Journal of Statistical Physics, Vol. 1, No. 3, 1969

Entropy, Information Theory, and the Approach to Equilibrium of Coupled Harmonic Oscillator Systems

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Received September 1, 1969; revised September 19, 1969

Finite segments of infinite chains of classical coupled harmonic oscillators are treated as models of thermodynamic systems in contact with a heat bath, i.e., canonical ensembles. The Liouville function ρ for the infinite chain is reduced by integrating over the "outside" variables to a function ρ_N of the variables of the N-particle segment that is the thermodynamic system. The reduced Liouville function ρ_N, which is calculated from the dynamics of the infinite chain and the statistical knowledge of the coordinates and momenta at $t = 0$, is a time-dependent probability density in the $2N$-dimensional phase space of the system. A Gibbs entropy defined in terms of ρ_N measures the evolution of knowledge of the system (more accurately, the growth of missing pertinent information) in the sense of information theory. As $|t| \to \infty$, energy is equipartitioned, the entropy evolves to the value expected from equilibrium statistical mechanics, and ρ_N evolves to an equilibrium distribution function. The simple chain exhibits diffusion in coordinate space, i.e., Brownian motion, and the diffusivity is shown to depend only on the initial distribution of momenta (not of coordinates) in the heat bath. The harmonically bound chain, in the limit of weak coupling, serves as an excellent model for the approach to equilibrium of a canonical ensemble of weakly interacting particles.

KEY WORDS: entropy; information theory; approach to equilibrium; coupled harmonic oscillators; Liouville function; nonequilibrium statistical mechanics.

1. INTRODUCTION

We consider the approach to equilibrium of a finite subsystem of an infinite chain of coupled harmonic oscillators—the subsystem representing the usual thermodynamic system, and the rest of the chain representing the heat bath. In this approach, we

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follow Blatt,(1) who argues that statistical mechanics is the mechanics of limited, not-completely-isolated systems, rather than of large, complicated ones. Interactions between the system and the outside world govern the approach to equilibrium, rather than the ergodicity of the system *per se.*

Our finite subsystem in an infinite heat bath is equivalent to the canonical ensemble of Gibbs. In this respect, we note that, in equilibrium statistical mechanics, calculations of canonical ensembles (systems open to energy flow) are usually easier and less strained than are those for the isolated, microcanonical ensembles, which must depend on ergodicity.

We define ρ_N, without reference to an ensemble, simply as the probability density in phase space appropriate for our N-particle subsystem, based on our knowledge of the system. (The phase space here considered is the $2s$ N-dimensional space, where s is the number of degrees of freedom of each particle, in which Gibbs represented each system of an ensemble by a point.) We calculate ρ_N as a reduced Liouville function, explicitly obtained from the Liouville function ρ of the infinite system, and automatically satisfying the condition

$$\int_\Gamma \rho_N \, d\Gamma = 1 \tag{1}$$

where Γ is the N-particle phase space. We then use for the entropy the expression

$$S_N = -k_B \int_\Gamma \rho_N \ln(h^{sN}\rho_N) \, d\Gamma \tag{2}$$

where h is (for present purposes) a constant with the units of action, introduced to make the argument of the ln term dimensionless. We regard ρ_N as a time-dependent function that evolves from its initial value via the equations of motion of the coupled-oscillator system, becoming, after a long time, an equilibrium distribution corresponding to the temperature of the heat bath.

Our approach modernizes that of Gibbs,(2) who used an expression similar to Eq. (2) for entropy. With Jaynes,(3) we regard the entropy in terms of information theory, and note that he has shown(4) that Eq. (2) gives the correct entropy of equilibrium thermodynamics when ρ_N is the canonical distribution function. We show in detail that, as the system moves away in time (in either direction) from its initial conditions, increasingly more distant members of the chain become pertinent to the behavior of the subsystem. We illustrate the point made by Katz(5), who states that, as we move away in time from the initial conditions, we move toward a state of knowledge that can only be described as equilibrium.

Mazur and Montroll(6) have studied ergodicity and irreversibility in systems of coupled harmonic oscillators, treating finite and infinite systems in one, two, and three dimensions in great generality. Much of the development presented here is at least implicit in their paper, and the mathematical techniques they exhibit are widely applicable to much more general systems of oscillators than are discussed here. They do not, however, calculate either ρ_N or any expression for the entropy.

By a process, the physical basis of which is not entirely clear to us, Ford *et al.*(7) obtain Brownian motion for a single particle, harmonically coupled to a system of coupled harmonic oscillators. We obtain Brownian motion of a single particle as a direct specialization of a more general result, simply as a consequence of the equations of motion and the dispersion of our knowledge of the initial conditions. The Brownian motion of a single oscillator follows also from the result of Mazur and Montroll[6] that its momentum is generated by a Gaussian random process when the oscillator is coupled properly to an infinite chain of other oscillators.

In Section 2, we develop the dynamics of two specific coupled-oscillator chains; in Section 3, the Liouville function ρ and its reduction ρ_N are calculated in general by means of the characteristic function. Section 4 presents the specific calculation of ρ_N and the entropy as functions of time for both types of chains, and, in Section 5, we show that, as $t \to \infty$, we obtain equipartition of energy from reversible dynamics as a direct consequence of the statistics. We discuss correlations and diffussion in Section 6, where we obtain Brownian motion for the simple chain. Liouville functions of particularly elementary subsystems are displayed explicitly in Section 7, and the entropies of these subsystems are developed in Section 8. In Section 9, we discuss some pertinent background material and the significance of the present work, and Section 10 is a brief historical note, citing earlier work and its relationship to the present paper.

2. DYNAMICS

In this section, we present the solutions to the two kinds of infinite systems to be considered: (a) An infinite chain of masses and springs, as shown in Fig. 1a, for which the Hamiltonian is

$$H_a = \sum_{n=-\infty}^{\infty} [(p_n^2/2m) + \tfrac{1}{2}k(x_{n+1} - x_n)^2] \tag{3}$$

and (b) an infinite chain of masses and springs, with each mass harmonically bound to its coordinate origin via an elastic bar, as shown in Fig. 1b. Here, the Hamiltonian is

$$H_b = \sum_{n=-\infty}^{\infty} [(p_n^2/2m) + \tfrac{1}{2}k(x_{n+1} - x_n)^2 + \tfrac{1}{2}Kx_n^2]. \tag{4}$$

The solution can be obtained by either of two methods: (1) a direct attack of the equations of motion of a particle, leading to an infinite series, or (2) a normal-mode analysis of a finite system, inversion to obtain $x(t)$ and $p(t)$, and calculation of the limit as the number of particles in the chain becomes infinite. In either case, the solutions of the equations of motion can be written

$$x_n(t) = \sum_{r=-\infty}^{\infty} [x_{n+r}(0) f_r(t) + p_{n+r}(0)\, g_r(t)/m\Omega] \tag{5a}$$

and

$$p_n(t) = m\, dx_n(t)/dt = m\dot{x}_n(t). \tag{5b}$$

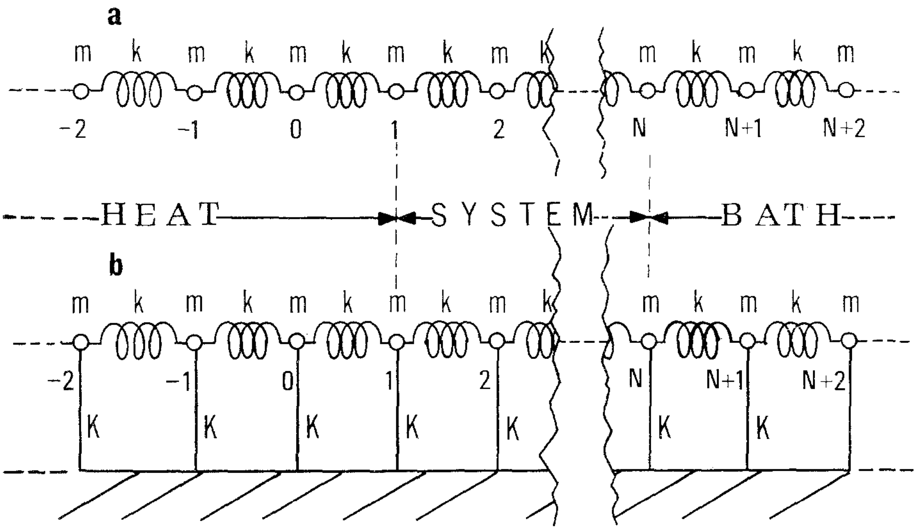

Fig. 1. The two coupled harmonic oscillator chains of this paper, consisting of a thermodynamic system of masses numbered 1 to N and their connecting springs, and a heat bath of the rest of the chain, extending infinitely far in both directions. Case (a) is a simple chain, whereas case (b) has each mass harmonically bound by a leaf spring of constant K to a rigid support structure.

