can be described by quantum Langevin equations which look formally the same as classical ones.[7] However, for Ohmic dissipation, i.e., a friction proportional to the momentary momentum of the damped particle, a Markovian description is valid only in the classical case whereas in the quantal case, long-living correlations of the fluctuating forces exist. With two independent heat baths attached to the ends of the chain, the quantum Langevin equations for the operators $x_n(t)$ and $p_n(t)$, $n=1,2,\ldots,N$, read

$$\frac{d}{dt}x_n(t)=p_n(t) \ , \tag{2.8a}$$

$$\frac{d}{dt}p_n(t)=-2x_n(t)+x_{n+1}(t)+x_{n-1}(t)-\gamma(\delta_{1n}+\delta_{Nn})p_n(t)+\delta_{1n}E_1(t)+\delta_{Nn}E_N(t) \ , \tag{2.8b}$$

subject to the boundary conditions $x_0(t)=x_{N+1}(t)=0$. The random force operators $E_i(t), i=1,N$, are Gaussian. They have vanishing means $\langle E_i(t)\rangle=0$, and their second moments are determined by the commutators

$$[E_i(t),E_j(s)]=\delta_{ij}2i\hbar\gamma\frac{\partial}{\partial t}\delta(t-s) \ , \tag{2.9}$$

and the symmetrized correlations

$$\frac{1}{2}\langle E_i(t)E_j(s)+E_j(s)E_i(t)\rangle=\delta_{ij}\frac{\gamma}{\pi}\int_0^\infty\hbar\omega\coth\left[\frac{\hbar\beta_i}{2}\omega\right]\cos[\omega(t-s)]d\omega \ . \tag{2.10}$$

Because the heat baths are assumed to be in equilibrium states, the correlation functions of the fluctuating force operators depend on time differences only. As a further consequence, the symmetrized correlations, Eq. (2.10), are related to the commutators, Eq. (2.9), by the Kubo-Martin-Schwinger (KMS) condition.[11,12] In the classical limit $\hbar\rightarrow 0$, the commutators vanish and the symmetrized correlations are proportional to δ functions. That is, the random force operators $E_i(t)$, $i=1,N$, become classical white random forces,

$$\langle E_i(t)E_j(s)\rangle=\delta_{ij}\frac{2\gamma}{\beta}\delta(t-s)\ . \tag{2.11}$$

Hence we recover the model discussed by Rieder, Lebowitz, and Lieb.[9]

We recall that we use dimensionless quantities. Correspondingly, the model is characterized by four dimensionless parameters. Because in the sequel we shall only use dimensionless operators and parameters, we indicate the parameters with the correct physical dimensions by the subscript "ph." The damping constant $\gamma_{\rm ph}$ has been written

$$\gamma_{\rm ph}=\frac{\omega_D}{2}\gamma\ . \tag{2.12}$$

The two parameters determining the fluctuations are

$$\hbar_{\rm ph}=\frac{a^2\omega_D m}{2}\hbar\ , \tag{2.13a}$$

$$(\hbar\beta_i)_{\rm ph}=\frac{2}{\omega_D}\hbar\beta_i,\quad i=1,N\ . \tag{2.13b}$$

Further, we set $k_B=1$ so that $T=\beta^{-1}$ is the dimensionless temperature. Then $\hbar=2(\hbar)_{\rm ph}/(a^2m\omega_D)$ is given by the ratio of the square of the uncertainty of the coordinate of an oscillator with mass m and frequency ω_D in its ground state and the square of the lattice constant. Quantal fluctuations become important for $\hbar\gtrsim 1$. Because $\Theta_D=\hbar\omega_D$ is the Debye temperature, we have $\hbar\beta=\Theta_D/2T$. Hence, for $\hbar\beta\ll 1$ all modes are excited and quantal effects can be neglected. For $\hbar\beta\gg 1$ a part of the eigenmodes "freezes out," and a quantal treatment becomes important.

The quantum Langevin equations may conveniently be written in matrix notation. We define a $2N$-dimensional column vector $\mathbf{X}$ with the displacement operators as the first N components followed by the momentum operators, $\mathbf{X}=(x_1,x_2,\ldots,x_N,p_1,p_2,\ldots,p_n)$. Defining further the random force vector $\mathbf{E}$ with the components $(\mathbf{E})_i=\delta_{i,N+1}E_1+\delta_{i,2N}E_N$, we obtain from Eqs. (2.8a) and (2.8b),

$$\frac{d}{dt}\mathbf{X}(t)=-\underline{A}\cdot\mathbf{X}(t)+\mathbf{E}(t)\ . \tag{2.14}$$

Here, $\underline{A}$ is the relaxation matrix which in block form reads

$$\underline{A}=\begin{bmatrix}\underline{0} & -\underline{1}\\ \underline{g} & \gamma\underline{r}\end{bmatrix}\ , \tag{2.15}$$

where $\underline{0}$ and $\underline{1}$ are the zero and unit $N\times N$ matrices, respectively, and where $\underline{g}$ and $\underline{r}$ are given by

$$(\underline{g})_{kl}=-\delta_{k-1,l}+2\delta_{kl}-\delta_{k+1,l}\ , \tag{2.16a}$$

$$(\underline{r})_{kl}=\delta_{kl}(\delta_{1k}+\delta_{Nk})\ . \tag{2.16b}$$

Because the deterministic parts of the quantum Langevin equations are linear, linear response is still exact; cf. Eq. (2.4). Due to the damping terms the eigenfrequencies of the chain are shifted and acquire imaginary parts. Consequently, the poles of the dynamic susceptibility move into the upper half of the complex frequency plane. In Appendix A, we find an expression for the dynamic susceptibility of the damped chain $\tilde{\chi}_{nm}(\omega)$ in terms of $\tilde{\chi}^0_{nm}(\omega)$; cf. Eqs. (A8) and (A9),

$$\tilde{\chi}_{nm}(\omega)=\tilde{\chi}^0_{nm}(\omega)-\frac{i\omega\gamma}{D(\omega)}\{[1+i\omega\gamma\tilde{\chi}^0_{11}(\omega)][\tilde{\chi}^0_{n1}(\omega)\tilde{\chi}^0_{1m}(\omega)+\tilde{\chi}^0_{nN}(\omega)\tilde{\chi}^0_{Nm}(\omega)]$$
$$-i\omega\gamma\tilde{\chi}^0_{1N}(\omega)[\tilde{\chi}^0_{n1}(\omega)\tilde{\chi}^0_{Nm}(\omega)+\tilde{\chi}^0_{nN}(\omega)\tilde{\chi}^0_{1m}(\omega)]\}\ , \tag{2.17}$$

where

$$D(\omega)=[1+i\omega\gamma\tilde{\chi}^0_{11}(\omega)]^2-[i\omega\gamma\tilde{\chi}^0_{1N}(\omega)]^2\ . \tag{2.18}$$

The damping leaves unchanged the symmetry relations in the indices n and m, and hence we have

$$\tilde{\chi}_{nm}(\omega)=\tilde{\chi}_{mn}(\omega)\ , \tag{2.19a}$$

$$\tilde{\chi}_{N+1-n,N+1-m}(\omega)=\tilde{\chi}_{nm}(\omega)\ . \tag{2.19b}$$

According to microscopic reversibility, the dynamic susceptibility has the symmetry

$$\tilde{\chi}_{nm}(\omega)=[\tilde{\chi}_{nm}(-\omega)]^*\ , \tag{2.20}$$

where the asterisk denotes the complex conjugate.

