ENTROPY OSCILLATION AND THE H THEOREM FOR FINITE SEGMENTS OF INFINITE COUPLED-HARMONIC-OSCILLATOR CHAINS

HARRY S. ROBERTSON AND MANUEL A. HUERTA

Department of Physics, University of Miami, Coral Gables, Florida 33124

ABSTRACT

Following a general discussion of the approach to equilibrium of a finite system in contact with a heat bath, an illustrative calculation is presented in terms of a weakly-coupled, harmonically-bound oscillator chain. A modified Gibbs entropy is defined in terms of ρ_N, the reduced Liouville function of the system, which is obtained from the total Liouville function of the system and heat bath by (in principle) integration over the heat-bath variables. Since the system and heat bath are mutually interacting, some structure is observable in the entropy function as the system evolves from its initial value toward equilibrium, but the entropy ultimately evolves to its correct equilibrium value, despite time-reversible dynamics, because ρ_N spreads from an initially sharp distribution to a final one that is characteristic of the heat bath in equilibrium. The entropy function is presented as an analytically defined, conceptually accurate substitute for Boltzmann's H.

1. INTRODUCTION

Compelling arguments have been offered in support of the point of view that no physical system of thermodynamic interest can properly be regarded as isolated[1,2]. Although the impossibility of shielding a system completely from cosmic rays and fluctuating gravitational fields is seldom questioned, the fundamental importance of these interactions of the system with the outside world is often either ignored or denied. Rather than provoke an unwanted emotional response to any position we might take on the ability of a general isolated system to approach equilibrium as a consequence of its own dynamics, we merely point out that, as in equilibrium statistical mechanics, the approach to equilibrium may be treated with complete validity in terms of open systems, and usually with greater ease than for closed ones. (Canonical theory is surely no less valid than microcanonical theory, and is usually simpler.)

The general system to be studied herein is a collection of interacting particles coupled to an infinite heat bath. The initial positions and momenta of the particles in the system are assumed to be known as well as measuring techniques permit, whereas the initial heat-bath variables are known only statistically. No assertion is made that the heat-bath variables are random, whatever that means; rather the initial choice that the heat-bath variables

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are canonically distributed is to be regarded only as a statement of our knowledge of them, and not as an assertion that the variables *are* so distributed.

Gibbs[3] used the Liouville function ρ of an N-particle system to define the entropy

$$S = -k_B \int \rho \ln \rho \, d\Gamma \qquad (1)$$

where the integration is over the entire $6N$-dimensional phase space, and at equilibrium the Liouville function is given by

$$\rho = \exp(-\lambda - \beta E) \qquad (2)$$

where λ is a normalization constant, $\beta = 1/k_B T$, and E is the energy variable of the N-particle system. Since ρ is a constant (its total time derivative, according to the Liouville theorem, is zero), Gibbs was unable to provide an analytical development of S, as the system evolves from some initial non-equilibrium state, to its final equilibrium value. Although the Gibbs entropy, with ρ given by equation 2, is the correct thermodynamic entropy, there is apparently no provision in Gibbs–Liouville theory for S to get to its equilibrium value, or even to change with time.
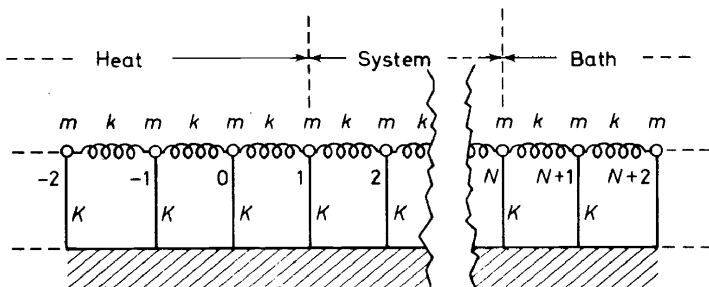

Figure 1. Infinite chain of oscillators, each harmonically bound to its home position by a leaf spring of constant K, and coupled to nearest neighbours by springs of constant k. A finite segment is regarded as the thermodynamic system, and the surroundings as the heat bath.