In case (a), $f_r(t)$ is given by a simple Bessel function as

$$f_r(t) = J_{2r}(2\omega t) \tag{6}$$

where $\omega^2 = k/m$, and $g_r(t)$ is given by

$$g_r(t)/\Omega = \int_0^t J_{2r}(2\omega t')\, dt'. \tag{7}$$

In case (b), we obtain

$$f_r(t) = \pi^{-1} \int_0^\pi d\phi \cos r\phi \cos[\Omega t(1 - 2\gamma \cos \phi)^{1/2}] \tag{8}$$

where $\Omega^2 = (K + 2k)/m$ and $\gamma = (\omega/\Omega)^2$. In the most useful subset of case (b), the coupling springs k are much weaker than the localizing spring K, so that we have $\gamma \ll 1$. In this case, Eq. (8) can be approximated as

$$f_r(t) = J_r(\gamma\Omega t) \cos[\Omega t - (r\pi/2)] \tag{9}$$

and the corresponding expression for $g_r(t)$ is

$$g_r(t) = J_r(\gamma\Omega t) \sin[\Omega t - (r\pi/2)]. \tag{10}$$

In both cases, the solutions are time reversible; i.e., $x_n(t) = x_n(-t)$, and $p_n(t) = -p_n(-t)$. The importance of any particle's initial conditions to its own future (or past) is seen to diminish as $|t|$ increases, and the distance of the most important members of the chain is seen to grow. Herein lies the key to the approach to equilibrium.

3. THE LIOUVILLE FUNCTION

One of the main results of this paper is the calculation of the Liouville function, or reductions of it, from a knowledge of the exact solutions of the dynamical variables $x_n(t)$ and $p_n(t)$ in terms of initial values, as given by Eqs. (5)–(10). Given an initial probability distribution for the set $\{x_n(0), p_n(0);\text{ all } n\}$, we seek the probability distribution for these quantities at time t; i.e., we solve for the Liouville function at time t in terms of its value at $t = 0$.

The solution can be given simply in terms of the characteristic function $\phi(\{k_n\}, \{q_n\}, t) \equiv \phi(\mathbf{k}, \mathbf{q}, t)$ as

$$\rho(\{x_n\}, \{p_n\}, t) = \int \exp[-i(\mathbf{k} \cdot \mathbf{x} + \mathbf{q} \cdot \mathbf{p})]\, \phi(\mathbf{k}, \mathbf{q}, t) \prod_n (dk_n/2\pi)(dq_n/2\pi) \tag{11}$$

where $\mathbf{k} \cdot \mathbf{x} = \sum_n k_n x_n$, $\mathbf{q} \cdot \mathbf{p} = \sum_n q_n p_n$, and n ranges over all the (infinite) set of particles. The ρ given by Eq. (11) for the infinite chain satisfies the Liouville equation. The characteristic function is defined as

$$\phi(\mathbf{k}, \mathbf{q}, t) = \int \exp[i(\mathbf{k} \cdot \mathbf{x} + \mathbf{q} \cdot \mathbf{p})]\, \rho(x, p, t) \prod_n dx_n\, dp_n \tag{12}$$

or

$$\phi(\mathbf{k}, \mathbf{q}, t) = \langle \exp[i(\mathbf{k} \cdot \mathbf{x} + \mathbf{q} \cdot \mathbf{p})] \rangle \tag{13}$$

where $\langle \cdots \rangle$ denotes the average over the entire phase space. But, since each $x_n(t)$ and $p_n(t)$ is given by Eqs. (5) in terms of the initial conditions $x_n(0)$, $p_n(0)$, and t, we may obtain the average of Eq. (13) by integrating over the initial conditions, or

$$\phi(\mathbf{k}, \mathbf{q}, t) = \int \exp[i\mathbf{k} \cdot \mathbf{x}(t) + i\mathbf{q} \cdot \mathbf{p}(t)]\, \rho[\{x_n(0)\}, \{p_n(0)\}, 0] \times \prod_n dx_n(0)\, dp_n(0). \tag{14}$$

We are interested principally in the Liouville function reduced for an N-particle subsystem of the chain. This function, denoted by $\rho_N(\{x_n\}, \{p_n\}, t)$, depends only on the positions and momenta of the particles in the subsystem and is obtained from ρ by integrating over all the x_n and p_n that are not in the subsystem. We obtain

$$\rho_N(\{x_n\}, \{p_n\}, t) = \int \exp[-i(\mathbf{k} \cdot \mathbf{x} + \mathbf{q} \cdot \mathbf{p})_N]\, \phi_N(\mathbf{k}, \mathbf{q}, t) \prod_{n=1}^{N} (dk_n/2\pi)(dq_n/2\pi) \tag{15}$$

where

$$\phi_N(\mathbf{k}, \mathbf{q}, t) = \int \exp[i\mathbf{k} \cdot \mathbf{x}(t) + i\mathbf{q} \cdot \mathbf{p}(t)]_N\, \rho[\{x_n(0)\}, \{p_n(0)\}, 0] \times \prod_n dx_n(0)\, dp_n(0). \tag{16}$$

Thus, the influence of the particles outside the subsystem is taken into account because the initial conditions of the entire chain enter the calculation of the reduced characteristic function ϕ_N in Eq. (16), which then determines ρ_N in Eq. (15).

4. CALCULATION OF ρ_N

The system to be studied consists of N adjacent particles of an infinite chain, the remainder of which is regarded as a heat bath. We suppose our knowledge of the initial positions and momenta of the particles in the system to be expressed as skewed Gaussian probability distributions that may be as narrow as techniques of measurement permit. The initial conditions of the heat bath are also expressed as Gaussian distributions, this time not skewed, since we assume no individual knowledge of members of the heat bath. We do, in a sense, make a *nonthermal* assertion about the heat bath when we assume the initial distributions to be uncorrelated Gaussians, rather than the canonical $\exp(-\beta H)$, but the resultant simplification almost justifies the procedure. Our principal justification, however, is our thesis that equilibrium is a state of knowledge; therefore, even when the initial distribution of the surroundings is nonthermal, the subsystem and its surroundings should evolve to a final state of equilibrium as a consequence of the temporal diffusion of ignorance, which is implicit in the dynamics developed in Section 2. We verify that this point of view is valid in Sections 5–7.

