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Statistical Dynamics

A. Tate[1]

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A way is suggested of incorporating the exact dynamics of a system into a statistical framework which is self-contained for low-order distribution functions.

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1. INTRODUCTION

In trying to predict the evolution of a system consisting of many constituent parts, three distinct problems are involved. First, the equations of motion of the constituents need to be known; second, their detailed initial state needs to be known; and finally, simple approximations valid within a certain range of physical conditions are required. Sometimes these problems have become intertwined with one another, possibly leading to some obscurity. We will examine the second of these problems, which is in many ways the simplest, and in so doing we make extensive use of the concept of entropy. Entropy is usually associated with systems in thermodynamic equilibrium and when we come to extend the ideas to unsteady conditions care must be taken to include the dynamics adequately. It is the concept of entropy that allows one to work only with the low-order distribution functions and yet include the dynamics of the system exactly.

The evolution of low-order distribution functions usually runs into logical difficulties because the equations do not form a closed system as is demonstrated by the BBGKY hierarchy of equations. The fact that the system may asymptotically tend to equilibrium in a determinable way, as has been shown by Prigogine,[7] does not really remove this difficulty, and indeed, for "short" times the closure difficulty recurs. What is not always stated explicitly is that there are really two problems. One problem is to find some simple way of expressing the dynamics in terms, for instance, of symmetry properties, collective coordinates, quasiparticles, or significant structures. The other, quite distinct problem is to find some way of determining a unique detailed

[1] Royal Armament Research and Development Establishment, Fort Halstead, Sevenoaks, Kent, England.

initial state for the system when only a knowledge of certain gross features exists. The way in which this latter problem can be resolved in an equilibrium theory was first suggested by Gibbs,[1] who derived the canonical distribution of the system by maximizing the entropy functional of the distribution function subject to a prescribed average energy. More recently, Shannon and Weaver[8] and Jaynes[3,4] set the theory on a firmer basis by showing that, under elementary consistency conditions, there exists an essentially unique functional that measures the amount of uncertainty represented by a distribution function. This particular functional we can associate with the entropy.

When we come to consider nonequilibrium situations, the dynamics of the system must clearly be taken into account. Previous work, such as that of Hall[2] and Lewis,[5] has used the entropy concept to derive approximate equations of motion for low-order distribution functions. This seems to be a misuse of entropy, which is not meant to be an approximation technique. Lewis' work is most interesting however, because his "principle" goes a long way to explaining the many definitions of entropy in physics and it does lead to closed systems of equations for low-order distribution functions. In this paper, we extend Lewis' principle so that the dynamics are contained exactly but the low-order distribution functions still form a closed system. No attempt is made in this paper to obtain approximate solutions.

2. EXTENSION OF LEWIS' PRINCIPLE

For completeness, we begin by outlining Lewis' work, using his notation. Consider a conservative classical mechanical system having r degrees of freedom and characterized by a Hamiltonian $H(z)$, where $z = (q, p) = (q_1, \ldots, q_i; p_1, \ldots, p_i)$, the q's and p's being generalized coordinates and their conjugate momenta. For certain conditions on H, there exists a one-parameter family of solution operators T_t such that[2]

$$z(t) = T_t z(0), \qquad T_0 = 1, \qquad T_t T_{t^1} = T_{t+t^1} \tag{1}$$

Next, we introduce a probability distribution P_t in phase space and a corresponding probability density $w(t, z)$ such that for every subset A

$$P_t(A) = \int_A w(t, z)\, dz \tag{2}$$

is the probability that, at time t, z is in A. Lewis then shows that w satisfies the Liouville equation

$$\partial w/\partial t = (H; w) \tag{3}$$

and that the solution of this equation is given by

$$w(t, z) = T_t w(0, z) \tag{4}$$

[2] Lewis uses S instead of T, but here S will be reserved for entropy.

The entropy functional of this distribution function has been shown by Shannon and Weaver[8] and Jaynes[3,4] to be

$$S[w] = -k \int w(t, z) \ln w(t, z)\, dz \tag{5}$$

Suppose we wish to find the evolution of a low-order distribution function such as the single-particle distribution function which is defined by

$$f_1(t, z_1) = \int w(t, z)\, dz_2 \cdots dz_n \tag{6}$$

Lewis' approach is to choose from the many possible w's satisfying Eq. (6) that one which will maximize the basic entropy functional given by Eq. (5), which he denotes by $w[f_1]$. Then, using Liouville's equation, Lewis shows that

$$\frac{\partial f_1}{\partial t} = \int w_t[f_1]\, dz_2 \cdots dz_n = \int (H; w[f_1])\, dz \cdots dz_n \tag{7}$$

and there exists a new entropy functional $S_1[f_1]$ defined by

$$S_1[f_1] = \max S[w] = S[w[f_1]] \tag{8}$$

Lewis calls a function such as w or f_1 a *state function* u and assumes that there exists a complete description consisting of an equation of motion

$$\partial u/\partial t = Mu \tag{9}$$

and an entropy functional

$$S = S[u] \tag{10}$$

Introducing a new state function of the form

$$f = Lu \tag{11}$$

where L is a linear operator, Lewis special principle is:

For given f, let $u[f]$ be the unique state function that maximizes Eq. (10) subject to Eq. (11) and possible other side conditions such as normalization or symmetry conditions. Then the equation of motion for f is

$$\partial f/\partial t = LMu[f] \tag{12}$$

and its entropy functional is

$$S_1[f] = S[u[f]] \tag{13}$$

Applying the principle in this form only leads to the Vlasov equation, however.

Lewis then suggests that a better description might result if the entropy is maximized after a short interval of time τ. Letting the solution operator for u be V_t, i.e.,

$$u(t) = V_t u(0) \tag{14}$$

he assumes that the equation of motion of f is of the form

$$\partial f/\partial t \sim (1/\tau)\, L\{V_r u[f(t)] - u[f(t)]\} \tag{15}$$

Lewis general principle is:

For given f, let $u[f]$ be the unique state function that maximizes Eq. (10) subject to Eq. (11) and possibly other side conditions such as normalization or symmetry conditions. Then, the equation of motion for f is given by Eq. (15) and its entropy functional by Eq. (13).

With a few extra assumptions, the principle leads to the Boltzmann equation. To find better approximations, the principle would presumably have to be refined even more.

Here, it is suggested that the maximization of the entropy functional can be used to form closed equations for low-order distribution functions in a unique way. If a low-order distribution function or macroscopic parameter is given initially, this defines the many possible w's forming an ensemble whose entropy is to assessed and from which the one with maximum entropy is to be chosen. It is this distribution function that must be used in all later averagings and not the distribution function whose entropy is maximized relative to the restrictive conditions (6) at some later time t.

If the restrictive conditions change, as in Lewis' work, then the members of the ensemble of w's change. But if we know how the system evolves from zero time, some apparently admissible N-particle distribution functions at time t should be rejected as not satisfying the initial conditions and this alters the maximum-entropy estimate.

3. GREENS FUNCTION APPROACH

To make the above formulation more explicit, it is convenient to use a Greens function approach. With appropriate boundary conditions, the evolution of each possible N-particle distribution function of the system is governed by an equation of the form

$$w(t, z) = \int G(tz \mid 0z^1)\, w(0z^1)\, dz^1 \tag{16}$$

where G is the N-particle Greens function of the Liouville equation. Suppose that the one-particle distribution function $f_1(0, z)$ and several macroscopic parameters P_r are known initially; then S must be maximized subject to these conditions and to the normalizing condition

$$\int w(t, z)\, dz = 1 \tag{17}$$

(Note that knowledge of f_1 is not sufficient to determine the total energy of the system. Using it, we can only calculate the average kinetic energy density, but we cannot determine the potential energy density due to the interactions of particles of the system.)

Using Lagrange's method of undetermined multipliers and the notation of Lewis,[5] we introduce the functional

$$J = S[w(0, z)] - \alpha \left\{ \int w(0, z)\, dz - 1 \right\} - \sum_r \beta_r \left\{ \int \hat{P}_r(z)\, w(0, z)\, dz - P_r \right\} - Q(w, \lambda) \tag{18}$$

where

$$Q(w, \lambda) = \int \lambda(z_1)\, w(0, z)\, dz - \int \lambda(z_1) f_1(z_1)\, dz_1 \tag{19}$$

and $\hat{P}_r$ are the microscopic operators equivalent to the macroscopic P_r parameters. Since w is symmetric, (19) can be rewritten

$$Q(w, \lambda) = \frac{1}{N} \sum_i \int \lambda(z_i)\, w(0, z)\, dz - \int \lambda(z_1) f_1(z_1)\, dz_1 \tag{20}$$

Setting $\partial J/\partial \alpha = 0$ and $\partial J/\partial \beta = 0$ yields the averaging equations, while setting $\partial J/\partial w = 0$ yields the condition

$$-k(1 + \ln w) - \alpha - \sum_r \beta_r \hat{P}_r - \frac{1}{N} \sum_{i=1}^{N} \lambda(z_i) = 0 \tag{21}$$