In the present development, ρ is the Liouville function for the entire system and heat bath; although it formally satisfies the Liouville equation, it is not used explicitly in the subsequent calculations. Instead, a reduced Liouville function ρ_N is obtained by integration (in principle) of ρ over the heat-bath variables. This ρ_N, no longer a phase-space constant, contains implicitly the interactions of the system with the heat bath, and an entropy defined as in equation 1, except with ρ_N, correctly expresses the evolution of the system to equilibrium.

The assumption that the heat-bath variables are canonically distributed can only be made as an *initial* state of knowledge, because the (presumably better known) system variables interact with the heat bath and transiently sharpen our knowledge of the heat-bath variables. (Analogously, a finite cold system in contact with a warmer heat bath transiently cools the heat bath in the neighbourhood of the contact area.) The sharpening of heat-bath

variables permits non-thermal transfers of energy across the boundaries of the system in such a way that the entropy evolution is not always a monotonic function of the time. This point is examined in detail in Section 4.

Notable features of the present treatment include the clear separation of dynamics from statistics, freedom from considerations of ergodicity, and easy clarification of the sometimes muddied process by which a system with time-reversible dynamics can evolve to equilibrium. These features are discussed explicitly in terms of a system of weakly-coupled, harmonically-bound oscillators, as shown in *Figure 1*. The dynamics is treated in Section 2, followed by the introduction of statistical features in Section 3. Specific results, particularly for small systems, are given in Section 4, and a short discussion of these results appears in Section 5. More detailed treatments of some aspects of this paper, and more extensive references to related work, appear elsewhere[4-7].

2. DYNAMICS

The Hamiltonian of the system shown in *Figure 1* is given by

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

The general solution to the equations of motion is of the form

$$x_n(t) = \sum_{r=-\infty}^{\infty} [x_{n+r}(0) f_r(t) + p_{n+r}(0) g_r(t)/m\Omega] \tag{4a}$$

$$\text{and } p_n(t) = m\dot{x}_n(t), \text{ where} \tag{4b}$$

$$f_r(t) = \pi^{-1} \int_0^\pi d\phi \cos r\phi \cos [\Omega t(1 - 2\gamma \cos \phi)^{\frac{1}{2}}] \tag{5}$$

$$g_r(t) = \Omega \int_0^t f_r(t') \, dt' \tag{6}$$

$\Omega^2 = (K + 2k)/m$, $\omega^2 = k/m$ and $\gamma = (\omega/\Omega)^2$. An exact treatment of this particular chain is available elsewhere[6], but for present purposes, when $\gamma \ll 1$ and the oscillators are thus weakly coupled, equations 5 and 6 may be quite accurately approximated as

$$f_r(t) = J_r(\gamma\Omega t) \cos (\Omega t - r\pi/2) \tag{7}$$

and

$$g_r(t) = J_r(\gamma\Omega t) \sin (\Omega t - r\pi/2) \tag{8}$$

After a long time, still for $\gamma \ll 1$, equations 7 and 8 differ from the exact expressions of equations 5 and 6 principally in the phase of the trigonometric term, but the essential ideas of the treatment are not affected by use of the approximate expressions.

Equations 7 and 8 exhibit the basic dynamic features that can lead to equilibrium: since $f_0(t)$ is proportional to $J_0(\gamma\Omega t)$, it is evident that the influence of each particle's own initial conditions in determining its future must vanish as $t \to \infty$, so that its ultimate state is determined by the initial

conditions of the other members of the chain. Even more strongly, since $J_n(x)$ vanishes as $x^{-\frac{1}{2}}$ for $x \gg n$, it is apparent that any finite segment of the chain must evolve to a state that is determined entirely by the initial conditions of increasingly remote parts of the surrounding heat bath.

