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Some Aspects of the "Harmonic Liquid" Away from Equilibrium[1]

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We deal with some aspects of the "harmonic liquid" away from equilibrium, namely, the correlation function formalism and its extension to the quantum domain. We have found some results similar to those for fluids subject to a temperature gradient. In the quantum case one obtains corrections which are significant at low temperatures.

KEY WORDS: dynamic structure factor; harmonic oscillators; nonequilibrium correlations; quantum oscillators.

1. INTRODUCTION

The linear chain of harmonic oscillators, usually referred to as the "harmonic liquid" [1, 2], is a model which enables one to derive rigorous results when the system is in or away from equilibrium. As an example we can quote work concerning the study of the Brownian motion of a particle in the chain [3–5] or heat conduction through a uniform or disordered chain [3, 6–8]. Our aim is precisely to analyze the harmonic chain in a nonequilibrium situation. To this end our first step must be to find an appropriate nonequilibrium stationary state and to develop the correlation function formalism. The stationary state can be obtained from the exact time evolution of an initial "local equilibrium" state in which the left and right parts of the chain have initial temperatures T_L and T_R, respectively.

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By means of some hypothesis about the interaction matrix it can be proved that the state of the system tends asymptotically to a homogeneous stationary state in which an energy flux is present [9].

From the stationary and time-dependent correlation functions we can arrive at the expressions of the nonequilibrium entropy or the dynamic structure factor. In this sense some previous results have been obtained in Ref. 10. The aforementioned program can be carried out at the classical or quantum levels. The quantum corrections become significant at low temperatures.

The paper is distributed as follows. In Section 2 we introduce the model and proceed to compute some quantities that are related to stationary and time-dependent correlation functions as the energy flux, the entropy, and the dynamic structure factor. Those quantities refer to the stationary state we consider. The nonequilibrium entropy depends on the stationary temperature and on the temperature difference, whereas the structure factor exhibits asymmetric peaks. We then stress the fact that the results we obtain by means of our model are similar to those for fluids subject to a temperature gradient. In Section 3 we generalize our model to the quantum case. We analyze the correlation of positions and momenta, the energy flux, and the entropy and compare them with their classical expressions. Finally, in Section 4 we collect our main results.

2. THE “HARMONIC LIQUID” AWAY FROM EQUILIBRIUM

The harmonic liquid introduced in Ref. 1 consists of a linear infinite chain of identical particles with pure harmonic interactions. Its Hamiltonian is given by

$$H = \sum_{n=-\infty}^{\infty} \frac{p_n^2}{2M} + \frac{1}{2} \sum_{n,m=-\infty}^{\infty} V_{nm} q_n q_m \tag{1}$$

where M is the mass of the particles, q_n the displacement of the nth particle with respect to its equilibrium position and p_n its momentum. As a consequence of the homogeneity of the system, the force constants V_{nm} must be functions of the distance between the particles only and constitute a symmetric positive definite matrix.

Translational invariance will permit us to introduce normal coordinates to diagonalize the Hamiltonian through a discrete Fourier transform. We then define the coordinates $\xi(\theta) = \sum_{n=-\infty}^{\infty} \exp(-in\theta) q_n$ and momenta $\pi(\theta) = \sum_{n=-\infty}^{\infty} \exp(-in\theta) p_n$, such that the Hamiltonian reads

$$H = \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} \left[\frac{1}{2M} \pi(-\theta)\, \pi(\theta) + \frac{1}{2} M\omega^2(\theta)\, \xi(-\theta)\, \xi(\theta) \right] \tag{2}$$

where $\omega^2(\theta) = (1/M) \sum_{n=-\infty}^{\infty} e^{-i(n-m)\theta} V_{nm}$ gives the frequency spectrum of the chain.