III. STATIONARY STATES

In order to study the stationary state, we first set up the equations of motion for the second moments of displacement and momentum operators. For example, we obtain from Eqs. (2.8a) and (2.8b) for the time rate of change of the moment $\langle x_n(t)p_m(t)\rangle$,

$$\frac{d}{dt}\langle x_n(t)p_m(t)\rangle=\langle p_n(t)p_m(t)\rangle-2\langle x_n(t)x_m(t)\rangle+\langle x_n(t)x_{m+1}(t)\rangle+\langle x_n(t)x_{m-1}(t)\rangle$$
$$-\gamma(\delta_{1m}+\delta_{Nm})\langle x_n(t)p_m(t)\rangle+\delta_{1m}\int_0^t ds\,\langle E_1(s)E_1(0)\rangle\chi_{1n}(s)+\delta_{Nm}\int_0^t ds\,\langle E_N(s)E_N(0)\rangle\chi_{Nn}(s)\ , \tag{3.1}$$

where we used the statistical independence of the two heat baths, i.e., $\langle E_1(t)E_N(s)\rangle=0$, the Gaussian nature of the random force operators, and, finally, $\chi_{nm}(t)=\chi_{mn}(t)$; cf. Eq. (2.19a). We note that the right-hand side consists of a linear combination of other second moments and integrals containing the correlation functions of the random forces. By splitting these correlation functions into antisymmetric and symmetric parts, which are given by the commutators, Eq. (2.9), and the symmetrized correlations, Eq. (2.10), respectively, the integrals in Eq. (3.1) may be decomposed into real and imaginary parts. With $\partial\chi_{1n}(t)/\partial t|_{t=0}=\delta_{1n}$ we find for the integrals in Eq. (3.1),

$$\int_0^t \langle E_i(s)E_i(0)\rangle\chi_{1n}(s)ds=i\hbar\gamma\delta_{1n}+D^{xp}(n,\beta_i;t)\ , \tag{3.2}$$

where

$$D^{xp}(n,\beta_i;t)=\tfrac{1}{2}\int_0^t \langle E_i(s)E_i(0)+E_i(0)E_i(s)\rangle\chi_{1n}(s)ds\ . \tag{3.3}$$

In this way one obtains a coupled set of linear inhomogeneous differential equations for the second moments which are most conveniently expressed in matrix notation. The time-dependent covariance matrix $\underline{\tilde{B}}(t)$ is a $2N\times 2N$ matrix with the elements

$$\underline{\tilde{B}}(t)=\begin{bmatrix}\langle x_k(t)x_l(t)\rangle & \langle x_k(t)p_l(t)\rangle\\ \langle p_k(t)x_l(t)\rangle & \langle p_k(t)p_l(t)\rangle\end{bmatrix}\ , \tag{3.4}$$

where, for example, the term $\langle x_k(t)x_l(t)\rangle$ represents an $N\times N$ matrix with the corresponding elements. We use the convention that the first index labels the rows and the second one labels the columns. In the following, we shall always write $2N\times 2N$ matrices in the same block form as in Eq. (3.4). The equation of motion for the covariance matrix then reads

$$\frac{d}{dt}\underline{\tilde{B}}(t)=-\underline{A}\cdot\underline{\tilde{B}}(t)-\underline{\tilde{B}}(t)\cdot\underline{A}^{t}+\underline{\tilde{D}}(t)\ , \tag{3.5}$$

where the matrix $\underline{A}$ is given by Eqs. (2.15) and (2.16) and where $\underline{A}^{t}$ denotes the transpose of $\underline{A}$. The matrix $\underline{\tilde{D}}(t)$ may be decomposed into its real and imaginary part, cf. Eq. (3.2),

$$\underline{\tilde{D}}(t)=i\hbar\gamma\underline{D}_1+\underline{D}(t)\ , \tag{3.6}$$

where $\underline{D}_1$ and $\underline{D}(t)$ are real matrices. $\underline{D}_1$ is an antisymmetric matrix

$$\underline{D}_1=\begin{bmatrix}\underline{0} & \underline{d}_1\\ -\underline{d}_1 & \underline{0}\end{bmatrix}\ , \tag{3.7a}$$

$$(\underline{d}_1)_{kl}=\delta_{kl}(\delta_{1k}+\delta_{Nk})\ . \tag{3.7b}$$

The time dependent symmetric matrix $\underline{D}(t)$ is given by

$$\begin{aligned}\underline{D}(t)=&\sum_{m=1}^{N}D^{xp}(m,\beta_1;t)\underline{D}_2(m)\\ &+\sum_{m=1}^{N}D^{xp}(m,\beta_N;t)\underline{D}_3(m)\\ &+\sum_{m=1}^{N}D^{pp}(m,\beta_1;t)\underline{D}_4(m)\\ &+\sum_{m=1}^{N}D^{pp}(m,\beta_N;t)\underline{D}_5(m)\ ,\end{aligned} \tag{3.8}$$

where $\underline{D}_i(m)$ are $2N\times 2N$ matrices with only a few nonvanishing elements on the Nth and $2N$th rows and columns,

$$\underline{D}_2(m)=\begin{bmatrix}\underline{0} & \underline{d}_2(m)\\ \underline{d}_2^{t}(m) & \underline{0}\end{bmatrix}\ , \tag{3.9a}$$

$$[\underline{d}_2(m)]_{kl}=\delta_{mk}\delta_{1l}\ ; \tag{3.9b}$$

$$\underline{D}_3(m)=\begin{bmatrix}\underline{0} & \underline{d}_3(m)\\ \underline{d}_3^{t}(m) & \underline{0}\end{bmatrix}\ , \tag{3.10a}$$

$$[\underline{d}_3(m)]_{kl}=\delta_{N+1-m,k}\delta_{Nl}\ ; \tag{3.10b}$$

$$\underline{D}_4(m)=\begin{bmatrix}\underline{0} & \underline{0}\\ \underline{0} & \underline{d}_4(m)\end{bmatrix}\ , \tag{3.11a}$$

$$[\underline{d}_4(m)]_{kl}=\delta_{mk}\delta_{1l}+\delta_{1k}\delta_{ml}\ ; \tag{3.11b}$$

$$\underline{D}_5(m)=\begin{bmatrix}\underline{0} & \underline{0}\\ \underline{0} & \underline{d}_5(m)\end{bmatrix}\ , \tag{3.12a}$$

$$[\underline{d}_5(m)]_{kl}=\delta_{Nk}\delta_{N+1-m,l}+\delta_{N+1-m,k}\delta_{Nl}\ ; \tag{3.12b}$$

and where the quantities $D^{xp}(m,\beta_i;t)$ are given by Eq. (3.3), and $D^{pp}(m,\beta_i;t)$ by

$$D^{pp}(m,\beta_i;t)=\tfrac{1}{2}\int_0^t ds\,\langle E_i(s)E_i(0)+E_i(0)E_i(s)\rangle\times\frac{d}{ds}\chi_{1m}(s)\ . \tag{3.13}$$

Using Eqs. (A11) and (2.10) we infer that for finite $\hbar$, $D^{xp}(1,\beta_i;t)$ and $D^{pp}(1,\beta_i;t)$ diverge due to the irregular behavior of the random force correlation functions on very short time scales. These irregularities stem from the unphysical assumption that the frequency spectra of the heat baths extend up to infinity. Thus these divergencies can be removed by introducing, e.g., an upper cutoff on the frequency spectra of the heat baths Ω_D. All other $D^{xp}(m,\beta)$'s and $D^{pp}(m,\beta)$'s are finite.

Analogously to the diffusion matrix $\underline{\tilde{D}}(t)$, the covariance matrix $\underline{\tilde{B}}(t)$ may be decomposed into its real and imaginary parts too, cf. Eq. (3.6),

$$\underline{\tilde{B}}(t)=\underline{B}(t)+\frac{i\hbar}{2}\begin{bmatrix}\underline{0} & \underline{1}\\ -\underline{1} & \underline{0}\end{bmatrix}\ , \tag{3.14}$$

where the imaginary part of $\underline{\tilde{B}}(t)$ is in accordance with the canonical commutation relations of the displacement and conjugate momentum operators and identically fulfills the imaginary part of the equation of motion, Eq. (3.5). The time dependent part $\underline{B}(t)$ is by definition real and symmetric, and obeys the following equation of motion:

$$\frac{d}{dt}\underline{B}(t)+\underline{A}\cdot\underline{B}(t)+\underline{B}(t)\cdot\underline{A}^{t}=\underline{D}(t)\ . \tag{3.15}$$

Using the classical limit of the fluctuating forces, Eq. (2.11), and the analytic behavior of the linear response function at $t=0$, cf. Eq. (A11), we readily obtain from Eqs. (3.3) and (3.13),

$$\lim_{\hbar\to 0} D^{xp}(m,\beta_i;t)=0 \;, \tag{3.16a}$$

$$\lim_{\hbar\to 0} D^{pp}(m,\beta_i;t)=\gamma T_i \delta_{1m} \;. \tag{3.16b}$$

With Eqs. (3.8), (3.16a), and (3.16b) we find

$$\underline{D}_{\rm cl}(t)=\underline{D}_{\rm cl}=\begin{bmatrix} \underline{0} & \underline{0} \\ \underline{0} & \underline{d}_{\rm cl} \end{bmatrix} \;, \tag{3.17a}$$

$$(\underline{d}_{\rm cl})_{kl}=\gamma(T_1\delta_{1k}+T_N\delta_{Nk})\delta_{kl} \;, \tag{3.17b}$$

and hence from Eqs. (3.15), (3.17a), and (3.17b) we recover the classical equation of motion for the covariance matrix studied by Rieder, Lebowitz, and Lieb.[9] As a consequence of long-living correlations of the fluctuating force operators, the quantum-mechanical diffusion matrix $\underline{D}(t)$, Eq. (3.8), turns out to be time dependent, to contain nondiagonal elements, and even to be not non-negative definite.

