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Statistical Mechanics of the Steady State

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The description of steady-state phenomena, near equilibrium, in terms of Gibbs ensembles is discussed. The Liouville equation is modified to include external nonconservative forces which prevent the system from reaching equilibrium. The steady state ensembles are then obtained as (approximately) time-independent solutions to the Liouville equation; such ensembles depend linearly on the thermodynamic parameters which characterize the deviation from equilibrium. With the aid of the steady state ensembles the linear relations between the thermodynamic fluxes and forces are obtained.

1. INTRODUCTION

THE description of transport phenomena in gases at low density may be based on the Boltzmann equation.[1] Discussions which are applicable to gases at higher density and to liquids have been given by a number of authors. In particular, Born and Green,[2] Bogoliubov,[3] and Kirkwood[4] have obtained kinetic equations which provide a generalization of the Boltzmann equation, and Green[5] and Hashitsume[6] have discussed transport phenomena from the point of view of Markoff random processes. The methods of Kirkwood[4] and of Green[5] have been carried to the point of yielding explicit formulas for such transport coefficients as the thermal conductivity and viscosity; however, general methods for evaluating these formulas have not been given.

The discussions of Born and Green, Bogoliubov, and Kirkwood are based on the distribution function method, the quantities of basic interest being the molecular distribution functions of low order. In the treatments of Green and Hashitsume the time dependence of the pertinent macroscopic variables is discussed directly. It is expected that some formal advantages may be offered by an approach to nonequilibrium phenomena in which the Gibbs ensemble plays a more prominent role. Here we wish to discuss the construction of Gibbs ensembles for the description of the steady state, near equilibrium; some comment will also be devoted to nonsteady phenomena. It will be seen that a steady-state ensemble can be simply expressed in terms of the external forces which maintain the deviation from equilibrium. With the aid of the steady-state ensemble one can obtain linear relations between the thermodynamic fluxes and forces, the coefficients in these relations being the transport coefficients.

Certain of the methods used here have also been applied by other authors. In particular we mention the work of Kubo,[7] Kohn and Luttinger,[8] Lax,[9] and Block[10] on electrical conductivity, and of Mori[11] on transport phenomena in fluids. In addition Bergmann and Lebowitz[12] have given a discussion of the steady state which in some respects is similar to ours.

2. LIOUVILLE EQUATION INCLUDING EXTERNAL FORCES

We consider first a classical system, surrounded by and interacting with external reservoirs and mechanical devices; the system and surroundings collectively will on occasion be referred to as the universe. We suppose the surroundings to be large compared to the system so that an approximate steady state can be attained in which variables referring to the system change slowly. We assume the Hamiltonian for the universe to be separated as

$$H_u = H + H_s + V, \tag{1}$$

where H and H_s depend on variables referring only to the system and surroundings, respectively, and the energy of interaction V is independent of the momentum variables. A Gibbs ensemble for the universe is described by a distribution function ρ satisfying the Liouville equation

$$\partial\rho/\partial t + \{\rho, H_u\} = 0, \tag{2}$$

where the curly brackets represent the Poisson bracket. An ensemble for the universe entails one for the system and surroundings separately, according to

$$f = \int d\psi\, \rho, \quad g = \int d\varphi\, \rho. \tag{3}$$

Here the integrations are taken over that part of phase space referring to the surroundings and to the system,

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[1] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, Cambridge, 1939).

[2] M. Born and H. S. Green, *A General Kinetic Theory of Liquids* (Cambridge University Press, Cambridge, 1949).

[3] N. Bogoliubov, J. Phys. U.S.S.R. **10**, 265 (1946).

[4] J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946); **15**, 72 (1947); Kirkwood, Buff, and Green, J. Chem. Phys. **17**, 988 (1949).

[5] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954).

[6] N. Hashitsume, Prog. Theoret. Phys. (Kyoto) **8**, 461 (1952).

[7] R. Kubo, J. Phys. Soc. (Japan) **12**, 570 (1957); Kubo, Yokota, and Nakajima, J. Phys. Soc. (Japan) **12**, 1203 (1957).

[8] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957); **109**, 1892 (1958).

[9] M. Lax, Phys. Rev. **109**, 1921 (1958).

[10] B. Block, Ann. Phys. **6**, 37 (1959).

[11] H. Mori, J. Phys. Soc. (Japan) **11**, 1029 (1956); Phys. Rev. **112**, 1829 (1958).