The one other feature of note in the dynamics is the time reversibility of equations 4, since the $p_r(0)$s change sign on time reversal. (A film of the motion of the chain would make sense when run in either direction.) Apparently, then, the approach to equilibrium of this system does not lie in the dynamics, though the loss-of-memory feature discussed in the last paragraph is necessary in order that equilibration is not dynamically precluded.

3. STATISTICS

Equations 4 are not statistical; they give definite values of $x_n(t)$ and $p_n(t)$ in terms of the presumably-known initial conditions. It is now appropriate to recognize that these initial conditions are not precisely known, but rather must be described as a distribution $\rho(0)$, the initial Liouville function of the entire system and heat bath.

It is convenient to specify the initial conditions of the system variables in terms of centred Gaussian distributions by writing

$$x'_n(0) = x_n(0) - u_n \tag{9a}$$

and

$$p'_n(0) = p_n(0) - v_n \tag{9b}$$

where u_n and v_n are the initial expectation values of the coordinates and momenta, respectively, of the system variables. The heat-bath initial conditions are distributed essentially canonically, so that $\rho(0)$ may be written

$$\rho(0) = \prod_{n=1}^{N} \frac{\exp\{-[x'_n(0)/\alpha]^2/2\}}{\alpha(2\pi)^{\frac{1}{2}}} \prod_{n=1}^{N} \frac{\exp\{-[p'_n(0)/\delta]^2/2\}}{\delta(2\pi)^{\frac{1}{2}}}$$

$$\times \prod{}' \frac{\exp\{-\beta[p_n^2(0)/2m + m\Omega^2 x_n^2(0)/2]\}}{(2\pi/\beta\Omega)} \tag{10}$$

where α and δ are the initial variances of system variables and $\beta = 1/k_B T_b$, with T_b as the temperature of the heat bath. The symbol $\prod'$ denotes a product over all variables outside the system. The heat-bath variables are distributed as if they were uncoupled classical oscillators of mass m and frequency Ω, in canonical equilibrium. The coupling terms $kx_n x_{n+1}$ have been omitted, both because they are small when $k \ll K$ and because they complicate the calculation. (They are included in the exact treatment of this problem[6].)

Any function of the variables $x_n(t)$ and $p_n(t)$ can now be averaged by using equations 4 to express the function in terms of the initial values and integrating with $\rho(0)$ over the initial phase space. Application of this procedure yields

$$\langle x_n(t) \rangle = \sum_{r=1}^{N} [u_r f_{r-n}(t) + (v_r/m\Omega) g_{r-n}(t)] \tag{11}$$

and $\langle p_n(t) \rangle = m\langle \dot{x}_n(t) \rangle$. Since equation 11 is a finite sum, it is evident from

equations 7 and 8 that $\langle x_n(t) \rangle \to 0$ and $\langle p_n(t) \rangle \to 0$ as $t \to \infty$. Primed variables may now be defined for all t as

$$x'_n(t) = x_n(t) - \langle x_n(t) \rangle \tag{12}$$

and similarly for $p'_n(t)$.

The proper function to represent the phase-space distribution of the system variables is $\rho_N[Y(t)]$, where $Y(t)$ is a column vector of the centred system variables, the transpose of which is $\tilde{Y} = (x'_1 x'_2 \ldots x'_N p'_1 \ldots p'_N)$, and $x'_j = x'_j(t)$. The function $\rho_N[Y]$, which is the reduced Liouville function mentioned in the introduction, is usually not directly obtained from the Liouville function of the entire chain. Instead, the characteristic function for the chain is found as

$$\phi_N(Z) = \int \exp\left[i\tilde{Y}(t)Z\right] \rho(0) \prod_{n=-\infty}^{\infty} dx_n(0)\, dp_n(0) \tag{13}$$

where Z is a $2N$-dimensional Fourier-transform vector. The inverse Fourier transform gives $\rho_N(Y)$ directly as

$$\rho_N(Y) = \int \exp\left[-i\tilde{Z}Y\right] \phi_N(Z) \prod_{j=1}^{2N} (dz_j/2\pi) \tag{14}$$