To analyze the dynamical properties of the system in thermal equilibrium we introduce the retarded Green function for the displacement

$$G_{nm}(t) = \Theta(t) \langle [q_n(t), q_m] \rangle \tag{3}$$

where $\Theta(t)$ is the Heaviside step function, $[\cdots, \cdots]$ is the classical Poisson bracket and $\langle \cdots \rangle$ is an equilibrium average. The Fourier transform, $\hat{G}_{nm}(\omega) = \int_{-\infty}^{\infty} (dt/2\pi)\, e^{-i\omega t} G_{nm}(t)$ satisfies the equation of motion

$$M\omega^2 \hat{G}_{nm}(\omega) = \sum_{k=-\infty}^{\infty} V_{nk} \hat{G}_{km}(\omega) + \frac{\delta_{nm}}{2\pi} \tag{4}$$

whose formal solution can be easily obtained through diagonalization by means of the discrete Fourier transform. We arrive at

$$\hat{G}_{nm}(\omega) = \frac{1}{2\pi M} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} \frac{e^{i(n-m)\theta}}{\omega^2 - \omega^2(\theta)} \tag{5}$$

Notice that, as a consequence of the linearity of the equations of motion, in particular of Eq. (4), the Green function does not depend on the state in which the average is computed. The relation of G_{nm} with the dynamics of the particles follows from the integration of the equations of motion. The formal solution for the coordinates and momenta are

$$\hat{q}_n(\omega) = -2\pi \sum_{k=-\infty}^{\infty} \hat{G}_{nk}(\omega) [p_k(0) + iM\omega q_k(0)] \tag{6}$$

$$\hat{p}_n(\omega) = 2\pi M \sum_{k=-\infty}^{\infty} \hat{G}_{nk}(\omega) \left[\sum_{l=-\infty}^{\infty} V_{kl} q_l(0) - i\omega p_k(0) \right] \tag{7}$$

where we have defined the Laplace transforms $\hat{q}_n(\omega) = \int_0^{\infty} dt\, e^{-i\omega t} q_n(t)$ and $\hat{p}_n(\omega) = \int_0^{\infty} dt\, e^{-i\omega t} p_n(t)$. Then the complete dynamics of the system is driven by the retarded Green function. Notice also that $G_{nm}(t)$ describes the position of the nth particle at t with the initial conditions $q_k(t=0) = 0$ and $p_k(t=0) = \delta_{km}/2\pi$.

Although the definition of $\hat{G}_{nm}(\omega)$ is valid only if ω belongs to the lower half of the complex plane, it can be analytically continued by means of the integral (5) to the entire plane out of the points $\omega = \pm\omega(\theta)$ of the spectrum of the interaction matrix. For large values of $|\omega|$ or, in other words, for frequencies much larger than the maximum frequency of the spectrum, we can expand $\hat{G}_{nm}(\omega)$ as

$$\hat{G}_{nm}(\omega) \approx \frac{1}{2\pi M\omega^2}\left[\delta_{nm} + \frac{V_{nm}}{M\omega^2} + \cdots\right] \tag{8}$$

Detailed information about the dynamics of the particles can be obtained by integrations of Eq. (5). This can be done formally in the case in which the interaction matrix has a finite range (there exists a finite N such that $V_{nm} = 0$ if $|n-m| > N$). Since $\omega^2(\theta)$ is then a rational function of $e^{i\theta}$ the integrand in Eq. (5) has a finite number of poles in the interval $-\pi < \operatorname{Re}\theta < \pi$ and can be expressed as a finite sum of residua. This enables one to obtain the form of $\hat{G}_{nm}(\omega)$ near its singularities.

In order to compute the integral in Eq. (5) let us define $\omega = s_0\omega(\phi) + is_1\varepsilon$ where $s_0, s_1 = \pm 1$ and $1 \gg \varepsilon > 0$. If $\varepsilon = 0$ the poles of the integrand in the region $\operatorname{Re}\theta \in [-\pi, \pi]$, $\operatorname{Im}\theta > 0$, form a finite set, $I[\phi]$. Then if $|\varepsilon| \to 0$ one has

$$\hat{G}_{nm}[s_0\omega(\phi) + is_1\varepsilon] \approx \frac{-i}{2\pi M}\left[\frac{\exp[|n-m|\,[is_0 s_1 s(\phi)\phi - 2\varepsilon f(\phi)]]}{s_0 s_1 |\omega^2(\phi)'|} + \sum_{\theta\in I(\phi)} \frac{e^{i|n-m|\theta}}{\omega^2(\theta)'}\right] \tag{9}$$

where $f(\phi) = |\omega(\phi)/\omega^2(\phi)'|$ and $s(\phi) = \operatorname{sign}[\omega^2(\phi)']$.