The formal solution of Eq. (3.15) reads

$$\underline{B}(t)=e^{-\underline{A}t}\underline{B}(0)e^{-\underline{A}^t t}+\int_0^t e^{-\underline{A}(t-s)}\underline{D}(s)e^{-\underline{A}^t(t-s)}ds \;, \tag{3.18}$$

where $\underline{B}(0)$ denotes the symmetrized covariance matrix at the initial time $t=0$. As in the classical case, the matrix $\underline{A}$ describes the relaxation of the initial state towards the stationary state of the chain; cf. Eq. (2.14). Because the poles of the dynamic susceptibility of the damped chain lie in the upper half of the complex frequency plane the eigenvalues of $\underline{A}$ have positive real parts. Hence the contributions from the initial conditions vanish in the limit $t\to\infty$, and a uniquely defined stationary covariance matrix $\underline{B}$ is obtained provided the diffusion matrix has a proper limit $\underline{D}$,

$$\underline{D}=\lim_{t\to\infty}\underline{D}(t) \;. \tag{3.19}$$

The elements of $\underline{D}$ are given by Eqs. (3.8)–(3.12b) where the time-dependent functions $D^{xp}(m,\beta;t)$ and $D^{pp}(m;\beta,t)$ are replaced by their $t\to\infty$ limits:

$$D^{xp}(m,\beta_i)=\tfrac{1}{2}\int_0^\infty \langle E_i(s)E_i(0)+E_i(0)E_i(s)\rangle \chi_{1m}(s)ds \;, \tag{3.20a}$$

$$D^{pp}(m,\beta_i)=\tfrac{1}{2}\int_0^\infty \langle E_i(s)E_i(0)+E_i(0)E_i(s)\rangle \frac{\partial}{\partial s}\chi_{1m}(s)ds \;. \tag{3.20b}$$

The expression for $\underline{D}$ can be further simplified for a long chain, i.e., in the thermodynamic limit. In this limit, it is possible to decompose $D^{pp}(m,\beta)$ into a part proportional to γ and a remaining part that can be expressed in terms of $D^{xp}(m,\beta)$; cf. Eq. (B8). Furthermore, utilizing the mirror symmetry about the middle of the chain of the dynamic susceptibility, one may split the diffusion matrix into an evenly and oddly transforming part under this mirror symmetry. Because the combined action of a reflection about the middle and an exchange of the heat baths leaves the system invariant, the even contribution to $\underline{D}$ may only depend evenly on the temperatures and the odd part oddly. Finally, we obtain

$$\begin{aligned}\underline{D}=&\tfrac{1}{2}\sum_{m=1}^{N}[D'^{pp}(m,\beta_1)+D'^{pp}(m,\beta_N)]\underline{S}_1(m)\\ &+\tfrac{1}{2}\sum_{m=1}^{N}[D^{xp}(m,\beta_1)+D^{xp}(m,\beta_N)]\underline{S}_2(m)\\ &+\tfrac{1}{2}\sum_{m=1}^{N}[D'^{pp}(m,\beta_1)-D'^{pp}(m,\beta_N)]\underline{T}_1(m)\\ &+\tfrac{1}{2}\sum_{m=1}^{N}[D^{xp}(m,\beta_1)-D^{xp}(m,\beta_N)]\underline{T}_2(m) \;,\end{aligned} \tag{3.21}$$

where the even matrices $\underline{S}_1(m)$ and $\underline{S}_2(m)$ are given by

$$\underline{S}_1(m)=\begin{bmatrix} \underline{0} & \underline{0} \\ \underline{0} & \underline{s}_1(m) \end{bmatrix} \;, \tag{3.22a}$$

$$\begin{aligned}[\underline{s}_1(m)]_{kl}=&\delta_{mk}\delta_{1l}+\delta_{1k}\delta_{ml}\\ &+\delta_{N+1-m,k}\delta_{Nl}+\delta_{Nk}\delta_{N+1-m,l} \;;\end{aligned} \tag{3.22b}$$

$$\underline{S}_2(m)=\begin{bmatrix} \underline{0} & \underline{s}_2(m) \\ \underline{s}_2^t(m) & \gamma\underline{s}_3(m) \end{bmatrix} \;, \tag{3.23a}$$

$$[\underline{s}_2(m)]_{kl}=\delta_{mk}\delta_{1l}+\delta_{N+1-m,k}\delta_{Nl} \;, \tag{3.23b}$$

$$\underline{s}_3(m)=-\underline{s}_1(m-2)+2\underline{s}_1(m-1)-\underline{s}_1(m) \;; \tag{3.23c}$$

and the odd matrices $\underline{T}_1(m)$ and $\underline{T}_2(m)$ by

$$\underline{T}_1(m)=\begin{bmatrix} \underline{0} & \underline{0} \\ \underline{0} & \underline{t}_1(m) \end{bmatrix} \;, \tag{3.24a}$$

$$\begin{aligned}[\underline{t}_1(m)]_{kl}=&\delta_{mk}\delta_{1l}+\delta_{1k}\delta_{ml}\\ &-\delta_{N+1-m,k}\delta_{Nl}-\delta_{Nk}\delta_{N+1-m,l} \;;\end{aligned} \tag{3.24b}$$

$$\underline{T}_2(m)=\begin{bmatrix} \underline{0} & \underline{t}_2(m) \\ \underline{t}_2^t(m) & \gamma\underline{t}_3(m) \end{bmatrix} \;, \tag{3.25a}$$

$$[\underline{t}_2(m)]_{kl}=\delta_{mk}\delta_{1l}-\delta_{N+1-m,k}\delta_{Nl} \;, \tag{3.25b}$$

$$\underline{t}_3(m)=-\underline{t}_1(m)+2\underline{t}_1(m-1)-\underline{t}_1(m-2) \;; \tag{3.25c}$$

we set $\underline{s}_i(m)=\underline{0}$ and $\underline{t}_i(m)=\underline{0}$ for $m\le 0$. Here, the quantities $D^{xp}(m,\beta)$ and $D'^{pp}(m,\beta)$ are given by Eqs. (B9a)–(B9c). Except for $D^{xp}(1,\beta)$, which diverges logarithmically with an upper cutoff Ω_D, all other quantities are finite.

The stationary covariance matrix follows from Eq. (3.18) as time tends to infinity

$$\underline{B}=\lim_{t\to\infty}\underline{B}(t)=\lim_{t\to\infty}\int_0^t e^{-\underline{A}(t-s)}\underline{D}(s)e^{-\underline{A}^t(t-s)}ds \;, \tag{3.26}$$

or, equivalently, by the solution of the algebraic equation

$$\underline{A}\cdot\underline{B}+\underline{B}\cdot\underline{A}^t=\underline{D} \;. \tag{3.27}$$

From Eq. (3.27) the uniqueness of $\underline{B}$ can readily be shown using a standard theorem of linear algebra which says that the solution $\underline{X}$ of $\underline{R}\cdot\underline{X}-\underline{X}\cdot\underline{S}=\underline{T}$ is uniquely determined if the matrices $\underline{R}$ and $\underline{S}$ have no common eigenvalue.[13] Here, $\underline{R}=\underline{A}$ and $\underline{S}=-\underline{A}^t$ may only have a common eigenvalue zero, which, however, does not exist for a chain with fixed boundary conditions.