We therefore write $\rho(\{x\},\{p\},0)$ as the product of four products, two over the coordinates of the subsystem, here numbered 1 to N, and two over the coordinates of the bath, where Π' denotes the omission of subsystem variables. We have

$$\rho(\{x\},\{p\},0) = \prod_{n=1}^{N} \frac{\exp\{-[x_n(0) - u_n]^2/2\alpha^2\}}{\alpha(2\pi)^{1/2}} \prod_{n=1}^{N} \frac{\exp\{-[p_n(0) - v_n]^2/2\delta^2\}}{\delta(2\pi)^{1/2}} \times \prod{}' \frac{\exp[-x_n^2(0)/2\epsilon^2]}{\epsilon(2\pi)^{1/2}} \prod{}' \frac{\exp[-p_n^2(0)/2\zeta^2]}{\zeta(2\pi)^{1/2}}\,. \tag{17}$$

The expressions needed for Eq. (16) may be written, by use of Eqs. (5), as

$$\begin{aligned}\mathbf{k}\cdot\mathbf{x}(t) &= \sum_{i=1}^{N} k_i \sum_{n=-\infty}^{\infty} [x_n(0) f_{n-i}(t) + p_n(0)\, g_{n-i}(t)/m\Omega] \\ &= \sum_{n=-\infty}^{\infty} x_n(0) \sum_{i=1}^{N} k_i f_{n-i}(t) + \sum_{n=-\infty}^{\infty} [p_n(0)/m\Omega] \sum_{i=1}^{N} k_i\, g_{n-i}(t)\end{aligned} \tag{18}$$

$$\mathbf{q}\cdot\mathbf{p}(t) = m \sum_{n=-\infty}^{\infty} x_n(0) \sum_{i=1}^{N} q_i \dot{f}_{n-i}(t) + m \sum_{n=-\infty}^{\infty} [p_n(0)/m\Omega] \sum_{i=1}^{N} q_i\, \dot{g}_{n-i}(t) \tag{19}$$

We now calculate $\phi_N(k, q, t)$ from Eqs. (16)–(19), using $\int_{-\infty}^{\infty} \exp(-ax^2 + bx)\, dx = (\pi/a)^{1/2} \exp(b^2/4a)$. The result is

$$\phi_N(\mathbf{k}, \mathbf{q}, t) = \prod_{r=1}^{6} P_r \tag{20}$$

where

$$P_1 = \exp\left\{i \sum_{n=1}^{N} u_n \sum_{j=1}^{N} [k_j f_{n-j}(t) + mq_j \dot{f}_{n-j}(t)]\right\} \tag{21a}$$

$$P_2 = \exp\left\{i \sum_{n=1}^{N} (v_n/m\Omega) \sum_{j=1}^{N} [k_j g_{n-j}(t) + mq_j \dot{g}_{n-j}(t)]\right\} \tag{21b}$$

$$P_3' = \exp\left(\sum_{n=1}^{N} (-\alpha^2/2) \left\{\sum_{j=1}^{N} [k_j f_{n-j}(t) + mq_j \dot{f}_{n-j}(t)]\right\}^2\right) \tag{21c$'$}$$

$$P_4' = \exp\left(\sum_{n=1}^{N} (-\delta^2/2m^2\Omega^2) \left\{\sum_{j=1}^{N} [k_j g_{n-j}(t) + mq_j \dot{g}_{n-j}(t)]\right\}^2\right) \tag{21d$'$}$$

$$P_5' = \exp\left(\sum_{n}{}' (-\epsilon^2/2) \left\{\sum_{j=1}^{N} [k_j f_{n-j}(t) + mq_j \dot{f}_{n-j}(t)]\right\}^2\right) \tag{21e$'$}$$

$$P_6' = \exp\left(\sum_{n}{}' (-\zeta^2/2m^2\Omega^2) \left\{\sum_{j=1}^{N} [k_j g_{n-j}(t) + mq_j \dot{g}_{n-j}(t)]\right\}^2\right) \tag{21f$'$}$$

are the naturally arising factors in the integration of Eq. (16). We note, however, that $\sum'$ in P_5' and P_6' can be replaced by $\sum_{n=-\infty}^{\infty}$ if appropriate changes are also made in P_3' and P_4'; therefore, we write

$$P_3 = \exp\left(\sum_{n=1}^{N} [(\epsilon^2 - \alpha^2)/2] \left\{\sum_{j=1}^{N} [k_j f_{n-j}(t) + mq_j \dot{f}_{n-j}(t)]\right\}^2\right) \tag{21c}$$

$$P_4 = \exp\left(\sum_{n=1}^{N} [(\zeta^2 - \delta^2)/2m^2\Omega^2] \left\{\sum_{j=1}^{N} [k_j g_{n-j}(t) + mq_j \dot{g}_{n-j}(t)]\right\}^2\right) \tag{21d}$$

$$P_5 = \exp\left(\sum_{n=-\infty}^{\infty} (-\epsilon^2/2) \left\{\sum_{j=1}^{N} [k_j f_{n-j}(t) + mq_j \dot{f}_{n-j}(t)]\right\}^2\right) \tag{21e}$$

$$P_6 = \exp\left(\sum_{n=-\infty}^{\infty} (-\zeta^2/2m^2\Omega^2) \left\{\sum_{j=1}^{N} [k_j g_{n-j}(t) + mq_j \dot{g}_{n-j}(t)]\right\}^2\right). \tag{21f}$$

The double finite sum in Eq. (21c) is now replaced by

$$\sum_{i,j=1}^{N} [k_i k_j A_{ij}(t) + 2k_i q_j B_{ij}(t) + q_i q_j C_{ij}(t)]$$

where

$$A_{ij}(t) = \sum_{n=1}^{N} f_{n-i}(t) f_{n-j}(t) = A_{ji}(t) \tag{22a}$$

$$B_{ij}(t) = m \sum_{n=1}^{N} f_{n-i}(t) \dot{f}_{n-j}(t) \tag{22b}$$

$$C_{ij}(t) = m^2 \sum_{n=1}^{N} \dot{f}_{n-i}(t) \dot{f}_{n-j}(t) = C_{ji}(t). \tag{22c}$$

The sum in Eq. (21e) is replaced in exactly the same manner by the expression

$$\sum_{i,j=1}^{N} [k_i k_j a_{ij}(t) + 2k_i q_j b_{ij}(t) + q_i q_j c_{ij}(t)]$$

where a_{ij}, b_{ij}, and c_{ij} differ from A_{ij}, B_{ij}, and C_{ij} only by having $\sum_{n=-\infty}^{\infty}$ instead of $\sum_{n=1}^{N}$. Also, since $f_j = f_{-j}$, it may be shown that $b_{ij} = b_{ji}$, a result that is not true for B_{ij}.

We use well-known properties of Bessel functions to calculate a_{ij}, b_{ij}, and c_{ij} in closed form for the two specific chains of Fig. 1. For case (a), we obtain

$$2a_{ij}(t) = \delta_{ij} + J_{2(i-j)}(4\omega t) \tag{23a}$$

$$2b_{ij}(t) = \omega m[J_{2i-2j-1}(4\omega t) - J_{2i-2j+1}(4\omega t)] = (m/2)\, d[J_{2i-2j}(4\omega t)]/dt \tag{23b}$$

$$\begin{aligned} 2c_{ij}(t) = {} & (m\omega)^2[J_{2i-2j+2}(4\omega t) + J_{2i-2j-2}(4\omega t) - 2J_{2i-2j}(4\omega t) \\ & + 2J_{2i-2j}(0) - J_{2i-2j+2}(0) - J_{2i-2j-2}(0)] \end{aligned} \tag{23c}$$

and, for case (b), the results are

$$2a_{ij}(t) = \delta_{ij} + J_{i-j}(2\gamma\Omega t)\cos[2\Omega t - \tfrac{1}{2}(i-j)\pi] \tag{24a}$$

$$2b_{ij}(t) = -m\Omega J_{i-j}(2\gamma\Omega t)\sin[2\Omega t - \tfrac{1}{2}(i-j)\pi] \tag{24b}$$

$$2c_{ij}(t) = (m\Omega)^2\, \delta_{ij} - (m\Omega)^2 J_{i-j}(2\gamma\Omega t)\cos[2\Omega t - \tfrac{1}{2}(i-j)\pi]. \tag{24c}$$