The knowledge of the retarded Green function will permit us to find the time evolution of the dynamic variables and their correlations through Eqs. (6) and (7). Let us assume that at time $t = 0$ the chain is in a "local equilibrium" state in which the right half of the chain is at temperature T_R and the left half is at zero temperature. The system evolves in time obeying the equations of motion, (6) and (7). If the interaction matrix has a finite range and the zero frequency is not present in the spectrum, then the state of the chain tends asymptotically to a stationary state [9].

In order to find the correlations in that statinary state, we first observe that if $f(t)$ is a function such that $\lim_{t\to\infty} f(t)$ exists, then its Laplace transform $\hat{f}(\omega) = \int_0^\infty dt\, e^{-i\omega t} f(t)$ satisfies $\lim_{\omega\to 0} i\omega\hat{f}(\omega) = \lim_{t\to\infty} f(t)$. We then study the Laplace transforms of the correlations. By using the convolution theorem one arrives at the stationary value of an unspecified binary correlation, C_{nm}

$$\lim_{t\to\infty} C_{nm}(t) = i \lim_{\omega\to 0} \omega \sum_{k,l>0} \int_L d\omega_1\, \hat{G}_{nk}(\omega_1)\, F_{kl}(\omega; \omega_1)\, \hat{G}_{lm}(\omega - \omega_1) \tag{10}$$

where the function F_{kl} depends on the specific correlation we compute. The integration path L is a horizontal line between the singularities of $\hat{G}_{nk}(\omega_1)$ at $\mathrm{Im}(\omega_1) = 0$ and those of $\hat{G}_{ml}(\omega - \omega_1)$ at $\mathrm{Im}(\omega_1) = \mathrm{Im}(\omega)$.

In order to estimate the limit in Eq. (10) we first introduce the expression (5) for the Green function $\hat{G}_{nk}(\omega_1)$ and close the integration path L by adding a semicircle in the upper half-plane. Then the integral in Eq. (10) transforms into

$$\frac{1}{2\pi M} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} e^{i(n-k)\theta} \oint_{C} d\omega_1 \frac{\hat{G}_{ml}(\omega - \omega_1) F_{kl}(\omega; \omega_1)}{\omega_1^2 - \omega^2(\theta)} \tag{11}$$

The integration contour includes the poles located at the zeros of the denominator, $\omega_1 = \pm\omega(\theta)$. Then the general form of the limit is

$$\begin{aligned} \lim_{t \to \infty} C_{nm}(t) = {} & -\lim_{\omega \to 0} \frac{\omega}{2M} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi\omega(\theta)} \\ & \sum_{k,l>0} e^{i(n-k)\theta} \, [\hat{G}_{ml}(\omega(\theta) - \omega) \, F_{kl}(\omega; \omega(\theta)) \\ & - \hat{G}_{ml}(\omega(\theta) + \omega) \, F_{kl}(\omega; \omega(\theta))] \end{aligned} \tag{12}$$

After computing the limit on the right-hand side of this last expression one arrives at

$$\lim_{t \to \infty} C_{nm}(t) = \frac{1}{8\pi M^2} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} \frac{e^{i(n-m)\theta}}{\omega^2(\theta)} \sum_{s=-\infty}^{\infty} F_{0s}(0; s(\theta)\, \omega(\theta)) e^{is\theta} \cdot \tag{13}$$

The displacement–momentum correlation $J_{nm} = \langle p_n q_m \rangle$ is a particular case of Eq. (13). By using the particular form of F_{kl} we arrive at the final expression

$$\lim_{t \to \infty} J_{nm}(t) = -\frac{k_{\mathrm{B}} T_{\mathrm{R}}}{2} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} \frac{\sin(n-m)\theta}{\omega(\theta)} \operatorname{sign}(\omega^2(\theta)') \tag{14}$$

where k_{B} is the Boltzmann constant.