In this and a following paper, we shall solve Eq. (3.27) for $\underline{B}$ and discuss its solution. Because both the chain and the heat baths are linear systems the stationary state of the chain is Gaussian with vanishing means, $\langle x_k \rangle = 0$ and $\langle p_k \rangle = 0$ for $k = 1, 2, \ldots, N$, and therefore completely determined once the solution of Eq. (3.27) is known.

IV. EQUILIBRIUM STATES

If both heat baths are at equal temperatures, $\beta_1 = \beta_N = \beta$, the chain eventually approaches a stationary equilibrium state. In this state, no heat flows through the chain. Because the thermal equilibrium ensemble of the chain is time reversal invariant, all mixed symmetrized moments $\frac{1}{2}\langle x_k p_l + p_l x_k \rangle$ vanish, and hence

$$\underline{B} = \begin{bmatrix} \underline{x} & \underline{0} \\ \underline{0} & \underline{y} \end{bmatrix} . \tag{4.1}$$

The equilibrium covariance matrix is uniquely given by, cf. Eqs. (3.27), (3.21), and (3.22a)–(3.23c),

$$\underline{A} \cdot \underline{B} + \underline{B} \cdot \underline{A}^{t} = \sum_{m=1}^{N} D'^{pp}(m,\beta) \underline{S}_1(m) + \sum_{m=1}^{N} D^{xp}(m,\beta) \underline{S}_2(m) . \tag{4.2}$$

By linearity, the matrix $\underline{B}$ may be decomposed into matrices $\underline{B}'$ and $\underline{B}''$

$$\underline{B} = \underline{B}' + \underline{B}'' = \begin{bmatrix} \underline{x}' & \underline{0} \\ \underline{0} & \underline{y}' \end{bmatrix} + \begin{bmatrix} \underline{x}'' & \underline{0} \\ \underline{0} & \underline{y}'' \end{bmatrix} , \tag{4.3}$$

which are the respective solutions of

$$\underline{A} \cdot \underline{B}' + \underline{B}' \cdot \underline{A}^{t} = \sum_{m=1}^{N} D'^{pp}(m,\beta) \underline{S}_1(m) , \tag{4.4a}$$

$$\underline{A} \cdot \underline{B}'' + \underline{B}'' \cdot \underline{A}^{t} = \sum_{m=1}^{N} D^{xp}(m,\beta) \underline{S}_2(m) . \tag{4.4b}$$

As is the matrix $\underline{B}$, $\underline{B}'$, and $\underline{B}''$ are uniquely determined; cf. the discussion following Eq. (3.27).

We begin determining the matrix $\underline{B}'$. For $\underline{x}'$ and $\underline{y}'$ we easily find the following system of coupled matrix equations:

$$\underline{x}' \cdot \underline{g} - \underline{y}' = \underline{0} , \tag{4.5a}$$

$$\underline{g} \cdot \underline{x}' - \underline{y}' = \underline{0} , \tag{4.5b}$$

$$\gamma \underline{r} \cdot \underline{y}' + \gamma \underline{y}' \cdot \underline{r} = \sum_{m=1}^{N} D'^{pp}(m,\beta) \underline{s}_1(m) , \tag{4.5c}$$

where the matrices $\underline{s}_1(m)$ are given by Eq. (3.22b). Using for the quantities $D'^{pp}(m,\beta)$ the representation in terms of the dynamic susceptibility of the undamped chain, Eq. (B9a), we transform the inhomogeneity in Eq. (4.5c) into

$$\sum_{m=1}^{N} D'^{pp}(m,\beta)[\underline{s}_1(m)]_{kl} = \gamma \sum_{i=1}^{N} (\underline{r})_{ki} \left[\frac{1}{\beta}\delta_{il} + \frac{4}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{il}(i\nu_n) - \frac{2}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{i,l-1}(i\nu_n) - \frac{2}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{i,l+1}(i\nu_n) \right] + \gamma \sum_{i=1}^{N} \left[\frac{1}{\beta}\delta_{ki} + \frac{4}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{ki}(i\nu_n) - \frac{2}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{k,i-1}(i\nu_n) - \frac{2}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{k,i+1}(i\nu_n) \right] (\underline{r})_{il} . \tag{4.6}$$

Because of Eqs. (4.5a) and (4.5b) the matrices $\underline{y}'$ and $\underline{g}$ commute, and hence they must be functions of each other. Recalling $(\underline{g}^{-1})_{kl} = \tilde{\chi}^{0}_{kl}(0)$, we find from Eqs. (4.5) and (4.6),

$$(\underline{x}')_{kl} = \frac{1}{\beta}\tilde{\chi}^{0}_{kl}(0) + \frac{2}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{kl}(i\nu_n) , \tag{4.7a}$$

$$(\underline{y}')_{kl} = \frac{1}{\beta}\delta_{kl} + \frac{4}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{kl}(i\nu_n) - \frac{2}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{k,l+1}(i\nu_n) - \frac{2}{\beta}\sum_{n=1}^{\infty} \tilde{\chi}^{0}_{k,l-1}(i\nu_n) . \tag{4.7b}$$

This is easily written in a well-known form. We insert the spectral representation of the dynamic susceptibility of the undamped harmonic chain, Eq. (2.7), and use the partial fraction expansion of the coth function.[14] Then we obtain for $\underline{x}'$ and $\underline{y}'$

$$(\underline{x}')_{kl} = \frac{\hbar}{N+1}\sum_{\kappa=1}^{N} \frac{1}{\omega^{\kappa}} \coth\left[\frac{\hbar\beta}{2}\omega^{\kappa}\right] \sin(kq^{\kappa})\sin(lq^{\kappa}) , \tag{4.8a}$$

$$(\underline{y}')_{kl} = \frac{\hbar}{N+1}\sum_{\kappa=1}^{N} \omega^{\kappa} \coth\left[\frac{\hbar\beta}{2}\omega^{\kappa}\right] \sin(kq^{\kappa})\sin(lq^{\kappa}) . \tag{4.8b}$$

These are the second moments of the displacement and momentum operators in the canonical ensemble $\rho = Z^{-1}\exp(-\beta H)$, where $Z = \mathrm{Tr}\exp(-\beta H)$ is the partition function and H denotes the Hamiltonian of the free harmonic chain; cf. Eq. (2.1).

Using $2\sin(kq^{\kappa})\sin(lq^{\kappa}) = \cos[(k-l)q^{\kappa}] - \cos[(k+l)q^{\kappa}]$, both $\underline{x}'$ and $\underline{y}'$ can be written as sums of two matrices with identical elements on the codiagonals [i.e., lines parallel to the diagonal $(1,1),(N,N)$] and cocrossdiagonals [i.e., lines parallel to the crossdiagonal $(1,N),(N,1)$], respectively, i.e., e.g., for $\underline{x}'$,

$$\underline{x}' = \underline{x}'_1 + \underline{x}'_2 , \tag{4.9}$$

where

$$(\underline{x}'_1)_{ij} = \Phi_{|i-j|} , \tag{4.10a}$$

$$(\underline{x}'_2)_{ij} = \Psi_{|N+1-i-j|} . \tag{4.10b}$$

From Eq. (4.8a) Φ_i and Ψ_i, $i=0,1,\ldots,N-1$, follow as

$$\Phi_i=\frac{\hbar}{2(N+1)}\sum_{\kappa=1}^{N}\frac{1}{\omega^\kappa}\coth\left[\frac{\hbar\beta}{2}\omega^\kappa\right]\cos[(i)q^\kappa]\ , \tag{4.11a}$$

$$\Psi_i=-\frac{\hbar}{2(N+1)}\sum_{\kappa=1}^{N}\frac{1}{\omega^\kappa}\coth\left[\frac{\hbar\beta}{2}\omega^\kappa\right]\cos[(N+1-i)q^\kappa]. \tag{4.11b}$$