Similarly, the double finite sum in Eq. (21d) is replaced by

$$\sum_{i,j=1} [k_i k_j D_{ij}(t) + 2k_i q_j E_{ij}(t) + q_i q_j A_{ij}(t)]$$

where A_{ij} appears again because $\dot{g}_j = \Omega f_j$, and

$$D_{ij}(t) = (m\Omega)^{-2} \sum_{n=1}^{N} g_{n-i}(t)\, g_{n-j}(t) = D_{ji}(t) \tag{25a}$$

$$E_{ij}(t) = m^{-1}\Omega^{-2} \sum_{n=1}^{N} g_{n-i}(t)\, \dot{g}_{n-j}(t) \tag{25b}$$

and the double sum in Eq. (21f) is replaced by

$$(m\Omega)^2 \sum_{i,j=1}^{N} [k_i k_j\, d_{ij}(t) + 2k_i q_j e_{ij}(t) + q_i q_j a_{ij}(t)]$$

where, as before, d_{ij} and e_{ij} differ from D_{ij} and E_{ij} only by having $\sum_{n=-\infty}^{\infty}$ instead of $\sum_{n=1}^{N}$. Also, as before, we obtain $e_{ij} = e_{ji}$, a result that is not valid in general for E_{ij}. The quantities $d_{ij}(t)$ and $e_{ij}(t)$ can be calculated in closed form; for case (a), we obtain

$$d_{ij}(t) = (t/2\omega m^2)\left[\int_0^{4\omega t} J_0(y)\, dy - J_1(4\omega t)\right] - (2\omega m)^{-2} \sum_{n=1}^{|i-j|} \int_0^{4\omega t} J_{2n-1}(y)\, dy \tag{26a}$$

and

$$e_{ij}(t) = (4\omega m)^{-1} \int_0^{4\omega t} J_{2i-2j}(y)\, dy \tag{26b}$$

and, for case (b), the results are

$$d_{ij}(t) = (m\Omega)^{-4} c_{ij}(t) \tag{27a}$$

and

$$e_{ij}(t) = -(m\Omega)^{-2} b_{ij}(t). \tag{27b}$$

Using these results, we now write Eq. (20) as

$$\phi_N(\mathbf{k}, \mathbf{q}, t) = \exp\left[-\tfrac{1}{2} \sum_{i,j=1}^{N} (k_i k_j M_{ij} + k_i q_j H_{ij} + q_i q_j Q_{ij}) + i \sum_j (k_j U_j + q_j V_j)\right] \tag{28}$$

where

$$M_{ij} = (\alpha^2 - \epsilon^2)\, A_{ij} + \epsilon^2 a_{ij} + (\delta^2 - \zeta^2)\, D_{ij} + \zeta^2\, d_{ij} = M_{ji} \tag{29a}$$

$$H_{ij} = (\alpha^2 - \epsilon^2)\, B_{ij} + \epsilon^2 b_{ij} + (\delta^2 - \zeta^2)\, E_{ij} + \zeta^2 e_{ij} \neq H_{ji} \tag{29b}$$

$$Q_{ij} = (\alpha^2 - \epsilon^2)\, C_{ij} + \epsilon^2 c_{ij} + (\delta^2 - \zeta^2)\, A_{ij} + \zeta^2 a_{ij} = Q_{ji} \tag{29c}$$

$$U_j = \sum_{n=1}^{N} [u_n f_{n-j}(t) + (v_n/m\Omega)\, g_{n-j}(t)] \tag{29d}$$

$$V_j = m \sum_{n=1}^{N} [u_n \dot{f}_{n-j}(t) + (v_n/m\Omega)\, \dot{g}_{n-j}(t)]. \tag{29e}$$

At this point, we adopt a more convenient matrix notation, defining a column matrix Z of the k_j, q_j components such that its transpose is

$$\tilde{Z} \equiv (k_1 k_2, \ldots, k_N q_1, \ldots, q_N) \tag{30}$$

and a real, symmetric matrix $W = (W_{ij})$ given by

$$W = \begin{pmatrix} M & H \\ \tilde{H} & Q \end{pmatrix} \tag{31}$$

where $M = (M_{ij})$, etc. We also include the initial Gaussian centers of the subsystem in the column matrix R, the tranpose of which is

$$\tilde{R} \equiv (U_1 U_2, \ldots, U_N V_1, \ldots, V_N). \tag{32}$$

The characteristic function of the subsystem may be rewritten, from Eq. (28), in the new notation as

$$\phi_N(\mathbf{k}, \mathbf{q}, t) = \exp[i\tilde{R}Z - (\tilde{Z}WZ/2)] \tag{33}$$

from which we proceed to calculate ρ_N by means of

$$\rho_N(\{x_n\}, \{p_n\}, t) = \int \exp[i(\tilde{R}Z - \tilde{X}Z) - (\tilde{Z}WZ/2)] \prod_{n=1}^{N} (dk_n/2\pi)(dq_n/2\pi) \tag{34}$$

where

$$\tilde{X} \equiv (x_1 x_2, ..., x_N p_1, ..., p_N). \tag{35}$$

Since W is a real, symmetric matrix, it can be diagonalized by an orthogonal transformation; we let L be the matrix that diagonalizes W, such that

$$L^{-1}WL = \Lambda \tag{36a}$$

where Λ is diagonal, with diagonal elements labelled $\lambda_1, ..., \lambda_{2N}$. We can then write

$$\tilde{Z}WZ = \tilde{Z}LL^{-1}WLL^{-1}Z = \tilde{Z}L\Lambda L^{-1}Z = \tilde{Z}L\Lambda\tilde{L}Z \tag{36b}$$

since $L^{-1} = \tilde{L}$. We now write

$$\tilde{L}Z = G \tag{37a}$$

or

$$Z = LG \tag{37b}$$

where G is a new column vector, and Eq. (36) becomes

$$\tilde{Z}WZ = \tilde{G}\Lambda G. \tag{38}$$

We transform X and R by the same matrix L, defining new column vectors

$$Y = \tilde{L}X \tag{39a}$$

and

$$F = \tilde{L}R \tag{39b}$$

so that Eq. (34) becomes

$$\rho_N = \int \exp[i(\tilde{F} - \tilde{Y})\, G - (\tilde{G}\Lambda G/2] \prod_{n=1}^{N} (dk_n/2\pi)(dq_n/2\pi). \tag{40}$$

We change the variables of integration from $\prod_{i=1}^{N} dk_n\, dq_n = \prod_{i=1}^{2N} dZ_n$ to $\prod_{i=1}^{2N} dG_n$. We note that the Jacobian of the transformation is simply $|\det L| = 1$. Thus, since Λ is diagonal, we obtain

$$\begin{aligned} \rho_N &= \prod_{n=1}^{2N} (2\pi)^{-1} \int \exp[i(F_n - Y_n)\, G_n - (G_n{}^2\Lambda_n/2)]\, dG_n \\ &= \prod_{n=1}^{2N} (2\pi\lambda_n)^{-1/2} \exp[-Y_n'^2/2\lambda_n] \end{aligned} \tag{41}$$

where

$$Y' = Y - F.$$

But, since we know that

$$\prod_{n=1}^{2N} (\lambda_n)^{-1} = 1/\det W \tag{42}$$

and

$$\prod_{n=1}^{2N} \exp[-Y_n'^2/2\lambda_n] = \exp\left[-\sum_{n=1}^{2N} Y_n'^2/2\lambda_n\right] = \exp[-\tilde{Y}'\Lambda^{-1}Y/2] \tag{43}$$

and since, from Eqs. (38)–(40), with $X' = X - R$, we have

$$\tilde{Y}'\Lambda^{-1}Y = \tilde{X}'L\Lambda^{-1}\tilde{L}X' = \tilde{X}'W^{-1}X' \tag{44}$$

we may finally write

$$\rho_N(\{x_n\}, \{p_n\}\, t) = (2\pi)^{-N}(\det W)^{-1/2} \exp[-\tilde{X}'W^{-1}X'/2] \tag{45}$$

The reduced Liouville function ρ_N is displayed in Eq. (45) as a function of the $2N$-square matrix W, and the column matrix X', both of which are time-dependent. The dependence on the initial most-probable values u_n and v_n enters only via $X' = X - R$; these values appear in R, or in its components U_j and V_j of Eqs. (29d, e). Note that, since all finite sums of the f_j, g_j, or their time derivatives will vanish as $t \to \infty$, ρ_N eventually loses all dependence on the initial measurement of the subsystem. The matrix W, through its elements given by Eqs. (29a–c), contains both finite sums (the capital letters) and infinite sums (the lower-case letters) of the f_j, g_j, and their time derivatives. The former vanish as $t \to \infty$, and the latter are explicitly given for our two cases by Eqs. (23), (24), (26), and (27).