These results can be easily generalized to the case in which both parts of the chain have an initial temperature different from zero. As a consequence of the linearity of the equations, the correlations are simply a superposition of those generated by each part. In this case the displacement–momentum correlation follows from Eq. (14) after substitution of T_{R} by $\Delta T = T_{\mathrm{R}} - T_{\mathrm{L}}$. The remaining correlations correspond to the equilibrium ones at temperature $T_{\mathrm{S}} = (T_{\mathrm{R}} + T_{\mathrm{L}})/2$.

Let us study some properties of the correlation (14). The contribution of each normal mode, θ, has the sign of the group velocity,

$c(\theta)=d[d\omega(\theta)/d\theta]$, where d is the space between the equilibrium positions of the particles and the asymptotic form for large distances can be obtained from the singularities in the integrand of Eq. (14) [11]. One obtains the expression

$$\langle p_n q_m\rangle \approx -\frac{k_B \Delta T}{2\pi}\frac{K_{nm}}{n-m} \tag{15}$$

where

$$K_{nm}=\sum_{\phi}\frac{\operatorname{sign}[\omega^2(\phi)'']}{\omega(\phi)}e^{i(n-m)\phi} \tag{16}$$

Here the sum extends over all the values of ϕ such that the group velocity $c(\phi)$ vanishes. One then concludes that the nonequilibrium correlation (15) exhibits long-range behavior.

The displacement–momentum correlation can be related to the mean energy flux through the chain [12]. One obtains

$$\langle j\rangle=\frac{1}{2M}\sum_{n=-N}^{N} nV_{n0}\langle p_0 q_n\rangle=-k_B \Delta T\int_0^{\pi}\frac{d\theta}{2\pi}|\omega(\theta)'| \tag{17}$$

Our result has the only restriction of considering interactions of finite range and therefore it generalizes previous analyses [3, 6, 7] in which nearest-neighbor interactions are assumed. Note the peculiar thermal behavior of the harmonic chain: the energy flux depends on the temperature difference but not on any temperature gradient. As a consequence the harmonic chain has an infinite heat conductivity. The physical meaning of Eq. (17) can be easily understood: phonons propagating from each part of the chain toward the opposite one contribute proportionally to their mean energy, $k_B T$, and their velocity, $c(\theta)$.

An entropy can be assigned to this stationary state through the usual Gibbs definition, $S=-k_B\langle \ln p\rangle$. Its value in terms of the parameters characterizing the stationary state can be easily obtained if we observe that this entropy is a constant of motion for the exact evolution of the system. Then the entropy is the same as in the initial state and can be computed from the equilibrium entropy $s_E(T)$. One arrives at

$$s(T_S,\Delta T)=\frac{1}{2}[s_E(T_R)+s_E(T_L)]=s_E(T_S)+\frac{k_B}{2}\ln(1-\lambda^2) \tag{18}$$

where $\lambda=\Delta T/2T_s$. Notice that $s(T_S,\Delta T)>s_E(T_S)$, and therefore the equilibrium state has the maximum entropy for a given value of the energy.

It is easy now to study dynamic correlations in this stationary state. The time evolution of the correlations can be obtained from the time evolution of the dynamic variables given in Eqs. (6) and (7). As an example let us study the time-dependent correlation defined as

$$Q_n(t) = \langle (q_m - q_m(t)) q_{m-n} \rangle \tag{19}$$

For the Laplace transform of this function we obtain

$$\hat{Q}_n(\omega) = 2\pi \sum_{k=-\infty}^{\infty} i\omega \left[M\hat{G}_{nk}(\omega) - \frac{\delta_{nk}}{2\pi\omega^2} \right] \langle q_k q_0 \rangle + \hat{G}_{nk}(\omega) \langle p_k q_0 \rangle \tag{20}$$

where use has been made of Eq. (6). Now transforming back we get

$$Q_n(t) = \frac{k_B T_S}{M} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} \frac{e^{i(n-m)\theta}}{\omega^2(\theta)} [\cos(\omega(\theta)t) + i\lambda s(\theta) \sin(\omega(\theta)t)] \tag{21}$$

From this result we can study some properties of the diffusion of particles through the chain. The asymptotic form of the dynamic correlation, valid for large distances and times, accounts for the "hydrodynamic-like" behavior of the motion of the particles through the chain. For large n and t we have

$$Q_n(t) \approx \begin{cases} (D/\omega_0)(\omega_0 t - |n| + \lambda n); & \omega_0 t \gg |n| \gg 1 \\ \lambda\, Dt \operatorname{sign}(n); & |n| \gg \omega_0 t \gg 1 \end{cases} \tag{22}$$

where $\omega_0 = c/d$, $c = c(\theta = 0)$ being the sound velocity, and $D = k_B T_S / 2M\omega_0$.