The actual integrations yield the result

$$\rho_N(Y) = (2\pi)^{-N}(\det W)^{-\frac{1}{2}} \exp\left[-\tilde{Y}W^{-1}Y/2\right] \tag{15}$$

where W is the covariance matrix given by

$$W = (W_{ij}) = (\langle y_i y_j \rangle) \tag{16}$$

and the y_ns are the components of Y.

The reduced Liouville function $\rho_N(Y)$, a function only of the system co-ordinates and momenta, is the correct distribution to represent the state of a system interacting with a heat bath. A Gibbs entropy can be written in terms of ρ_N as

$$S_N = -k_B \int \rho_N(Y) \ln\left[h^N \rho_N(Y)\right] \prod_{i=1}^{N} dx'_i\, dp'_i \tag{17}$$

where h is, for classical purposes, a constant with units of action, required to make the argument of the logarithm dimensionless. Substitution of ρ_N from equation 15 into equation 17 yields

$$S_N = Nk_B + k_B \ln\left[\hbar^{-N}(\det W)^{\frac{1}{2}}\right] \tag{18}$$

where $\hbar = h/2\pi$. Thus S_N is seen to be given entirely by the covariance matrix W, the elements of which are time dependent, as in S_N. Specific results for the weakly-coupled, harmonically bound chain are given in Section 4.

4. RESULTS

For simplicity, it is assumed that the initial variances of the system satisfy the relation

$$\delta^2/2m = m\Omega^2\alpha^2/2 = k_B T_0/2 \tag{19}$$

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where T_0 is regarded as the initial temperature of the system. The covariance matrix W is now written

$$W = \begin{pmatrix} M & G \\ \tilde{G} & Q \end{pmatrix} \tag{20}$$

where $M = (M_{ij})$, etc., and $M_{ij} = \langle x_i'(t)x_j'(t) \rangle$; $Q_{ij} = \langle p_i'(t)p_j'(t) \rangle$, and $G_{ij} = \langle x_i'(t)p_j'(t) \rangle$. After some modest algebra, these matrix elements are found to be:

$$M_{ij} = (k_B/m\Omega^2) \{ T_b \delta_{ij} + (T_0 - T_b)(1, N; n - i, n - j) \cos [(i - j)\pi/2] \} \tag{21}$$

$$G_{ij} = [k_B(T_0 - T_b)/\Omega] (1, N; n - i, n - j) \sin [(i - j)\pi/2] = -G_{ji} \tag{22}$$

and

$$Q_{ij} = (m\Omega)^2 M_{ij} \tag{23}$$

where the parenthesized expression denotes

$$(a, b; c, d) = \sum_{n=a}^{b} J_c(\gamma\Omega t) J_d(\gamma\Omega t) \tag{24}$$

and the sum is always over the index n, which must appear in c and d. We may now write

$$\det W = \det \begin{pmatrix} M & G \\ \tilde{G} & Q \end{pmatrix} = (m\Omega)^{2N} \det \begin{pmatrix} M & G/m\Omega \\ -G/m\Omega & M \end{pmatrix} \tag{24}$$

The final matrix of equation 24 may be written as a sum of direct matrix products:

$$\begin{pmatrix} M & G/m\Omega \\ -G/m\Omega & M \end{pmatrix} = M \times \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + (G/m\Omega) \times \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \tag{25}$$

Rotation in 2×2 space to diagonalize the final matrix of equation 25 permits equation 24 to be written

$$\det W = (m\Omega)^{2N} \det \begin{pmatrix} M + iG/m\Omega & 0 \\ 0 & M - iG/m\Omega \end{pmatrix} \tag{26}$$