The entropy of the subsystem is, from Eq. (2),

$$S_N = -k_B \int \rho_N \ln(h^N \rho_N) \prod_{j=1}^{N} dx_j\, dp_j \tag{46}$$

which, after straightforward calculations, becomes

$$S_N = k_B N + k_B \ln[\hbar^{-N}(\det W)^{1/2}] \tag{47}$$

where $\hbar = h/2\pi$, and h is, for classical purposes, only dimensionally equal to Planck's constant. The entropy S_N does not involve u_n and v_n ; it measures missing pertinent information in the sense of information theory,$^{(3-5)}$ starting with the correct information-theoretic entropy, based on the observations at $t = 0$, and evolving in time to the correct thermodynamic entropy as calculated from conventional equilibrium statistical mechanics. We shall examine in more detail several specific, simple cases in Sections 7 and 8, and discuss the results more generally in Section 9.

5. EQUIPARTITION OF ENERGY

In this section, we demonstrate equipartition of energy for both types of chains. The kinetic energy of the rth particle is $p_r^2/2m$, and the potential energy for the harmonically bound particle of case (b), when $K \gg k$, is approximately $m\Omega^2 x_r^2/2$. For the simple chain of case (a) however, the meaningful potential energy is that of a spring, given by $k(x_{r+1} - x_r)^2/2$. From the initial distribution of Eq. (17), it is easily seen that, for the chain outside the subsystem, the initial energy expectation values are

$$\langle p_r^2 \rangle_0 / 2m = \zeta^2/2m \tag{48}$$

$$m\Omega^2 \langle x_r^2 \rangle_0 / 2 = m\Omega^2 \epsilon^2/2 \tag{49}$$

and

$$k\langle (x_{r+1} - x_r)^2 \rangle_0 / 2 = k\epsilon^2. \tag{50}$$

Thus, we see that, unless ϵ and ζ are chosen for the purpose, the kinetic and potential energies in the outside system are not initially equipartitioned, and, inside the subsystem, the energies can be anything. We now proceed to calculate, using ρ_N of Eq. (45), the time-evolved energy terms corresponding to those of Eqs. (48)–(50). Since we are interested at present in limits as $t \to \infty$, we replace X' in Eq. (45) by X, since the effects of initial conditions will have vanished. We first calculate $\langle x_r^2 \rangle$ for r in the subsystem as

$$\begin{aligned}\langle x_r^2 \rangle &= \int x_r^2 \rho_N(\{x_n\}, \{p_n\}, t) \prod_{n=1}^{N} dx_n \, dp_n \\ &= (2\pi)^{-N} (\det W)^{-1/2} \int x_r^2 \exp[-\tilde{X} W^{-1} X/2] \prod_{n=1}^{N} dx_n \, dp_n \, . \end{aligned} \tag{51}$$

We write, by Eq. (39a), $x_r = \sum_{j=1}^{2N} L_{rj} Y_j$, and use Eq. (43) to obtain

$$\begin{aligned}\langle x_r^2 \rangle &= (2\pi)^{-N} (\det W)^{-1/2} \int \sum_{i,j=1}^{2N} L_{ri} L_{rj} Y_i Y_j \exp\left[- \sum_{n=1}^{2N} Y_n^2 / 2\lambda_n \right] \prod_{s=1}^{2N} dY_s \\ &= \sum_{j=1}^{2N} L_{rj}^2 \lambda_j \end{aligned} \tag{52}$$

$$\langle x_r^2 \rangle = \tilde{L}_r \Lambda L_r \tag{53}$$

where L_r is the rth column vector of the matrix L. Therefore, we obtain simply that

$$\langle x_r^2 \rangle = W_{rr} = M_{rr} \tag{54}$$

by Eq. (31). Then, from Eq. (29a), we have

$$\langle x_r^2 \rangle = (\alpha^2 - \epsilon^2) A_{rr} + \epsilon^2 a_{rr} + (\delta^2 - \zeta^2) D_{rr} + \zeta^2 d_{rr} \, . \tag{55}$$

Similar calculations yield

$$\langle p_r^2 \rangle = Q_{rr} = (\alpha^2 - \epsilon^2) C_{rr} + \epsilon^2 c_{rr} + (\delta^2 - \zeta^2) A_{rr} + \zeta^2 a_{rr} \tag{56}$$

and

$$\begin{aligned}\langle(x_{r+1} - x_r)^2\rangle &= M_{r+1,r+1} - 2M_{r,r+1} + M_{rr}\\ &= (\alpha^2 - \epsilon^2)(A_{rr} + A_{r+1,r+1}) + \epsilon^2(a_{rr} + a_{r+1,r+1})\\ &\quad + (\delta^2 - \zeta^2)(D_{rr} + D_{r+1,r+1}) + \zeta^2(d_{rr} + d_{r+1,r+1})\\ &\quad - 2(\alpha^2 - \epsilon^2)\, A_{r,r+1} - 2\epsilon^2 a_{r,r+1}\\ &\quad 2(\delta^2 - \zeta^2)\, D_{r,r+1} - 2\zeta^2 d_{r,r+1}\,. \end{aligned} \tag{57}$$

We now evaluate the quantities needed for the final energy in the two cases, noting, first, that all upper-case letters in these results represent finite sums of functions that vanish as $t \to \infty$, and that we need only the lower-case letters already expressed in Eqs. (23), (24), (26), and (27).

For case (a), the simple chain, the kinetic energy is

$$\begin{aligned}\langle p_r{}^2\rangle/2m &= (\epsilon^2/2m)(m\omega)^2[J_0(0) + J_2(4\omega t) - J_0(4\omega t)] + (\zeta^2/4m)[1 + J_0(4\omega t)]\\ &\to \tfrac{1}{2}[(\zeta^2/2m) + m\omega^2\epsilon^2]\end{aligned} \tag{58}$$

and the potential energy of a spring is

$$\begin{aligned}k\langle(x_{r+1} - x_r)^2\rangle/2 &= (k\epsilon^2/2)[1 + J_0(4\omega t) - J_2(4\omega t)] + (k\zeta^2/4m^2\omega^2)[1 - J_0(4\omega t)]\\ &\to \tfrac{1}{2}[\zeta^2/2m) + m\omega^2\epsilon^2]\end{aligned} \tag{59}$$

since $k = m\omega^2$. Equations (58) and (59) show not only that all the masses of the system have the same final kinetic energy, which is equal to the final potential energy of each spring, but also that energy is really shared, since the term in square brackets in these equations is just the sum of the initial kinetic energy of an outside mass, from Eq. (48), and the initial potential energy of an outside spring, as given by Eq. (50). It is convenient here to define an equilibrium temperature for system (a) by

$$k_B T_a = (\zeta^2/2m) + m\omega^2\epsilon^2 \tag{60}$$

so that Eqs. (58) and (59) may be written

$$\langle p_r{}^2\rangle/2m \to k\langle(x_{r+1} - x_r)^2\rangle/2 \to k_B T_a/2 \tag{61}$$

A similar calculation for the harmonically bound chain, case (b), yields

$$\begin{aligned}\langle p_r{}^2\rangle/2m &= (m\Omega^2\epsilon^2/4)[1 - J_0(2\gamma\Omega t)\cos(2\Omega t)] + (\zeta^2/4m)[1 + J_0(2\gamma\Omega t)\cos(2\Omega t)]\\ &\to \tfrac{1}{2}[(\zeta^2/2m) + (m\Omega^2\epsilon^2/2)]\end{aligned} \tag{62}$$

and

$$\begin{aligned}m\Omega^2\langle x_r{}^2\rangle/2 &= (m\Omega^2\epsilon^2/4)[1 + J_0(2\gamma\Omega t)\cos(2\Omega t)] + (\zeta^2/4m)[1 - J_0(2\gamma\Omega t)\cos(2\Omega t)]\\ &\to \tfrac{1}{2}[(\zeta^2/2m) + (m\Omega^2/2)\epsilon^2].\end{aligned} \tag{63}$$

Again we have found equipartition, and again we define an equilibrium temperature by

$$k_B T_b = (\zeta^2/2m) + (m\Omega^2/2)\epsilon^2 \tag{64}$$

where, this time, the energy on the right-hand side of Eq. (64) is the total average initial energy of a particle in the heat bath. (Here the, coupling energy has been neglected; its inclusion still leaves the average equilibrium values of kinetic and potential energy equal, but apportions the potential energy between the two kinds of springs.)