The self-diffusion of a particle is described through the mean square displacement, $\langle [q_n - q_n(t)]^2 \rangle = 2Q_0(t)$. For long times its behavior is linear, with a diffusion coefficient D, whereas for finite times a frequency dependent diffusion coefficient must be introduced through the well-known relation $D(\omega) = \frac{1}{2} \int_{-\infty}^{\infty} dt\, e^{i\omega t} \langle v(t)\, v(0) \rangle$. In the low-frequency limit one recovers the diffusion coefficient, $D(\omega = 0) = D$.

A more detailed description of the dynamics of the chain can be carried out through the density–density correlation function. We then study its spatial Fourier transform,

$$S(k, t) \equiv \int_{-\infty}^{\infty} \frac{dx}{2\pi} e^{-ikx} \langle \rho(x, t)\, \rho(0, 0) \rangle = \frac{1}{d} \sum_{n=-\infty}^{\infty} \langle e^{-ik[x_n(t) - x_0(0)]} \rangle \tag{23}$$

where $x_n(t) = q_n(t) + nd$ is the absolute position of the particle n at time t. That function can be expressed in terms of the correlations of positions,

$Q_n(t)$. Finally, its Fourier transform, the dynamic structure factor, can be obtained for small values of k and $q = k \bmod(2\pi/d)$,

$$S(k,\omega) = \frac{4(1-\lambda^2)}{\pi c} \frac{\gamma_k^2}{[(\omega - cq)^2 + \gamma_k^2(1+\lambda)^2][(\omega + cq)^2 + \gamma_k^2(1-\lambda)^2]} \tag{24}$$

where $\gamma_k = Dk^2$ is the attenuation constant of sound waves in terms of the diffusion coefficient. The form of the dynamic structure factor reveals the fact that the Brillouin peaks are not symmetric, which is due to the presence of the factor λ.

3. THE QUANTUM LINEAR CHAIN

Our purpose in this section is to study the properties of the stationary state of the chain when a quantum description is used. One should realize that, as a consequence of the linear character of our system, the analysis carried out in the classical case applies also to the quantum case. To proceed it is convenient to use the Heisenberg representation of the position and momentum operators

$$q_n(t) = e^{iHt} q_n e^{-iHt} \tag{25}$$

$$p_n(t) = e^{iHt} p_n e^{-iHt} \tag{26}$$

Notice that these operators satisfy the same linear equations of motion as their corresponding classical variables. One can also define the retarded Green function by means of the same expression (3) where the classical variables are substituted again by the Heisenberg operators and the Poisson bracket by $-i/\hbar$ times the commutator. As in the classical case the time evolution of the Heisenberg operators can be expressed in terms of the Green function. Furthermore, the time evolution of the pair correlations and their asymptotic limit differ from the classical case only in the initial equilibrium value of the correlations.

The local equilibrium initial state can be described by means of a canonical density matrix, which is Gaussian. Notice that now the ordering of the operators should be taken into account: correlations of a given number of coordinates and momenta can be expressed as a sum of products of all possible pair correlations with order preserved. Then it is also sufficient to study the evolution of the pair correlations. As indicated in Ref. 4 the difficulties arising from the noncommutative character of the operators can be solved by using the normal product. The equilibrium averages of the normal products are

$$\langle :p_n p_m: \rangle = Mk_B T \left[\frac{\hbar\Omega/k_B T}{\exp[\hbar\Omega/k_B T] - 1} \right]_{nm}$$

$$= \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} e^{i(n-m)\theta} \frac{M\hbar\omega(\theta)}{\exp[\hbar\omega(\theta)/k_B T] - 1} \tag{27}$$

$$\langle :q_n q_m: \rangle = \frac{\hbar}{M} \left[\frac{\Omega^{-1}}{\exp[\hbar\Omega/k_B T] - 1} \right]_{nm}$$

$$= \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} e^{i(n-m)\theta} \frac{\hbar/M\omega(\theta)}{\exp[\hbar\omega(\theta)/k_B T] - 1} \tag{28}$$

$$\langle :p_n q_m: \rangle = 0 \tag{29}$$

At zero temperature, the normal product averages vanish. Then we can see that to take the normal product is equivalent to subtract the "zero-point" fluctuations.