Rearranging (21) gives the w of maximum entropy w_m as

$$w_m(0, z) = A \exp\left[-\sum_r B_r \hat{P}_r \right] \prod_{i=1}^{N} \phi(z_i) \tag{22}$$

where A, B_r, and ϕ are determined from the equations

$$A \int \exp\left[-\sum_r B_r \hat{P}_r \right] \prod_{i=1}^{N} \phi(z_i)\, dz = 1 \tag{23a}$$

$$A \int P_r \exp\left[-\sum_r B_r \hat{P}_r \right] \prod_{i=1}^{w} \phi(z_i)\, dz = P_r \tag{23b}$$

$$A \int \exp\left[-\sum_r B_r \hat{P}_r \right] \prod_{i=1}^{w} \phi(z_i)\, dz_2 \cdots dz_n = f_1(0, z_1) \tag{23c}$$

If the system is of finite extent, then the boundary conditions will be reflected in the form of G, as is shown in Morse and Feshback.[6] The N-particle distribution with the maximum entropy at any later time is thus given by

$$w_m(t, z) = \int G(tz \mid 0z^1)\, w_m(0, z^1)\, dz^1 \tag{24}$$

The P_r must form a complete set of macroscopic parameters in the sense that the macroscopic state of the sytem must be completely determined by them. If the total energy of the system, which we will denote by H, is known, then w_m takes on a familiar form, namely

$$w_m(t, z) = A \exp(-B\hat{H}) \tag{25}$$

If the the macroscopic variables or the low-order distribution functions are given for an interval of time, the formalism becomes a little more complex. First, as the microscopic motion is reversible, we can write

$$w(t', z') = \int \tilde{G}(t'z' \mid t''z'')\, w(t'', z'')\, dz'', \qquad t' < t'' \tag{26}$$

where $\tilde{G}$ is the adjoint Greens function to G and is defined so that

$$\tilde{G}(t'z' \mid t''z'') = 0 \qquad \text{for} \quad t' > t'' \tag{27}$$

Now, we wish to maximize (5) subject to the normalizing condition and to the restricting macroscopic conditions,

$$\int \hat{P}_r(z')\, w(t', z')\, dt' = P_r(t'), \qquad t' < t \tag{28}$$

Using (26) with $t'' = t$, $z'' = z$,

$$\int\int \hat{P}_r(z')\, \tilde{G}(t'z' \mid tz)\, w(t, z)\, dz'\, dz = P_r(t'), \qquad t' < t \tag{29}$$

Now, proceeding as above to find $\delta/\delta w$ and using (27) gives

$$\ln w_m(t, z) + \alpha + \sum_r \int_{-\infty}^{\infty} \beta_r(t')\, \hat{P}_r(z')\, \tilde{G}(t'z' \mid tz)\, dz'\, dt' = 0 \tag{30}$$

where α and β_r are Lagrange's undetermined multipliers, which are calculated by substituting the above form of w into the normalizing conditions and Eq. (28).

Once $w_m(t, z)$ is known, then all average quantities can be calculated. The above theory thus gives a way of determining the most probable evolution of the system given only certain coarse averages. The scope of the predictions are thus determined by the limits of knowledge, as one might reasonably expect, and yet no knowledge is arbitrarily discarded.

4. A PARTICULAR FORM OF INTERACTION POTENTIAL

In order to proceed further, it is necessary to consider a special form for the interaction potential V. We will therefore suppose

$$V = \sum_{i>j} V_{ij}(1q_i - q_j1) \tag{31}$$

Taking the only known macroscopic parameter to be total energy H, then, by using suitable units,

$$H = \sum \tfrac{1}{2} p_i^2 + V \tag{32}$$

If $f_1(0, z_1)$ is also known, then (22) becomes

$$w_m(0, z) = A \exp(-BH) \prod_{i=1}^{N} \phi(z_i) \tag{33}$$

Substituting in (23c),

$$\phi(z_i) \exp(-Bp_1^2/2)/g = f_1(0, z_i) \tag{34}$$

where g is a constant. Substituting for ϕ into (33),

$$w_m(0, z) = Ag^N \exp(-BV) \prod_{i=1}^{N} f(0, z_i) \tag{35}$$

The two-particle distribution function then takes the simple form

$$f_2(0, z_1, z_2) = \exp(-BV_{12}) f(0, z_1) f(0, z_2) \tag{36}$$

The evolution of the system is given by substituting (35) into (24), and in general no simple solution exists. The next step is thus to find suitable ways of approximating the Greens function.

5. CONCLUSION

In the previous work of Hall[2] and Lewis,[5] the ensemble of N-particle distribution functions is chosen so that the members fit the one-particle distribution function some infinitesimal or at most some very short time earlier. In this way, the members of the ensemble keep changing as f_1 changes and it is not clear how far the statistics are blurring out the dynamics rather than genuinely approximating them.

It has been shown above how a closed equation for the one-particle distribution function can be obtained in such a way that, in Jaynes words, it is maximally noncommital with regard to missing information, but nevertheless incorporates the dynamics of the system exactly.

The next and far more difficult problem is to find some suitable approximation to the N-particle Greens function in order that simple equations for the evolution of f_1 and the macroscopic parameters may be determined.

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