Note that both matrices are symmetrical with respect to the reflection along the diagonal and crossdiagonal. Matrices of the form of $\underline{x}'_1$ and $\underline{x}'_2$ are referred to as "Toeplitz" and "Hankel" matrices, respectively.[15]

For finite γ, the corrections to the weak-coupling results $\underline{x}'$ and $\underline{y}'$ are given by the matrices $\underline{x}''$ and $\underline{y}''$, respectively, which are the solutions of the following equations, cf. Eqs. (4.3) and (4.4b):

$$\underline{x}''\cdot\underline{g}-\underline{y}''=\sum_{m=1}^{N}D^{xp}(m,\beta)\underline{s}_2(m)\ , \tag{4.12a}$$

$$\underline{g}\cdot\underline{x}''-\underline{y}''=\sum_{m=1}^{N}D^{xp}(m,\beta)\underline{s}_2^{t}(m)\ , \tag{4.12b}$$

$$\underline{r}\cdot\underline{y}''+\underline{y}''\cdot\underline{r}=\sum_{m=1}^{N}D^{xp}(m,\beta)\underline{s}_3(m)\ , \tag{4.12c}$$

where $D^{xp}(m,\beta)$ are given by Eqs. (B9b) and (B9c) and the matrices $\underline{s}_2(m)$ and $\underline{s}_3(m)$ by Eqs. (3.23a)–(3.23c). We note that the quantities $D^{xp}(m,\beta)$, $m=1,2,\ldots$, vanish as $\hbar\rightarrow 0$; cf. Eq. (3.16a). Thus, in the classical limit, the weak-coupling expressions become exact in accordance with the findings for single-particle systems.[8] We may expect that the matrices $\underline{x}''$ and $\underline{y}''$ too, can be represented as linear combination of Toeplitz and Hankel matrices. Indeed, it is easily verified that the solution of Eqs. (4.12a)–(4.12c) is

$$\underline{x}''=\sum_{m=1}^{N}D^{xp}(m+1,\beta)\underline{h}(m)\ , \tag{4.13a}$$

$$\underline{y}''=\sum_{m=1}^{N}[-D^{xp}(m+2,\beta)+2D^{xp}(m+1,\beta)-D^{xp}(m,\beta)]\underline{h}(m)\ , \tag{4.13b}$$

where the Hankel matrices $\underline{h}(m)$ are given by

$$[\underline{h}(m)]_{kl}=\delta_{k+l,m+1}+\delta_{2(N+1)-k-l,m+1}\ . \tag{4.14}$$

That is, the matrices $\underline{h}(m)$ are symmetrical both with respect to the reflection along the diagonal and crossdiagonal, and their nonvanishing elements are placed on the $(N-m)$th cocrossdiagonals. This guarantees the mirror symmetry about the middle of the chain of the second moments $\langle x_kx_l\rangle=\langle x_kx_l\rangle'+\langle x_kx_l\rangle''$ and $\langle p_kp_l\rangle=\langle p_kp_l\rangle'+\langle p_kp_l\rangle''$.

Now the covariance matrix $\underline{B}$ is determined by Eqs. (4.3), (4.7a), (4.7b), (4.13a), and (4.13b). We begin the discussion of $\underline{B}$ by noting that the quantities $D^{xp}(m+1,\beta)$ are negative while the linear combinations $-D^{xp}(m+2,\beta)+D^{xp}(m+1,\beta)-D^{xp}(m,\beta)$ are positive. Hence the covariance of the displacement operators is reduced and that of the momentum operators is increased. This behavior has been found in other open quantum systems if heat baths are coupled via their coordinates.[16–19]

We see from Eqs. (4.13a), (4.13b), and (4.14) that only $\langle p_1^2\rangle''$ and $\langle p_N^2\rangle''$ depend on $D^{xp}(1,\beta)$, which diverges logarithmically with the frequency cutoff Ω_D,

$$\langle p_1^2\rangle''=\langle p_N^2\rangle''\simeq\gamma\frac{\hbar}{\pi}\ln\left[\frac{\hbar\beta}{2\pi}\Omega_D\right]\ , \tag{4.15}$$

whereas all other second moments remain finite. Hence both the weak coupling and the classical limit have to be done for large but finite Ω_D.

From the asymptotic low-temperature behavior of $D^{xp}(m,\beta)$ for small and large damping constants, cf. Eqs. (C10) and (C12), and using Eqs. (4.13a) and (4.13b) we find for the corrections to the weak-coupling result

$$\langle x_k^2\rangle''\simeq-\gamma\frac{\hbar}{2\pi}\frac{1}{k^2},\quad \gamma\ll 1,\quad k<\frac{\hbar\beta}{\pi}\ , \tag{4.16a}$$

$$\langle x_k^2\rangle''\simeq-\frac{\hbar}{\pi}\frac{1}{k},\quad \gamma\rightarrow\infty,\quad k<\frac{\hbar\beta}{\pi}\ ; \tag{4.16b}$$

and

$$\langle p_k^2\rangle''\simeq\gamma\frac{\hbar}{\pi}\frac{4}{k^4},\quad \gamma\ll 1,\quad 2\le k<\frac{\hbar\beta}{\pi}\ , \tag{4.17a}$$

$$\langle p_k^2\rangle''\simeq\frac{\hbar}{\pi}\frac{2}{k^3},\quad \gamma\rightarrow\infty,\quad 2\le k<\frac{\hbar\beta}{\pi}\ . \tag{4.17b}$$

Due to the mirror symmetry the same behavior holds for $k>N/2$, of course. Outside the indicated boundary layer the deviations are exponentially small by a factor of $\exp(-\pi k/\hbar\beta)$.

A boundary layer behavior can be seen in the weak-coupling limit as well. Proceeding along the same lines as in Appendix C, from Eq. (4.7b) we find the low-temperature approximation for $\langle p_k^2\rangle'$ in terms of elementary functions,

$$\langle p_k^2\rangle'\simeq\frac{1}{\beta}\left[\coth\left[\frac{\pi}{2\hbar\beta}\right]+\tfrac{1}{2}\coth\left[\frac{\pi}{2\hbar\beta}(4k-1)\right]-\tfrac{1}{2}\coth\left[\frac{\pi}{2\hbar\beta}(4k+1)\right]\right]\ . \tag{4.18}$$

Hence $\langle p_k^2\rangle'$ exponentially approaches a constant value outside a boundary layer of thickness $\hbar\beta/(2\pi)$ near both ends of the chain,

$$\langle p_k^2\rangle'\simeq\frac{1}{\beta}\coth\left[\frac{\pi}{2\hbar\beta}\right]+\frac{4\pi\hbar}{(\hbar\beta)^2}\exp\left[-\frac{4\pi k}{\hbar\beta}\right]\ ,\quad \frac{\hbar\beta}{2\pi}<k<N/2\ . \tag{4.19}$$

Inside this smaller boundary layer, the enhancement of the momenta decreases like k^{-2} towards the middle of the chain,

$$\langle p_k^2\rangle'\simeq\frac{1}{\beta}\coth\left[\frac{\pi}{2\hbar\beta}\right]+\frac{\hbar}{8\pi}\frac{1}{k^2},\quad 2\le k<\frac{\hbar\beta}{2\pi}\ . \tag{4.20}$$