If we use these values in the asymptotic expressions for the correlations (13), we obtain the following results: the correlations $\langle :p_n p_m: \rangle$ and $\langle :q_n q_m: \rangle$ are one-half of the equilibrium ones at temperature T_R and the $\langle :p_n q_m: \rangle$ correlation is given by

$$\langle :p_n q_m: \rangle = -\frac{\hbar}{2} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} \frac{\sin((n-m)\theta)}{\exp[\hbar\omega(\theta)/k_B T_R] - 1} \operatorname{sign}(\omega^2(\theta)') \tag{30}$$

It is interesting to compare this result with the classical one given in Eq. (14). The energy of the particles extends homogeneously over the chain, but the correlations of momenta and displacements differ from their equilibrium counterparts. The reason lies in the fact that in the quantum case the correlations are nonlinear functions of the temperature. On the other hand, the contribution of each normal mode to the momentum–displacement correlation is proportional to its occupation number in the initial state, $N(\theta, T) = (\exp[\hbar\omega(\theta)/k_B T] - 1)^{-1}$. In the limit $\hbar\omega(\theta)/k_B T \ll 1$, it reduces to the classical expression.

In the case in which both parts of the chain have a nonzero initial temperature, the correlations can be expressed as a linear superposition of those originated when only one of the parts was initially at nonzero temperature. In contrast with the classical case, these correlations cannot be simply expressed as a function of a "stationary temperature" and of the difference of the initial temperatures. To simplify the result we restrict ourselves to the case of a small temperature difference and study the "linear response" of the system. Then to first order in $\Delta T = T_R - T_L$ one obtains

$$\langle :p_n q_m: \rangle = -\frac{\hbar \Delta T}{2} \int_{-\pi}^{\pi} \frac{d\theta}{2\pi} \frac{\partial N(\theta, T)}{\partial T} \sin((n-m)\theta) \operatorname{sign}(\omega^2(\theta)') \tag{31}$$

The form of this correlation follows from Fig. 1, in which we have plotted such a quantity as a function of the distance between oscillators in the case of nearest-neighbor interactions. From Fig. 1 one concludes that for large distances the correlation decays in the same form (15) as in the classical case, where now K_{nm} is given by

$$K_{nm} = \frac{\hbar}{k_B} \sum_{\phi} \operatorname{sign}(\omega^2(\phi)'') \frac{\partial N(\phi, T)}{\partial T} e^{i(n-m)\phi} \tag{32}$$

Then the correlations depend also on the mean temperature and increase when increasing the temperature. Moreover, they are smaller than in the classical case because only those normal modes for which $\hbar\omega(\theta)/k_B T \leqslant 1$ are excited.

We can also study the energy flux by means of the procedure outlined above. In this case, however, we should employ the expression of the momenta-displacements correlations given in Eq. (31). One arrives at

$$\langle j \rangle = -\Delta T \frac{\hbar}{2} \int_0^{\pi} \frac{d\theta}{2\pi} |\omega^2(\theta)'| \frac{\partial N(\theta, T)}{\partial T} \tag{33}$$