[12] P. G. Bergmann and J. L. Lebowitz, Phys. Rev. **99**, 578 (1955); Ann. Phys. **1**, 1 (1957).

respectively, $d\psi$ and $d\varphi$ being the corresponding elements of volume. If ρ is normalized,

$$\int d\psi\, d\varphi\, \rho = 1, \tag{4}$$

then it follows immediately that f and g are normalized,

$$\int d\varphi\, f = 1, \quad \int d\psi\, g = 1. \tag{5}$$

If we write

$$\rho = fg(1+\chi), \tag{6}$$

then χ is a measure of the statistical correlation between the system and surroundings.

We now wish to obtain a Liouville equation for f. Integration of Eq. (2) over the phase space for the surroundings yields

$$\partial f/\partial t + \{f,H\} + \int d\psi \{\rho, H_s\} + \int d\psi \{\rho, V\} = 0. \tag{7}$$

The integrand in the third term above is a divergence in the phase space of the surroundings; the integral then vanishes if ρ is assumed to vanish sufficiently rapidly in the remote regions of phase space. The last term may be transformed to give

$$\partial f/\partial t + \{f,H\} + \partial f F_i/\partial p_i = 0, \tag{8}$$

where

$$F_i = -\int d\psi\, g(1+\chi)\partial V/\partial q_i. \tag{9}$$

The q_i and p_i here are the coordinates and momenta of the system. We have used the summation convention that terms containing repeated indices are to be summed; the number of terms in the sum will be evident from the context.

The F_i are effective external forces representing the effect of the surroundings on the system. They are in general time-dependent, if the universe is not in equilibrium. However, if the surroundings are large compared to the system we expect that in some situations the time dependence of the F_i will be sufficiently slow that over long periods of time they may be treated as constant; we further assume that under such conditions the system will attain an approximately steady state in which its distribution function is substantially constant.

If $\chi = 0$, that is, if the system and surroundings are uncorrelated, the external forces are conservative. Their effect may then be described by adding a suitable term to the system Hamiltonian; this will simply lead to a modification of the equilibrium properties of the system. In general, however,

$$\partial F_i/\partial p_i \neq 0, \tag{10}$$

and the effect of the external forces cannot be included in the Hamiltonian formalism. We note that in such a case $f=1$ is not a solution to the Liouville equation (8); as a consequence the principle of equal *a priori* probabilities is not valid, in the system phase space.

3. STEADY-STATE SOLUTION TO THE LIOUVILLE EQUATION

Our problem is now to obtain solutions to the Liouville equation (8), under the assumption that F_i and f are nearly time-independent. We further assume the F_i to be small in the sense that the steady-state solution is near equilibrium, that is, that

$$f = f_0(1+\Delta\eta), \tag{11}$$

where $\Delta\eta$ is small and f_0 corresponds to an equilibrium ensemble. We first choose for f_0 the canonical ensemble,

$$f_0 = e^{\alpha - \beta H}; \tag{12}$$

the grand canonical ensemble will be introduced below. Here $\beta = 1/kT$ where k is Boltzmann's constant and T the Kelvin temperature, and α is $1/kT$ times the Helmholtz function.

The equation for the determination of $\Delta\eta$ is

$$\partial\Delta\eta/\partial t + \{\Delta\eta, H\} - \beta F_i \partial H/\partial p_i + \partial F_i/\partial p_i = 0,$$

where terms containing the product of $\Delta\eta$ and F_i have been neglected. Rewrite this equation as

$$\partial\Delta\eta/\partial t + \{\Delta\eta, H\} = h, \tag{13}$$

where

$$h = \beta F_i \partial H/\partial p_i - \partial F_i/\partial p_i. \tag{14}$$

We solve Eq. (13) by introducing an adiabatic turning-on of the external forces. That is we imagine that in the remote past ($t=-\infty$) the system is in equilibrium without interaction with the surroundings. The external forces are then slowly turned on (for example by the removal of adiabatic walls), reaching their full value at $t=0$. If the turning-on is sufficiently slow we expect that the system will at all times adjust itself to the instantaneous values of the external forces, reaching the desired steady state at $t=0$. Presumably the results will be independent of the particular manner in which the forces are increased; we will make the choice

$$F_i(t) = e^{\epsilon t} F_{0i},$$

or

$$h(t) = e^{\epsilon t} h_0. \tag{15}$$

Here ϵ is small, that is, $1/\epsilon$ is large compared to the time necessary for the system to attain a steady state.