Evidently, we could have chosen any part of the chain for the calculation of the equilibrium value; our result therefore shows that the entire chain approaches equilibrium, and that equipartition is a directly-derived consequence of the use of the reduced Liouville function ρ_N to calculate averages. We discuss this result further in Sections 7 and 9.

6. CORRELATIONS AND DIFFUSION

Two different kinds of correlations may be examined—those relating the value of a dynamical variable at time t to the value of a dynamical variable at $t = 0$, and those relating two dynamical variables at time t. The former follow almost trivially from Eqs. (5) and (17), without the necessity for further statistical analysis. As an example, the first kind of correlation coefficient for two momenta can be calulated as

$$\begin{aligned} P[p_r(t), p_{r+n}(0)] &\equiv \langle p_r(t)\, p_{r+n}(0)\rangle / [\langle p_r{}^2(0)\rangle \langle p^2_{r+n}(0)\rangle]^{1/2} \\ &= \zeta^{-2} \int p_r(t)\, p_{r+n}(0)\, \rho(\{x\}, \{p\}, 0) \prod_{j=-\infty}^{\infty} dx_j(0)\, dp_j(0) \end{aligned} \tag{65}$$

provided both masses are members of the heat bath (for simplicity) and $p_{r+n}(t)$ is given in terms of the initial conditions by Eq. (5b). The integrand is an infinite sum of terms, each of which is odd in $p_{n+r}(0)$ except for the one term in $p_r(t)$ that depends on $p_{n+r}(0)$; its coefficient is $\dot{g}_r(t)/\Omega = f_r(t)$, and the integral of that single nonzero term is $\zeta^2 f_r(t)$. Thus, we have

$$P[p_r(t), p_{r+n}(0)] = f_n(t) \tag{66}$$

where $f_n(t)$ is given by Eq. (6) for case (a) and by Eq. (8) or (9) for case (b). Similarly, we find, for the coordinates of the heat bath,

$$P[x_r(t), x_{r+n}(0)] = f_n(t) \tag{67}$$

the same result as for the momenta. These results and their implications have been discussed by Mazur and Montroll,[6] who obtained (66) differently.

The second kind of correlation is more interesting; it may be calculated either directly, by the method of Eq. (65) with both dynamical variables time-dependent and expressed in terms of the initial conditions by Eqs. (5), or by the method displayed in Section 5 for such quantities as $\langle x_r{}^2\rangle$. In either case, the results may be conveniently expressed in terms of the already-defined elements of the matrix W of Eq. (31). We obtain

$$P[x_r(t), x_{r+n}(t)] = M_{r,r+n}/[M_{rr}M_{r+n,r+n}]^{1/2} \tag{68}$$

$$P[p_r(t), p_{r+n}(t)] = Q_{r,r+n}/[Q_{rr}Q_{r+n,r+n}]^{1/2} \tag{69}$$

and

$$P[x_r(t), p_{r+n}(t)] = H_{r,r+n}/[M_{rr}Q_{r+n,r+n}]^{1/2}. \tag{70}$$

For case (a) as $t \to \infty$, Eq. (69) gives

$$P[p_r(t), p_{r+n}(t)] \to [\zeta^2\delta_{0n} + (m\omega\epsilon)^2(2\delta_{0n} - \delta_{1n} - \delta_{1n})]/[\zeta^2 + 2(m\omega\epsilon)^2] \tag{71}$$

so that momenta of adjacent particles are seen to be anticorrelated, with a correlation coefficient of $-1/4$ (when $\zeta^2/2m = m\omega^2\epsilon^2 = kT_a/2$), and no other momentum correlations exist. For case (b), all off-diagonal momentum correlations vanish as $t \to \infty$, as do the position correlations.

Before examining the limit of Eq. (68) for case (a), we first evaluate $\langle x_r{}^2\rangle$, as expressed by Eq. (55). Only a_{rr} and d_{rr} persist for large values of t; these yield

$$\langle x_r{}^2\rangle \to \epsilon^2/2 + (\zeta^2 t/2\omega m^2)\left[\int_0^{4\omega t} J_0(y)\,dy - J_1(4\omega t)\right]. \tag{72}$$

For large $|t|$, the integral approaches ± 1, depending on the sign of t, and $J_1(2\omega t) = O(t^{-1/2})$, so that Eq. (72) becomes, with $\sigma = t/|t| = \pm 1$,

$$\langle x_r{}^2\rangle \to (\zeta^2\sigma t/2\omega m^2) + O(t^{1/2}). \tag{73}$$

This result may be understood as a Brownian motion of the particles of chain (a), which are not harmonically bound to any home position, and thus may be expected to drift. We may identify a coefficient of diffusivity from the relation $\langle x^2\rangle = 2D|t|$, as

$$D = \zeta^2/4\omega m^2. \tag{74}$$

If the heat bath energies were initially equipartioned, so that $\zeta^2/2m = m\omega^2\epsilon^2 = k_BT_a/2$, as in Eq. (60), then Eq. (74) becomes

$$D = k_BT_a/4m\omega \tag{75}$$

We note, however, that Eq. (74) correctly relates D to the initial variance in the momentum distribution of the heat bath, but not to ϵ, a result we believe to be new.

We now calculate $\langle x_r(t)\, x_{r+n}(t)\rangle$, for large values of t, as

$$\langle x_r x_{r+n}\rangle \to \langle x_r x_r\rangle - (\zeta/2\omega m)^2 \sum_{k=1}^{n} \int_0^{4\omega t} J_{2k-1}(y)\,dy. \tag{76}$$

For large times, the integrals in Eq. (76) are very nearly unity, so we may write

$$\langle x_r x_{r+n}\rangle \to \langle x_r x_r\rangle - (\zeta/2\omega m)^2 n \tag{77}$$

showing that the correlation deteriorates as the separation increases. However, for any finite separation, the correlation coefficient approaches unity as $t \to \infty$, or

$$\begin{aligned} P[x_r(t), x_{r+n}(t)] &\equiv \langle x_r x_{r+n}\rangle / [\langle x_r{}^2\rangle\langle x_{r+n}^2\rangle]^{1/2} \\ &\to 1 - (n/\omega t\sigma) \to 1. \end{aligned} \tag{78}$$

The complete correlation, in the limit, of all positions of a finite length of the chain simply implies that the Brownian drift cannot lead to appreciable storage of energy in the coupling springs. We examine another aspect of this Brownian motion in the next section.