Hence, in the quantal case, two boundary layers are observed in which the thermal properties of the particles depend on the damping constant γ and in which the weak-coupling expressions for the variance of the momenta depend on the particle site k. Note that the former boundary layer is twice as thick as the latter. In the classical case, both boundary layers vanish. The weak-coupling expressions become exact, and in accordance with the equipartition theorem, the variance of the momenta is independent of the particle site k,

$$\lim_{\hbar\to 0}\langle p_k^2\rangle|_{\rm eq}=T\ . \tag{4.21}$$

Finally, we briefly discuss the mean square of the difference of displacement operators $\langle (x_k-x_l)^2\rangle$. In the classical case, we recover from Eq. (4.8a) the well-known result

$$\lim_{\hbar\to 0}\langle (x_k-x_l)^2\rangle=|k-l|T\ . \tag{4.22}$$

In the quantal case, $\langle (x_k-x_l)^2\rangle$ depends only on the difference $k-l$ outside the boundary layer of thickness $\hbar\beta/\pi$ near both ends of the chain. We choose $\hbar\beta/\pi<k$, $l<N/2$, and let $N\to\infty$. Using the low-temperature approximation of Appendix C, we find

$$\langle (x_k-x_l)^2\rangle\simeq\begin{cases}\dfrac{\hbar}{\pi}[\ln(|k-l|)+2],\ |k-l|<\dfrac{\hbar\beta}{\pi} & (4.23a)\\[2ex] |k-l|T+\dfrac{\hbar}{\pi}\left[\ln\left[\dfrac{\hbar\beta}{\pi}\right]+1\right], & \\[2ex] \qquad |k-l|>\dfrac{\hbar\beta}{\pi}\ . & (4.23b)\end{cases}$$

It is interesting that a similar behavior is found for a Brownian particle with coordinate x where the particle site corresponds to time and $\langle (x_k-x_l)^2\rangle$ goes over to the mean square of the displacement $\langle [x(t)-x(s)]^2\rangle$. At finite temperatures, the Brownian particle moves diffusively as in the classical case,

$$\langle [x(t)-x(s)]^2\rangle\sim|t-s|T\ , \tag{4.24}$$

while at zero temperature $T=0$, a quantal treatment yields[3,20]

$$\langle [x(t)-x(s)]^2\rangle\sim\hbar\ln(\gamma|t-s|)\ . \tag{4.25}$$

In the classical limit, the close analogy of properties of the harmonic chain in thermal equilibrium and the motion of a Brownian particle can be made clear by noting that in thermal equilibrium, the distribution function of the classical harmonic chain is given by

$$\rho_{\rm cl}=Z^{-1}\prod_{n=1}^{N}\exp\left[-\frac{\beta}{2}p_n^2\right]\prod_{n=0}^{N}\exp\left[-\frac{\beta}{2}(x_n-x_{n+1})^2\right]\ . \tag{4.26}$$

Thus interpreting n as a discrete time variable, the increments x_n-x_{n+1} of the process x_n become independent Gaussian random variables and the part of $\rho_{\rm cl}$ depending on the coordinates becomes the path probability of a random walk with diffusion constant T. In the quantal case, the density matrix for the thermal equilibrium state no longer factorizes. For this reason the increments x_n-x_{n+1} are no longer independent from each other. This corresponds to the non-Markovian nature of a quantum diffusion process. Because a quantum analog of the classical path probability is not known as yet, we do not understand the analogy in the quantum case as well as in the classical one.

V. SUMMARY AND OUTLOOK

We studied properties of large open quantum systems for the simple model of a harmonic chain to whose ends independent heat baths are attached. Starting from quantum Langevin equations for operators we derived the equation of motion for the covariance matrix. We showed that as time goes to infinity, the chain approaches a unique stationary state. In the limit as the length of the chain goes to infinity, we obtained a simplified algebraic equation for the stationary covariance matrix from which equilibrium and nonequilibrium properties of the chain may be inferred. Then we assumed that the two heat baths are at equal temperatures so that the chain approaches thermal equilibrium. We showed that in the quantal case, a Gibbs state describes the thermal properties of the whole chain in the weak-coupling limit only. For arbitrary coupling strengths, corrections to the weak-coupling expressions are appreciable only within a boundary layer of thickness $\Theta_D/(2\pi T)$ near both ends of the chain. Finally, we showed that outside this boundary layer thermal properties of the harmonic chain are related to a discrete random walk. The square of the difference of displacement operators shows the absence of long-range order in the harmonic chain. This property is common to all one-dimensional systems with short-range interactions where fluctuations prevent the formation of long-range order and drive the critical temperature to absolute zero. Quantum fluctuations remove this transition even at $T=0$.

In a following paper, we shall investigate the case when the heat baths are at different temperatures, and the chain approaches a stationary nonequilibrium state. Typical nonequilibrium properties as, e.g., the heat flux through the chain and the temperature profile along the chain shall be discussed there.

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APPENDIX A: DYNAMIC SUSCEPTIBILITY

The dynamic susceptibility of the damped harmonic chain $\tilde{\chi}_{jm}(\omega)$ is defined by, cf. Eqs. (2.8a) and (2.8b),

$$(2-\omega^2)\tilde{\chi}_{jm}(\omega)-\tilde{\chi}_{j-1,m}(\omega)-\tilde{\chi}_{j+1,m}(\omega)+\delta_{j1}[i\gamma\omega\tilde{\chi}_{1m}(\omega)]+\delta_{jN}[i\gamma\omega\tilde{\chi}_{Nm}(\omega)]=\delta_{jm}\ , \tag{A1}$$

subject to the boundary conditions

$$\tilde{\chi}_{0m}(\omega)=\tilde{\chi}_{N+1,m}(\omega)=0 \ . \tag{A2}$$

To solve Eq. (A1) we employ a method which takes into account that $\tilde{\chi}^0_{nm}(\omega)$ is the solution of Eq. (A1) for $\gamma=0$. For the time being we assume to know the susceptibilities $\tilde{\chi}_{1m}(\omega)$ and $\tilde{\chi}_{Nm}(\omega)$ and solve for the others in terms of these. For this purpose we introduce the new inhomogeneity

$$F_{jm}=-\delta_{j1}[i\gamma\omega\tilde{\chi}_{1m}(\omega)]-\delta_{jN}[i\gamma\omega\tilde{\chi}_{Nm}(\omega)]+\delta_{jm} \ , \tag{A3}$$

and obtain with Eq. (A1)

$$(2-\omega^2)\tilde{\chi}_{jm}(\omega)-\tilde{\chi}_{j+1,m}(\omega)-\tilde{\chi}_{j-1,m}(\omega)=F_{jm} \ . \tag{A4}$$

The solution of Eq. (A4) reads

$$\tilde{\chi}_{jm}(\omega)=\sum_{l=1}^{N}\tilde{\chi}^0_{jl}(\omega)F_{lm} \ . \tag{A5}$$

In order to determine the as yet unknown susceptibilities $\tilde{\chi}_{1m}(\omega)$ and $\tilde{\chi}_{Nm}(\omega)$, we insert the expression (A3) for F_{lm} and set $j=1,N$. Using $\tilde{\chi}^0_{nm}(\omega)=\tilde{\chi}^0_{N+1-n,N+1-m}(\omega)$ we find in matrix notation

$$\begin{bmatrix} [1+i\gamma\omega\tilde{\chi}^0_{11}(\omega)] & i\gamma\omega\tilde{\chi}^0_{1N}(\omega) \\ i\gamma\omega\tilde{\chi}^0_{1N}(\omega) & [1+i\gamma\omega\tilde{\chi}^0_{11}(\omega)] \end{bmatrix} \times \begin{bmatrix} \tilde{\chi}_{1m}(\omega) \\ \tilde{\chi}_{Nm}(\omega) \end{bmatrix} = \begin{bmatrix} \tilde{\chi}^0_{1m}(\omega) \\ \tilde{\chi}^0_{Nm}(\omega) \end{bmatrix} . \tag{A6}$$