With the assumption (15) for h, a solution to Eq. (13) is

$$\Delta\eta(P,t) = \int_{-\infty}^{t} e^{\epsilon t'} h_0(P_{t'-t})\, dt'.$$

Here P denotes the position of a point in phase space and P_t is the position at time t of that point which was at P initially. At $t=0$ we have

$$\Delta\eta(P)=\int_{-\infty}^{0} e^{\epsilon t'} h_0(P_{t'})dt', \tag{16}$$

and the steady-state ensemble is

$$f=f_0\left[1+\int_{-\infty}^{0} e^{\epsilon t'} h_0(P_{t'})dt'\right]. \tag{17}$$

4. SPECIFICATION OF THE EXTERNAL FORCES

To proceed further it is necessary to specify the external forces, or h_0, in more detail. For this purpose we consider first the interaction of the system with a single reservoir. We suppose the forces F_i^r due to this reservoir to be such that the system can reach an equilibrium state described by a canonical distribution

$$f_r=e^{(\alpha-\beta_r H)},$$

where $1/k\beta_r$ is the temperature of the reservoir. Substituting this expression into the Liouville equation (8) (with only the forces F_i^r being included) we find the condition

$$\partial e^{(-\beta_r H)} F_i^r/\partial p_i=0,$$

or

$$\partial F_i^r/\partial p_i=\beta_r F_i^r \partial H/\partial p_i. \tag{18}$$

In the presence of more than one reservoir the quantity h of Eq. (14) is

$$h=\sum_r[\beta F_i^r\partial H/\partial p_i-\partial F_i^r/\partial p_i],$$

which reduces with the help of Eq. (18) to

$$h=\sum_r(\beta-\beta_r)F_i^r\partial H/\partial p_i.$$

Now $F_i^r\partial H/\partial p_i$ is the rate at which energy is transferred from the rth reservoir to the system. Denoting this quantity by q_r,

$$q_r=F_i^r\partial H/\partial p_i,$$

we have

$$h=\sum_r(\beta-\beta_r)q_r.$$

Consider next the interaction with an external mechanical device. For concreteness we may imagine the system to be a fluid enclosed in the annular region between two concentric cylinders. A relative rotation of the two cylinders will produce a transport of momentum across the fluid. Evidently for such mechanical devices one can choose the external forces to be momentum independent,

$$\partial F_i/\partial p_i=0. \tag{19}$$

(However, the forces are still nonconservative and cannot be represented by a potential added to the Hamiltonian.) Their contribution to h is simply

$$\beta F_i\partial H/\partial p_i=-\beta W,$$

where W is the rate at which work is done by the system.

In the presence of both reservoirs and mechanical devices

$$h=\sum_r(\beta-\beta_r)q_r-\beta W. \tag{20}$$

For any particular system, q_r and W can be expressed as functions of the q_i and p_i; the specification of h is then complete.

Maintenance of a steady state requires that, on the average, the energy of the system be constant, or

$$\sum_r\langle q_r\rangle-\langle W\rangle=0,$$

where the angular brackets denote an average taken with respect to the steady state ensemble. Thus

$$\langle h\rangle=-\sum_r\beta_r\langle q_r\rangle.$$

This is just $1/k$ times the entropy production σ familiar in nonequilibrium thermodynamics,[13]

$$\langle h\rangle=\sigma/k.$$

The formalism has so far been restricted to closed systems. For the treatment of such phenomena as electrical conduction and diffusion it is necessary to consider open systems, able to interchange particles with the environment. We will defer the discussion of open systems, as they are somewhat more easily handled in the quantum theory. It will be shown below that the quantity h for an open system is

$$h=\sum_r(\beta-\beta_r)q_r-\beta W-\sum_r(\beta\mu-\beta_r\mu_r)j_r. \tag{21}$$

Here j_r is the rate at which particles are added to the system from the rth reservoir; μ and μ_r are the chemical potentials for the system and rth reservoir. The average of h is

$$\langle h\rangle=-\sum_r\beta_r\langle q_r\rangle-\sum_r(\beta\mu-\beta_r\mu_r)\langle j_r\rangle,$$

or, for the steady state,

$$\sum_r\langle j_r\rangle=0,$$

and

$$\langle h\rangle=-\sum_r\beta_r\langle q_r\rangle+\sum_r\beta_r\mu_r\langle j_r\rangle.$$

This is again $1/k$ times the entropy production σ.