7. LIOUVILLE FUNCTIONS FOR SIMPLE SYSTEMS

In this section, we display ρ_N from Eq. (45) explicitly for a one-particle system of both types and for an N-particle system, after a long time, for case (b). The calculation of ρ_N requires that we obtain W^{-1}, which is given, for $N = 1$, by

$$W^{-1} = (\det W)^{-1} \begin{pmatrix} Q_{11} & -H_{11} \\ -H_{11} & M_{11} \end{pmatrix} \tag{79}$$

leading directly to the result

$$\begin{aligned} \rho_1(x, p, t) = {} & [(2\pi)^2 (M_{11}Q_{11} - H_{11}^2)]^{-1/2} \\ & \times \exp[-(Q_{11}x'^2 - 2H_{11}x'p' + M_{11}p'^2)/2(M_{11}Q_{11} - H_{11}^2)] \end{aligned} \tag{80}$$

where

$$x' = x - U_1 = x - u_1 f_0(t) - (v_1/m\Omega) g_0(t) \tag{81a}$$

and

$$p' = p - V_1 = p - u_1 m\dot{f}_0(t) - (v_1/\Omega)\,\dot{g}_0(t). \tag{81b}$$

For case (a) at large $|t|$, M_{11} is given by Eq. (73), Q_{11} by Eq. (58), and H_{11} is obtainable from Eq. (29b) in the limit as

$$H_{11} \to \epsilon^2 b_{11} + \zeta^2 e_{11} \to \sigma\zeta^2/4\omega m. \tag{82}$$

Using Eq. (74) for D, we write, still for case (a),

$$\begin{aligned} \rho_1(x, p, t) = {} & (2\pi)^{-1} \left[2k_B T_a m D\sigma t - \left(\frac{mD}{2}\right)^2\right]^{-1/2} \\ & \times \exp \frac{-(mk_B T_a x^2 - \sigma m D x p + 2p^2 D\sigma t)}{2[2k_B T_a m D\sigma t - (mD/2)^2]} \end{aligned} \tag{83}$$

a result that depends on time, but not in an obviously understandable way .To expose ρ_1 for better analysis, we reduce it again, first integrating $\rho_1(x, p, t)$ over x to obtain the momentum distribution function, and then integrating $\rho_1(x, p, t)$ over p to obtain the coordinate distribution function. We have

$$\begin{aligned}\rho_1(p, t) &\equiv \int_{-\infty}^{\infty} \rho_1(x, p, t)\, dx \\ &= (2\pi m k_B T_a)^{-1/2} \exp(-p^2/2mk_B T_a) \qquad (84)\end{aligned}$$

the proper canonical distribution function for the momentum. Similarly, the integral over p gives

$$\begin{aligned}\rho_1(x, t) &\equiv \int_{-\infty}^{\infty} \rho_1(x, p, t)\, dp \\ &= (4\pi D\sigma t)^{-1/2} \exp[-x^2/4D\sigma t] \qquad (85)\end{aligned}$$

which is just the proper distribution function to satisfy the one-dimensional diffusion equation

$$\partial\rho/\partial t = D\, \partial^2\rho/\partial x^2 \qquad (86)$$

in agreement with the results of the previous section.

Brownian motion is usually obtained from the motion of a particle in a viscous medium, subject to a stochastic force. The presence of the viscous drag destroys time-reversibility in the dynamics. Here, the result was obtained without an irreversible force, and the result of Eq. (85) *is* time reversible in the sense that $\rho_1(x, t) = \rho_1(x, -t)$, since $\sigma t = |t|$. The diffusion as expressed by ρ_1 in Eq. (85) is a *statistical* result, representing the fact that our knowledge of the system becomes increasingly poorer in both directions of time as we move away from $t = 0$. From our limited knowledge of the present, we can neither predict the future nor unravel the past.

For case (b), the harmonic binding prevents diffusion, and Eq. (80) yields, for large values of t,

$$\rho_1(x, p, t) = (\Omega/2\pi k_B T_b) \exp[-(m\Omega^2 x^2 + p^2/m)/2k_B T_b] \qquad (87)$$

a result that is seen without further analysis to be the product of two canonical distributions, one for x and the other for p, at the equilibrium temperature T_b.

Since W becomes diagonal as $t \to \infty$ for case (b), we easily obtain $\rho_N(\{x\}, \{p\}, t)$ from Eq. (45) as

$$\begin{aligned}\rho_N(\{x\}, \{p\}, t) &= (\Omega/2\pi k_B T_b)^N \exp\left[-(2k_B T_b)^{-1} \sum_{n=1}^{N} (m\Omega^2 x_n^2 + p_n^2/m)\right] \\ &= \prod_{n=1}^{N} \rho_1(x_n, p_n, t). \qquad (88)\end{aligned}$$

This is the expected result for a canonical distribution of very weakly interacting oscillators.

8. THE ENTROPY FOR SIMPLE SYSTEMS

Equation (47) gives the information-theoretic entropy of the system at any time, through the time dependence of W. We shall examine the entropy for the three simple systems of the previous section, all for large values of time. The one-particle, case (a) system gives

$$S_1 = k_B + k_B \ln \hbar^{-1}[2k_BT_a mD\sigma t - (mD/2)^2]^{1/2}. \tag{89}$$

Here, we find the entropy increasing without limit as ln t, a result that agrees with the previously derived Brownian motion.

The one-particle, case (b) system gives

$$S_1 = k_B[1 + \ln(k_BT_b/\hbar\Omega)] \tag{90}$$

and the N-particle system gives $S_N = NS_1$, as it should. The entropy of Eq. (90) arose as $t \to \infty$ through our information state being describable only as equilibrium; yet, it agrees exactly with the classical canonical entropy of a harmonic oscillator in equilibrium with a heat bath. Thus, we have demonstrated that our procedure leads to the correct thermodynamic equilibrium.

9. DISCUSSION

Systems of coupled oscillators have been studied extensively in the attempt to establish a dynamical basis for equilibrium statistical mechanics. A finite, isolated system of coupled harmonic oscillators does not approach equilibrium or share energy among its normal modes. Fermi *et al.*(8) carried out computer studies of a finite, isolated system of coupled *anharmonic* oscillators, believing, as J. Ford(9) did later, that the nonlinear forces would produce a Gibbs-like stirring in phase space, thereby leading to ergodicity, energy sharing among the normal modes of the linearized system, and equilibration. They found very little tendency toward equipartition, though Ford and Waters(10) did succeed in demonstrating that the energy of a single oscillator in a finite, nonlinear system has a Boltzmann distribution.

Apparently, the fundamental difficulty with the finite, nonlinear systems as models in statistical mechanics is that, although ergodicity is *their* only pathway to equipartition, they are not, in general, ergodic; indeed, Kolmogorov(11) has shown that fairly complicated nonlinear systems are *not* ergodic. Northcote and Potts,(12) however, seem to have achieved time-reversible ergodicity and complete energy sharing in a finite system of harmonically-coupled hard spheres that can redistribute the normal-mode energies by collision.

The practical objection to the use of most of these nonlinear models in statistical mechanics is that, for most purposes, only numerical analysis is possible. For harmonic systems, on the other hand, analytic techniques are well developed and lead to intuition-guiding results.

Since we wish to establish a generally valid basis for the approach of dynamical systems to equilibrium, we do not regard ergodicity as fundamental, because it is demonstrably not a property of many common dynamical systems that are important in statistical physics. We have chosen, instead, what seems to be a natural synthesis of the views of Blatt,(1) Jaynes,(3,4) and Katz.(5) Blatt states that interactions between the system and the outside world govern the approach to equilibrium, rather than interactions within the system itself. We have expressed this point of view mathematically in terms of the Liouville function for an infinite chain of coupled harmonic oscillators, reduced by integrating over the coordinates of the "outside world," to a function $\rho_N(\{x\}, \{p\}, t)$, given by Eq. (45). This function, which depends only on the variables of the system at time t, is a probability density in the $2N$-dimensional phase space of the segment of chain that is regarded as the thermodynamic system. The temporal evolution of ρ_N is influenced, and ultimately dominated, by the "outside world"; therefore, ρ_N cannot satisfy the Liouville equation for the N-particle system, although the original ρ formally satisfies the Liouville equation for the infinite chain.

The entropy, defined in accord with information theory,(3,5) turns out to be the Gibbs entropy,(2) except that we use the ρ_N of Eq. (45) rather than the Liouville function for the isolated N-particle system. This modification of the Gibbs expression is evidently the one Gibbs should have used in discussing the approach of canonical systems to equilibrium, since it takes into account interaction of the system with the heat bath. We show that ρ_N approaches the canonical distribution as $t \to \pm\infty$ for the harmonically bound chain, and note that Jaynes(4) has shown the Gibbs entropy to yield the correct thermodynamic value when ρ_N is the canonical distribution.