A matrix inversion yields

$$\begin{bmatrix} \tilde{\chi}_{1m}(\omega) \\ \tilde{\chi}_{Nm}(\omega) \end{bmatrix} = \frac{1}{D(\omega)} \begin{bmatrix} [1+i\gamma\omega\tilde{\chi}^0_{11}(\omega)] & -i\gamma\omega\tilde{\chi}^0_{1N}(\omega) \\ -i\gamma\omega\tilde{\chi}^0_{1N}(\omega) & [1+i\gamma\omega\tilde{\chi}^0_{11}(\omega)] \end{bmatrix} \times \begin{bmatrix} \tilde{\chi}^0_{1m}(\omega) \\ \tilde{\chi}^0_{Nm}(\omega) \end{bmatrix} , \tag{A7}$$

where $D(\omega)$ is the determinant of the coefficient matrix, i.e.,

$$D(\omega)=[1+i\gamma\omega\tilde{\chi}^0_{11}(\omega)]^2-[i\gamma\omega\tilde{\chi}^0_{1N}(\omega)]^2 \ . \tag{A8}$$

inserting Eqs. (A3) and (A7) into Eq. (A5), we obtain $\tilde{\chi}_{nm}(\omega)$,

$$\begin{aligned}\tilde{\chi}_{nm}(\omega)=\tilde{\chi}^0_{nm}(\omega)-i\gamma\omega\frac{1}{D(\omega)}\{&[1+i\gamma\omega\tilde{\chi}^0_{11}(\omega)][\tilde{\chi}^0_{n1}(\omega)\tilde{\chi}^0_{1m}(\omega)+\tilde{\chi}^0_{nN}(\omega)\tilde{\chi}^0_{Nm}(\omega)] \\ &-i\gamma\omega\tilde{\chi}^0_{1N}(\omega)[\tilde{\chi}^0_{n1}(\omega)\tilde{\chi}^0_{Nm}(\omega)+\tilde{\chi}^0_{nN}(\omega)\tilde{\chi}^0_{1m}(\omega)]\} \ .\end{aligned} \tag{A9}$$

It is readily seen from Eq. (A11) that the dynamic susceptibility is symmetrical both with respect to the reflection along the diagonal and crossdiagonal, i.e.,

$$\tilde{\chi}_{nm}(\omega)=\tilde{\chi}_{mn}(\omega) \ , \tag{A10a}$$

$$\tilde{\chi}_{nm}(\omega)=\tilde{\chi}_{N+1-n,N+1-m}(\omega) \ . \tag{A10b}$$

Furthermore, the high-frequency behavior is not altered by the damping. In particular, we have

$$\tilde{\chi}_{1n}(\omega)\simeq\tilde{\chi}^0_{1n}(\omega)\sim\frac{1}{\omega^{2n}}, \quad \omega\to\infty \ . \tag{A11}$$

In the thermodynamic limit, for purely imaginary arguments, the dynamic susceptibility of the damped chain can be simplified to give

$$\tilde{\chi}_{1n}(-i\Omega)=\frac{\tilde{\chi}^0_{1n}(i\Omega)}{1+\gamma\Omega\tilde{\chi}^0_{11}(i\Omega)} \ . \tag{A12}$$

The dynamic susceptibility of the undamped harmonic chain can exactly be evaluated; see, for example, Ref. 10,

$$\tilde{\chi}^0_{nm}(i\Omega)=\frac{1}{2\sinh(\alpha)}(e^{-|n-m|\alpha}-e^{-(n+m)\alpha}) \ , \quad n,m<N/2 \ , \tag{A13}$$

where α is given by

$$\Omega=2\sinh\left[\frac{\alpha}{2}\right] . \tag{A14}$$

APPENDIX B: ELEMENTS OF THE DIFFUSION MATRIX

Using the condition of causality, the lower limits of integration in Eqs. (3.20) can be set equal to minus infinity. Thus these integrals may be evaluated in the frequency regime

$$D^{xp}(m,\beta)=\frac{\gamma}{2\pi}\int_{-\infty}^{+\infty}\hbar\omega\coth\left[\frac{\hbar\beta}{2}\omega\right]\tilde{\chi}_{1m}(\omega)d\omega \ , \tag{B1a}$$

$$D^{pp}(m,\beta)=\frac{\gamma}{2\pi}i\int_{-\infty}^{+\infty}\hbar\omega\coth\left[\frac{\hbar\beta}{2}\omega\right]\omega\tilde{\chi}_{1m}(\omega)d\omega \ , \tag{B1b}$$

where we used Eq. (2.10). The integrands are well behaved near $\omega=0$, and hence taking the limit $t\to\infty$ in Eq. (3.19) is justified. The dynamic susceptibility $\tilde{\chi}_{nm}(\omega)$ may be split into its real and imaginary parts, which have different high-frequency behavior

$$\lim_{\omega\to\infty}\mathrm{Re}\tilde{\chi}_{1m}(\omega)\sim\frac{1}{\omega^{2m}} \ , \tag{B2a}$$

$$\lim_{\omega\to\infty}\mathrm{Im}\tilde{\chi}_{1m}(\omega)\sim\frac{1}{\omega^{2m+1}} \ , \tag{B2b}$$

where we have used Eqs. (2.7), (2.17), and (2.18). The short-time behavior of the random force correlation function is different in the quantal case and classical case. For finite $\hbar$, we have

$$\lim_{\omega\to\infty} \omega \coth\left[\frac{\hbar\beta}{2}\omega\right] \sim \omega \ , \tag{B3}$$

whereas performing the limit $\hbar\to 0$ first we find in the classical limit

$$\lim_{\omega\to\infty}\lim_{\hbar\to 0} \frac{\hbar\omega}{2}\coth\left[\frac{\hbar\beta}{2}\omega\right] = \lim_{\omega\to\infty}\frac{1}{\beta} = \text{const} \ . \tag{B4}$$

From Eqs. (B1a), (B1b), (B3), and (B4) it is readily seen that in the quantal case, the quantities $D^{xp}(m,\beta)$ and $D^{pp}(m,\beta)$ are divergent for $m=1$, but are finite in the classical case. These divergencies are a consequence of the assumption that the frictional forces are proportional to the momentary momenta. In reality, the damping depends on the frequency and vanishes as the frequency tends to infinity. In the following, we shall treat a Drude model with the frequency dependent damping coefficient

$$\gamma(\omega)=\gamma\frac{\Omega_D}{\Omega_D+i\omega} \ , \tag{B5}$$

which corresponds to a damping kernel with a finite memory time Ω_D^{-1}.

$$\gamma p(t)\to\gamma\int_{-\infty}^{t}\Omega_D e^{-\Omega_D(t-s)}p(s)ds \ . \tag{B6}$$

The evaluation of the frequency integrals in Eqs. (B1a) and (B1b) is straightforward. We use the defining equation of the dynamic susceptibility, Eq. (A1), and remove the emerging divergencies stemming from the pole of the coth function at $\omega=0$ by taking the Cauchy principal value. Because the poles of the dynamic susceptibility lie in the upper half of the complex frequency plane, we close the path of integration in the lower half of the complex frequency plane enclosing the poles of $\coth(\hbar\beta\omega/2)$ at the imaginary Matsubara frequencies,

$$-i\frac{2\pi}{\hbar\beta}n\equiv -i\nu_n, \quad n=1,2,\ldots \ . \tag{B7}$$

It turns out that it is very convenient to split the terms proportional to γ in $D^{pp}(k,\beta)$. By using

$$[1+\gamma\nu_n\tilde{\chi}^0_{11}(i\nu_n)]^{-1} = 1-\gamma\nu_n\tilde{\chi}^0_{11}(i\nu_n)[1+\gamma\nu_n\tilde{\chi}^0_{11}(i\nu_n)]^{-1}$$

and

$$\tilde{\chi}^0_{1n}(i\Omega)\tilde{\chi}^0_{1m}(i\Omega)=\tilde{\chi}^0_{1,n+m}(i\Omega)$$

as $N\to\infty$, cf. Eq. (A12), we obtain

$$D^{pp}(m,\beta)=D'^{pp}(m,\beta)-D^{xp}(m,\beta) +2D^{xp}(m+1,\beta)-D^{xp}(m+2,\beta) \ , \tag{B8}$$

where

$$D'^{pp}(m,\beta)=\gamma\left[\frac{1}{\beta}\delta_{1m}+\frac{4}{\beta}\sum_{n=1}^{\infty}\tilde{\chi}^0_{1m}(i\nu_n) -\frac{2}{\beta}\sum_{n=1}^{\infty}\tilde{\chi}^0_{1,m-1}(i\nu_n) -\frac{2}{\beta}\sum_{n=1}^{\infty}\tilde{\chi}^0_{1,m+1}(i\nu_n)\right], \quad m=1,2,\ldots, \tag{B9a}$$

$$D^{xp}(1,\beta)=\gamma\frac{\hbar}{\pi}\ln\left[\frac{\hbar\beta}{2\pi}\Omega_D\right] +\gamma\left[\frac{4}{\beta}\sum_{n=1}^{\infty}\frac{1}{\nu_n}\frac{\tilde{\chi}^0_{11}(i\nu_n)}{1+\gamma\nu_n\tilde{\chi}^0_{11}(i\nu_n)} -\frac{2}{\beta}\sum_{n=1}^{\infty}\frac{1}{\nu_n}\frac{\tilde{\chi}^0_{12}(i\nu_n)}{1+\gamma\nu_n\tilde{\chi}^0_{11}(i\nu_n)} +\gamma\frac{2}{\beta}\sum_{n=1}^{\infty}\frac{\tilde{\chi}^0_{11}(i\nu_n)}{1+\gamma\nu_n\tilde{\chi}^0_{11}(i\nu_n)}\right], \tag{B9b}$$

$$D^{xp}(m,\beta)=-\gamma\frac{2}{\beta}\sum_{n=1}^{\infty}\nu_n\frac{\tilde{\chi}^0_{1m}(i\nu_n)}{1+\gamma\nu_n\tilde{\chi}^0_{11}(i\nu_n)} \ , \quad m=2,3,\ldots \ . \tag{B9c}$$