5. LINEAR RELATIONS BETWEEN FLUXES AND FORCES

The quantity h can be written in the form

$$h=(1/k)\sum_\alpha X_\alpha J_\alpha, \tag{22}$$

where the X_α are thermodynamic forces representing the deviation from equilibrium, and the $J_\alpha(P)$ are phase functions whose averages are the thermodynamic fluxes. Combining Eqs. (17) and (22) gives for the steady state ensemble

$$f(P)=f_0(P)\left[1+\frac{1}{k}\sum_\alpha X_\alpha\int_{-\infty}^{0} e^{\epsilon t}J_\alpha(P_t)dt\right].$$

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[13] S. R. De Groot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1952).

With the help of this ensemble we find for the thermodynamic fluxes

$$\langle J_\beta\rangle = \left\langle J_\beta(P)\left[1+\frac{1}{k}\sum_\alpha X_\alpha \int_{-\infty}^{0} e^{\epsilon t}J_\alpha(P_t)dt\right]\right\rangle_0,$$

where $\langle\ \rangle_0$ denotes an average taken with respect to the equilibrium ensemble f_0. Since the fluxes vanish in equilibrium,

$$\langle J_\beta\rangle = \frac{1}{k}\sum_\alpha X_\alpha \int_{-\infty}^{0} e^{\epsilon t}dt\langle J_\beta(P)J_\alpha(P_t)\rangle_0. \tag{23}$$

With Eq. (23) we have derived the familiar linear relations between fluxes and forces,

$$\langle J_\beta\rangle = \textstyle\sum_\alpha L_{\beta\alpha}X_\alpha, \tag{24}$$

with the transport coefficients being given by

$$L_{\beta\alpha} = \frac{1}{k}\int_{-\infty}^{0} e^{\epsilon t}\langle J_\beta(P)J_\alpha(P_t)\rangle_0 dt. \tag{25}$$

Onsager's theorem[13] is an immediate consequence of Eq. (25) and the reversibility of the mechanical equations of motion.

The positive-definite nature of the entropy production is readily demonstrated. Consider the inequality

$$I \equiv \left\langle\left[\int_{-\infty}^{0} e^{\epsilon t}J_\alpha(P_t)dt\right]^2\right\rangle_0 \geqslant 0.$$

It follows from invariance under a translation of the origin of time that

$$\langle J_\alpha(P_t)J_\alpha(P_{t'})\rangle_0 = \langle J_\alpha(P)J_\alpha(P_{t'-t})\rangle_0,$$

and therefore

$$I = \int_{-\infty}^{0} e^{\epsilon t}dt\int_{-\infty}^{0} e^{\epsilon t'}dt'\langle J_\alpha(P)J_\alpha(P_{t'-t})\rangle_0$$

$$= \int_{-\infty}^{0} e^{\epsilon t}dt\int_{-\infty}^{-t} e^{\epsilon(s+t)}ds\langle J_\alpha(P)J_\alpha(P_s)\rangle_0.$$

An integration by parts yields

$$I = \frac{1}{\epsilon}\int_{-\infty}^{0} e^{\epsilon t}\langle J_\alpha(P)J_\alpha(P_t)\rangle_0 dt.$$

Consequently,

$$L_{\alpha\alpha} = \epsilon I/k \geqslant 0.$$

Thus the diagonal elements of L are non-negative, in any representation. This has the result that the entropy production, which can be written

$$\sigma = \textstyle\sum_{\alpha,\beta} X_\alpha L_{\alpha\beta}X_\beta,$$

is non-negative.

6. NONSTEADY PHENOMENA

The above formalism is readily modified to include slowly varying time-dependent phenomena. Supposing the external forces to depend on the time, we consider a single Fourier component. Including also the adiabatic factor, we have

$$X_\alpha(t) = e^{(i\omega+\epsilon)t}X_{\alpha 0}.$$

The frequency ω must be assumed to be sufficiently small that the system can at all times adjust itself to the instantaneous values of the external forces, that is $1/\omega$ must be large compared to the relaxation times characteristic of the system. As in the previous discussion, we then find the ensemble

$$f(P) = f_0(P)\left[1+\frac{1}{k}\sum_\alpha X_{\alpha 0}e^{i\omega t}\int_{-\infty}^{0} e^{(i\omega+\epsilon)t}J_\alpha(P_t)dt\right].$$

The linear relations between fluxes and forces are

$$\langle J_\beta\rangle = \textstyle\sum_\alpha L_{\beta\alpha}(\omega)X_\alpha,$$

with the frequency-dependent transport coefficients being

$$L_{\beta\alpha}(\omega) = \frac{1}{k}\int_{-\infty}^{0} e^{(i\omega+\epsilon)t}\langle J_\beta(P)J_\alpha(P_t)\rangle_0 dt. \tag{26}$$