In our view, then, the approach to equilibrium lies entirely in the statistics, in the evolution of our knowledge of the system, and not in dynamics or ergodicity. The equations of motion here are time reversible, as is usual,(8–10,12) but, as Katz has emphasized,(5) the system reaches what we call "equilibrium" because of our increasing inability to supply the information required for utilization of the equations of motion to describe the system. During evolution toward equilibrium, no information is lost; everything we knew at $t = 0$ can be kept on record. But, from an examination of, say, Eqs. (5) and (6), we see that, near $|t| = 0$, only $x_r(0)$ is important in determining $x_r(t)$, since only $J_0(2\omega t)$ is nonnegligible for small $|t|$. As $|t|$ increases, the higher-order Bessel functions successively become important, while the lower-order ones decay in amplitude as $|t|^{-1/2}$. Thus, it is evident that the significance of its own initial condition fades, and increasingly remote events become pertinent to any particle in the system as time evolves. Therefore, no matter how well we know the initial conditions of our system, we ordinarily do not expect to have detailed knowledge of the surroundings, and we see that, ultimately, the only *pertinent* data for our system are the initial conditions of increasingly remote parts of the surroundings. Our only choice is to express our knowledge of the distant parts of the "outside world" statistically. In the absence of further measurements, we describe our finite system as approaching equilibrium as the inwardly diffusing statistical fog blankets our ability to extract useful information from the equations of motion.

In this formulation of the approach to equilibrium, ergodicity is not a consideration, and there are no paradoxes of reversibility or recurrence, simply because the information required or the description of the open system grows monotonously with $|t|$.

If one adopts Blatt's attitude(1) that all systems are, in reality, open, and that statistical mechanics properly pertains only to these imprecisely known systems, then the kind of reduced Liouville function developed here seems to be the proper one for studying the approach to equilibrium. Even if one regards Blatt's view as an overstatement, since it would exclude microcanonical ensembles from statistical mechanics, our reduced Liouville function still seems to be the proper one for the treatment of canonical ensembles.

Equipartition of energy was demonstrated in Section 5, and an equilibrium temperature was obtained, both as consequences of statistics, and not of dynamics. Temperature is generally regarded as a statistical concept, related to our inability to assign detailed energies to the individual particles, and it is appropriate that it should be specified in terms of equipartitioned energies. We note that equipartition of energy is not sufficient for equilibrium; our case (a), for example, succeeds in equipartitioning energy, but the Brownian motion, which must exist for a chain that is not bound to any home position, is not an attribute of true equilibrium. The system of Northcote and Potts(12) also succeeds in equipartitioning energy, but the Gibbs entropy is a constant of the motion, and the missing pertinent information does not change. All the information necessary for a complete dynamical description of their system persists, and the decision to describe it in terms of thermodynamic variables is tantamount to a decision to throw away or disregard a considerable body of information. (One can, by this choice, attain equilibrium in a microcanonical ensemble. We expect to compare definitions of entropy, and means of attaining the state of information described as "equilibrium," in a forthcoming paper.)

We note also that the information-theoretic approach to equilibrium may lead to a final, stationary, equipartioning distribution that differs nontrivially from the canonical one. In a future paper, we expect to discuss the simple chain with one point fixed, so that Brownian motion is eliminated. The noncanonical momentum correlations of Eq. (71) still exist, when initial conditions are chosen as in this paper, and the final state is clearly one of equilibrium, but the distribution is not of the canonical form.

The entropy, as given by Eq. (47), has the interesting property that it is determined entirely by the time-dependent bilinear expectation values of the coordinates and momenta of the system; i.e., we may write the matrix W as

$$W = \begin{pmatrix} M & H \\ \tilde{H} & Q \end{pmatrix}$$

where $M_{ij} = \langle x_i x_j \rangle$, $Q_{ij} = \langle p_i p_j \rangle$, and $H_{ij} = \langle x_i p_j \rangle$. The initial conditions were chosen by us (though not necessarily so) such that W begins as a diagonal matrix. As t increases, the off-diagonal elements become important as a consequence of interactions. For the harmonically-bound oscillator chain, the growth of off-diagonal terms may be pictured as a pair of wavefronts moving toward opposite corners of W from the main diagonal, leaving behind a decaying, finite-amplitude oscillation. The "wave" moves out of W, into the outside world, the off-diagonal elements decay to zero, and the diagonal elements decay to their equilibrium values, leaving W once again diagonal. But, for the simple chain, off-diagonal elements persist, illustrating the necessity for retaining the complete matrix W in the calculation of the entropy, rather than adopting a Boltzmann-like approach of calculating the entropy of an N-particle system from ρ_1, the single-particle, reduced Liouville function.

10. HISTORICAL NOTE

In this section, we attempt to cite some of the most important contributions to the ever-popular problem of coupled harmonic oscillators in statistical physics.

The dynamics of the infinite, simple chain of our case (a) was solved elegantly by Schrödinger,(13) who obtained results equivalent to our Eqs. (6) and (7). These results were used by Klein and Prigogine,(14) who obtained equipartition of energy, corresponding to our Eqs. (58) and (59), for the infinite chain with uncorrelated Gaussian initial distributions of the Schrödinger variables. They did not, however, discover the Brownian motion, since they looked only at the Schrödinger variables (which show spring stretchings, but not displacements).

The most detailed treatment of the simple chain is that by Hemmer,(15) who obtains Brownian motion, as we do, as a consequence of the distribution of initial values. He uses an initially-thermal heat bath, rather than our independent Gaussian distributions of x's and p's, and obtains a diffusivity twice the value given by Eq. (75). (We have not yet discovered the reason for the discrepancy.) Hemmer obtains essentially our Eq. (80) for the single-particle distribution function, although his matrix elements differ somewhat from ours because of the different initial conditions. He discusses a number of points not yet treated by us, such as finite chains, quantized systems, thermal conductivity, and the Brownian motion of a massive particle in an infinite chain.

Henley and Thirring(16) treat the dynamics of a finite, harmonically bound chain by the normal coordinate method, obtaining results that can easily generate our Eq. (8) in the limit. We have seen no other explicit treatment of this system. The work of Mazur and Montroll,(6) however, is sufficiently general to yield our Eq. (66) for the time-relaxed momentum correlations of any chain of harmonic oscillators.

We have seen no other calculations of ρ_N, given by Eq. (45), as a reduced Liouville function for a general N-oscillator subsystem of an infinite chain, nor have we seen the entropy of such a system, as given by Eq. (47). A calculation of ρ_1 for the simple chain is given by Klein and Prigogine(14) and by Hemmer,(15) but entropy is not mentioned.

The covariance matrix W has been used in various calculations of distributions of initially Gaussian variables(17–19), and we have found one suggestion(18) that the entropy could be written in terms of W.

When the initial distribution of the heat bath in the simple chain is taken to be canonical (a convenient procedure with Schrödinger variables(14,15)) the anticorrelation of adjacent momenta vanishes. This result is displayed explicitly by Rubin,(20) for example, and is easily derived from Hemmer's work. We have seen no analysis of the approach to equilibrium, other than the present one, in which the initial distribution in the heat bath was chosen to be nonthermal.

11. CONCLUSION

Finite subsystems of infinite chains of coupled harmonic oscillators have been shown to be useful and instructive models for study of the approach of a thermodynamic system to equilibrium. The Gibbs, or information-theoretic, entropy, defined in terms of the N-particle reduced Liouville function, exhibits the correct temporal behavior and decays to the value expected from equilibrium statistical mechanics. We conclude, then, that our approach is a valid one that is direct, analytically not very difficult, physically acceptable, and free of the conceptual difficulties related to ergodicity and the paradoxes of time reversibility and Poincaré recurrence. We expect treatments in terms of the reduced Liouville function to be useful and enlightening in a variety of problems of nonequilibrium statistical mechanics, many-body theory, and plasma physics.

ACKNOWLEDGMENTS

The senior author (HSR) thanks Elliott Montroll for a stimulating discussion, particularly on the significance of the Northcote–Potts paper,(12) before the present work was begun. We thank J. M. Blatt and J. Ford for interesting and enlightening correspondence. We also thank H. Reiss for constructive editorial comment. This work was supported in part by the United States Atomic Energy Commission.

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