According to the definition of $N(\theta, T)$, in the classical limit the energy

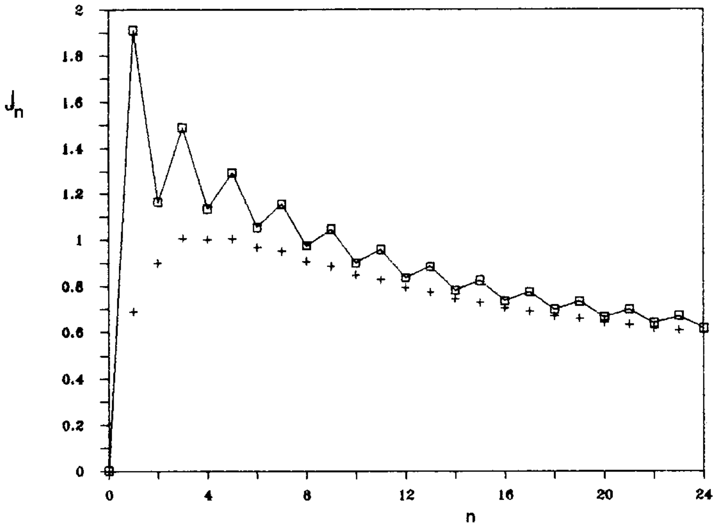

Fig. 1. The dimensionless momentum–displacement correlation function $J_n = 2\pi\omega_0\langle p_0 q_n\rangle/\Delta T$ is plotted as a function of n for $k_B T_S/\hbar\omega_0 = 0.5$ in the case of nearest neighbor interaction. Squares and crosses correspond to the classical and quantum result, respectively.

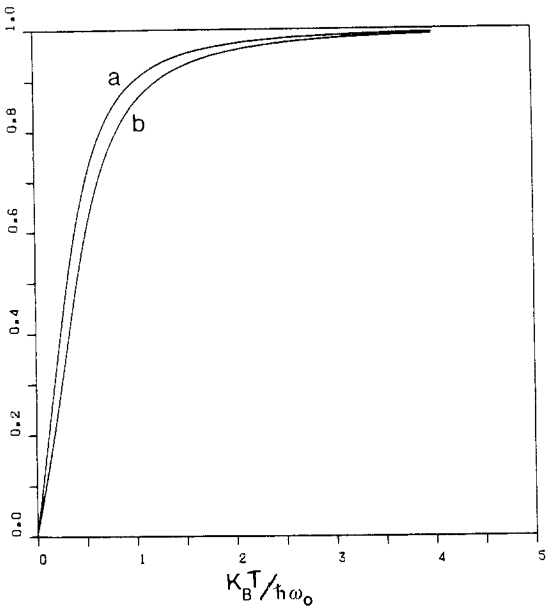

Fig. 2. The ratio between the quantum and classical values of the energy flux (curve a) and the specific heat (curve b) are plotted as a function of the dimensionless quantity $k_B T_S/\hbar\omega_0$.

flux reduces to the classical expression (17). In Fig. 2 we have plotted the ratio between the quantum and classical expressions for the energy flux and the dimensionless quantity $k_B T/\hbar\omega_0$. One observes that it increases with increasing temperature and tends to one.

Finally, we are interested in computing the nonequilibrium entropy of the chain in the quantum case. Following the lines indicated in Section 2 we arrive at the lowest order correction to the equilibrium entropy

$$s(T, \Delta T) = s_E(T) - \frac{C(T)}{8T^2} (\Delta T)^2 \tag{34}$$

where $C(T)$ is the specific heat per particle. Again, with increasing temperature the specific heat tends to k_B; therefore the entropy approaches its corresponding classical value given through the limit $\lambda \to 0$ of Eq. (18). This fact may be observed in Fig. 2, where we have also depicted the specific heat.

4. CONCLUSIONS

To clarify some of the points raised in this paper the following comments may be useful.

We have shown that the "harmonic liquid" is a model that permits us to study the peculiar behavior of the correlation functions away from equilibrium [13] from a Hamiltonian description. In particular, the existence of long-range correlations away from equilibrium is also found in our system. Such a behavior is related to the presence of "external forces" keeping the system away from equilibrium.

Our theory can be extended to the case in which quantum effects become relevant. Correlation functions between coordinates and momenta can also be computed. Such quantities are now operators in the Heisenberg representation and correlations correspond to nonequilibrium averages of their normal products. We have found that the correlations differ from the classical ones. The quantum corrections are negligible in the limit $\hbar\omega(\theta)/k_B T \ll 1$. Our analysis permits us to arrive at expressions for the energy flux and the nonequilibrium entropy that tend to their corresponding classical values when increasing temperature.

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