But $(M + iG/m\Omega)$ is Hermitean, and $\det (M + iG/m) = \Pi\lambda_i$, where the λ_i are all real. Therefore we obtain

$$|\det W|^{\frac{1}{2}} = (m\Omega)^N \det (M + iG/m\Omega) \tag{27}$$

with the matrix elements given by

$$(M + iG/m\Omega)_{ij} = (k_B/m\Omega^2) \{ T_b \delta_{ij} + (T_0 - T_b)(1, N; \\ n - i, n - j) \exp [i(r - s)\pi/2] \tag{28}$$

Since the coefficient of $T_0 - T_b$ in equation 28 is a finite sum of Bessel-function products that vanish as $t \to \infty$, the matrix $M + iG/m\Omega$ is seen to become scalar, and the equilibrium entropy is given by equation 18, as $|t| \to \infty$, as

$$S_N = Nk_B + Nk_B \ln (k_B T_b/\hbar\Omega) \tag{29}$$

the correct canonical entropy for a system of N independent classical oscil-

lators. At $t = 0$, the matrix is also diagonal, and the initial entropy is easily seen to be

$$S_N(0) = Nk_B[1 + \ln(k_B T_0/\hbar\Omega)] \tag{30}$$

Thus the entropy correctly evolves from its initial value to the final equilibrium value, in accordance with the expectations implicit in Gibbs's formulation of statistical mechanics.

The temporal evolution of S_N is most easily presented in terms of a temperature function $T(N, t)$, such that $T(N, 0) = T_0$ and $T(N, \infty) = T_b$, but at other times the function is to be regarded only as a mathematical convenience. In terms of $T(N, t)$, S_N can be written as

$$S_N/Nk_B = 1 + \ln[k_B T(N, t)/\hbar\Omega] \tag{31}$$

where $T(N, t)$ is calculated from equations 18 and 27. The results for the first few Ns are:

$$T(1, t) = T_b + (T_0 - T_b) J_0^2(\gamma\Omega t) \tag{32}$$

$$T(2, t) = T_b + (T_0 - T_b)(J_0^2 + J_1^2) \tag{33}$$

$$
\begin{aligned}
T(3, t) = [\![\{ T_b + (T_0 - T_b) [2J_1^2 + (J_0 - J_2)^2] \} \{ T_b^2 + T_b(T_0 - T_b) \\
\times [J_0^2 + 2J_1^2 + (J_0 + J_2)^2] + (T_0 - T_b)^2 [J_0^2(J_0^2 + J_2^2) \\
+ 2J_1^2(J_0 + 2J_2)] \}]\!]^{\frac{1}{3}}
\end{aligned}
\tag{34}
$$

and

$$
\begin{aligned}
T(4, t) = [\![\{ [T_b + (T_0 - T_b)(J_0^2 + J_1^2 + J_2^2 + J_3^2)] \\
\times [T_b + (T_0 - T_b)(J_0^2 + 2J_1^2 + J_2^2)] - (T_0 - T_b)^2 J_2^2(J_1 + J_3)^2 \}^2 \\
+ \{ 2(T_0 - T_b)^4 J_2^2(J_1 + J_3)^2 (2J_0 J_2 - J_1^2 + J_1 J_3)^2 \} \\
+ \{ (T_0 - T_b)^4 (2J_0 J_2 - J_1^2 + J_1 J_3)^4 \} - \{ 2[T_b + (T_0 - T_b) \\
\times (J_0^2 + J_1^2 + J_2^2 + J_3^2)] [T_b + (T_0 - T_b)(J_0^2 + 2J_1^2 + J_2^2)] \\
\times (T_b - T_0)^2 (2J_0 J_2 - J_1^2 + J_1 J_3)^2 \}]\!]^{\frac{1}{4}}
\end{aligned}
\tag{35}
$$