Note that the diverging part of $D^{pp}(1,\beta)$ is identical to that of $D^{xp}(1,\beta)$. From Eqs. (B8) and (B9a)–(B9c) we easily recover the classical limit; cf. Eqs. (3.16a) and (3.16b).

APPENDIX C: LOW-TEMPERATURE APPROXIMATION

Using Eqs. (A13) and (A14) the series representation for $D^{xp}(m,\beta)$, $m=1,2,\ldots$, cf. Eq. (B9c), can be written

$$D^{xp}(m,\beta)=-\gamma\frac{2}{\beta}\sum_{n=1}^{\infty}\frac{2\sinh(\alpha_n/2)e^{-m\alpha_n}}{1+\gamma 2\sinh(\alpha_n/2)e^{-\alpha_n}} \ , \tag{C1}$$

where the quantities α_n are related to the Matsubara frequencies ν_n by

$$\nu_n=2\sinh\left[\frac{\alpha_n}{2}\right] \ . \tag{C2}$$

The right-hand side of Eq. (C1) may be represented as

$$D^{xp}(m,\beta)=-\gamma\frac{2}{\beta}\int_0^{\infty}\sum_{n=-\infty}^{\infty}\delta(x-n)\frac{2\sinh[\alpha(x)/2]e^{-m\alpha(x)}}{1+\gamma^2\sinh[\alpha(x)/2]e^{-\alpha(x)}}dx \ , \tag{C3}$$

where we defined the function $\alpha(x)$ by, see Eq. (C2),

$$2\sinh\left[\frac{\alpha(x)}{2}\right]=\frac{2\pi}{\hbar\beta}x \ . \tag{C4}$$

Using the Poisson summation formula

$$\sum_{n=-\infty}^{\infty} \delta(x-n) = \sum_{l=-\infty}^{\infty} e^{i2\pi l x} , \tag{C5}$$

we obtain from Eq. (C3)

$$D^{xp}(m,\beta) = -\gamma \frac{2}{\beta} \sum_{l=-\infty}^{\infty} \int_0^{\infty} e^{i2\pi l x} \frac{2\sinh[\alpha(x)/2] e^{-m\alpha(x)}}{1+\gamma 2\sinh[\alpha(x)/2] e^{-\alpha(x)}} dx , \tag{C6}$$

where we interchanged the order of summation and integration. Next, we change the integration variable to $\alpha = \arcsin(\pi x/\hbar\beta)$, and obtain

$$D^{xp}(m,\beta) = -\gamma \frac{2\hbar}{\pi} \sum_{l=-\infty}^{\infty} \int_0^{\infty} e^{i2\pi l \hbar\beta \sinh(\alpha)} \frac{2\sinh(\alpha) e^{-m\alpha}}{1+\gamma^2 \sinh(\alpha/2) e^{-\alpha}} d\alpha . \tag{C7}$$

It is only here that an approximation is made. For $\hbar\beta \gg 1$, we approximate $\exp[i2\pi l\hbar\beta\sinh(\alpha)] \simeq \exp(i2\pi l\hbar\beta\alpha)$,

$$D^{xp}(m,\beta) \simeq -\gamma \frac{2\hbar}{\pi} \sum_{l=-\infty}^{\infty} \int_0^{\infty} e^{i2\pi l \hbar\beta\alpha} \frac{2\sinh(\alpha) e^{-m\alpha}}{1+\gamma^2 \sinh(\alpha/2) e^{-\alpha}} d\alpha . \tag{C8}$$

The rest is straightforward. In the two limits $\gamma \ll 1$ and $\gamma \to \infty$, the integration over α is easily done and the emerging series over l are related to the partial fraction of the coth function.[14] For small damping constants, we find in leading order

$$D^{xp}(m,\beta) \simeq -\frac{\gamma}{2\beta} \left[\coth\left[\frac{\pi}{2\hbar\beta}(2m-1) \right] - \coth\left[\frac{\pi}{2\hbar\beta}(2m+1) \right] \right] . \tag{C9}$$

Using the Laurent series expansion for the coth-function, we find

$$D^{xp}(m,\beta) \simeq -\gamma \frac{\hbar}{2\pi} \frac{1}{m^2}, \quad m < \frac{\hbar\beta}{\pi} . \tag{C10}$$

This algebraic decrease goes over into an exponential one,

$$D^{xp}(m,\beta) \simeq -\gamma\hbar\pi \frac{1}{(\hbar\beta)^2} \exp\left[-\frac{\pi m}{\hbar\beta} \right], \quad m > \frac{\hbar\beta}{\pi} . \tag{C11}$$

Similarly, for large γ we obtain from Eq. (C8)

$$D^{xp}(m,\beta) \simeq -\frac{\hbar}{\pi} \frac{1}{m}, \quad m < \frac{\hbar\beta}{\pi} \tag{C12}$$

and

$$D^{xp}(m,\beta) \simeq -\hbar\pi \frac{1}{\hbar\beta} \exp\left[-\frac{\pi m}{\hbar\beta} \right], \quad m > \frac{\hbar\beta}{\pi} . \tag{C13}$$

A more complete discussion may be found in Ref. 21.

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[1] A. J. Leggett, Suppl. Prog. Phys. **69**, 80 (1980).
[2] *SQUID'85*, edited by H. D. Hahlblom and H. Lübbig (de Gruyter, Berlin, 1985).
[3] H. Grabert, P. Schramm, and G. L. Ingold, Phys. Rep. **168**, 115 (1988), and references cited therein.
[4] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 250 (1990).
[5] H. B. Callen and W. A. Welton, Phys. Rev. **83**, 34 (1951).
[6] P. Talkner, Ann. Phys. (N.Y.) **167**, 390 (1985).
[7] G. W. Ford, M. Kac, and P. Mazur, J. Math. Phys. **6**, 504 (1965).
[8] R. Benguria and M. Kac, Phys. Rev. Lett. **46**, 1 (1981).
[9] Z. Rieder, J. L. Lebowitz, and E. Lieb, J. Math. Phys. **8**, 1073 (1967).
[10] A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic, New York, 1965).
[11] R. Kubo, J. Phys. Soc. Jpn. **12**, 1570 (1957).
[12] P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959).
[13] F. R. Gantmacher, *Matrizenrechung I* (Deutscher Verlag der Wissenschaften, Berlin, 1958).
[14] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series, and Products* (Academic, New York, 1980).
[15] M. Kac, Ark. Fys. Semin. Trondheim **11** (1968).
[16] H. Grabert, U. Weiss, and P. Talkner, Z. Phys. B **55**, 87 (1984).
[17] P. Riseborough, P. Hänggi, and U. Weiss, Phys. Rev. A **31**, 471 (1985).
[18] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, (1), 1 (1987).
[19] F. Guinea, V. Hakim, and A. Muramatsu, Phys. Rev. Lett. **54**, 263 (1985).
[20] V. Hakim and V. Ambegaokar, Phys. Rev. A **32**, 423 (1985).
[21] U. Zürcher, Ph.D. thesis, University of Basel, 1989.