where the arguments of the Bessel functions are all $\gamma\Omega t$. These temperature functions become increasingly complicated as N increases, with no apparent general expression or simplification. The first three are shown in *Figure 2*. The single-particle temperature function $T(1, t)$, which could reasonably be called the temperature of the system, starts at T_0, increases to T_b when $\gamma\Omega t = 2\cdot405$, and bounces back to lower temperature, returning to T_b at successive zeros of J_0. These pre-equilibrium swings to $T = T_b$, with subsequent bounces, seem to be at odds with the ideas of the H theorem and with the simplistic 'time's-arrow' concept of entropy. The reason for this behaviour is clear, however, when one realizes that when $J_0 = 0$, the system's initial conditions have (at those instants) no influence on its behaviour, and its motion is determined entirely by the initial conditions of heat-bath variables. At other times, the system's initial influence on the heat bath returns from the heat bath to reduce its temperature, but ever more feebly.
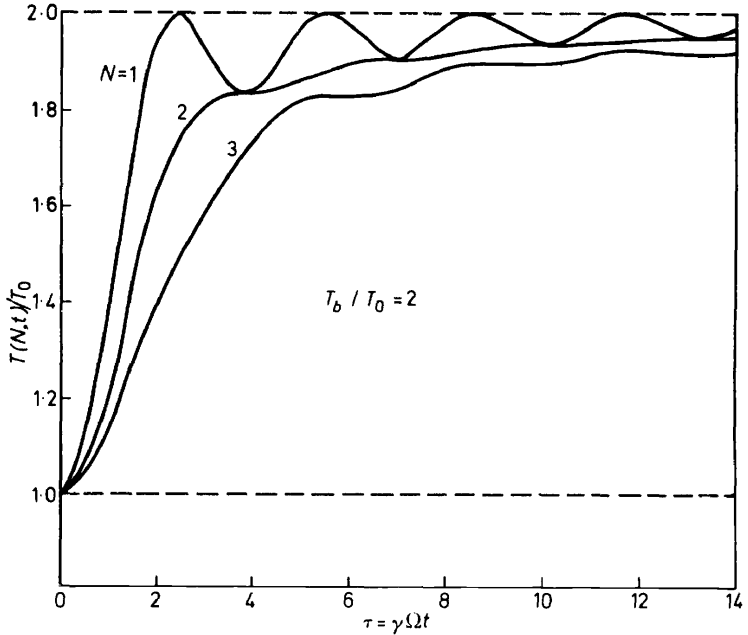
Figure 2. Plots of $T(N, \tau)/T_0$ for $N = 1, 2$ and 3, and $T_b/T_0 = 2$, where $\tau = \gamma\Omega t$.

The two-particle system shows no bounces of the temperature function, since $J_0^2 + J_1^2$ is a monotonic non-increasing function of its argument, but the slope of $T(2, t)$ is zero at values corresponding to the zeros of J_1. At no pre-equilibrium time is the two-particle system completely determined by the heat-bath variables, since internal influence is shared. The three-particle system shows an even smoother temperature function, and it is conjectured that $T(N, t)$ and $S_N(t)$ become increasingly structureless as N increases.

5. DISCUSSION

Boltzmann's H is, except for sign, the conceptual (though not, in general, the theoretically correct) equivalent of the entropy function. The entropy exhibited in equation 17 has the property that it evolves from the initial value, determined entirely by system variables at $t = 0$, to the canonical equilibrium value as $|t| \to \infty$. The evolution, except for $N = 1$ and 2, seems to be sufficiently smooth to satisfy the conceptual content of the H theorem, though the temporal development is somewhat bumpy because of the interaction of system and heat bath. The evolution is time-reversible at $t = 0$, showing that from a given set of initial conditions, *retro*diction is no better than *pre*diction, and that as the system evolves in either direction of time away from the initial state, our *description* of it, ρ_N of equation 14, evolves to a state of knowledge that can only be described as equilibrium.

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6. ACKNOWLEDGEMENT

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