7. QUANTUM THEORY

We consider next the modifications necessary for quantum mechanical systems. An ensemble for the universe is described by the density matrix ρ, satisfying the Liouville equation

$$\partial\rho/\partial t + \frac{1}{i\hbar}[\rho, H_u] = 0.$$

Let q' and Q' be the eigenvalues of a complete set of commuting variables referring to the system and surroundings, respectively. Then the density matrix f for the system is given by

$$\langle q'|f|q''\rangle = \textstyle\sum_{Q'}\langle q',Q'|\rho|q'',Q'\rangle.$$

Assuming the Hamiltonian operator for the universe to be separated as in Eq. (1), we find the Liouville equation for f

$$\partial f/\partial t + \frac{1}{i\hbar}[f,H] + \frac{1}{i\hbar}\,\mathrm{Ts}[\rho,V] = 0.$$

Here Ts denotes a trace taken over the eigenvalues of variables referring to the surroundings, that is

$$\langle q'|\mathrm{Ts}A|q''\rangle = \textstyle\sum_{Q'}\langle q',Q'|A|q'',Q'\rangle.$$

If we define X by

$$\rho = fX,$$

we have

$$\partial f/\partial t + \frac{1}{i\hbar}[f,H] + \frac{1}{i\hbar}\,\mathrm{Ts}[fX,V] = 0. \tag{27}$$

Proceeding now as before we assume f to be close to an equilibrium ensemble

$$f=f_0(1+\Delta\eta).$$

In order to treat open systems we choose for f_0 a grand canonical ensemble,

$$f_0=e^{\alpha-\beta H+\beta\mu n},$$

where μ is the chemical potential and n the number of particles. (For simplicity we consider systems containing one type of particle only; the generalization to a variety of particles is immediate.) We then find the equation for $\Delta\eta$

$$\partial\Delta\eta/\partial t+\frac{1}{i\hbar}[\Delta\eta,H]=h, \tag{28}$$

where to lowest order

$$h=-\frac{1}{i\hbar f_0}\,\mathrm{Ts}[f_0X,V].$$

Equation (28) can be solved as before; we find

$$\Delta\eta=\int_{-\infty}^{0}e^{\epsilon t}h(t)dt,$$

where $h(t)$ is the Heisenberg representation operator

$$h(t)=e^{(i/\hbar)Ht}h_0e^{-(i/\hbar)Ht}.$$

To relate h to the thermodynamic forces, consider as before the interaction with a single reservoir (thermal or particle). Suppose this interaction to be such that the equilibrium state of the system is described by the grand canonical ensemble.

$$f_r=e^{\alpha-\beta_rH+\beta_r\mu_rn}. \tag{29}$$

Here $1/k\beta_r$ is the temperature of the rth reservoir and μ_r its chemical potential. Including in Eq. (27) the interaction with the rth reservoir only, and requiring that the ensemble (29) be a solution to this equation, we find the condition

$$\mathrm{Ts}[f_0X_r,V_r]=0. \tag{30}$$

To first order in $\beta-\beta_r$ and $\mu-\mu_r$,

$$f_0=[1+(\beta_r-\beta)H-(\beta_r\mu_r-\beta\mu)]f_r,$$

and, with the help of Eq. (30), h is reduced to

$$\begin{aligned}h&=-\frac{1}{i\hbar f_0}\sum_r\mathrm{Ts}[f_rX_r,V_r]\\&=-\frac{1}{i\hbar f_0}\sum_r\{(\beta_r-\beta)\,\mathrm{Ts}[H,V_r]f_rX_r\\&\qquad-(\beta_r\mu_r-\beta\mu)\,\mathrm{Ts}[n,V_r]f_rX_r\}.\end{aligned}$$

Now $[H,V_r]/i\hbar$ is the rate of change of the system energy, due to the interaction with the rth reservoir; that is, it is the flux of energy into the system from the rth reservoir. Similarly $[n,V_r]/i\hbar$ is the flux of particles into the system from the rth reservoir. While such fluxes presumably do not commute with H, n, or f_r, we may in the present context neglect the effects of the uncertainty principle as applied to H, n, and the fluxes. One may in fact replace these quantities by commuting "macroscopic variables," as discussed by von Neumann[14] and van Kampen.[15] Then

$$\begin{aligned}h=-\frac{1}{i\hbar f_0}\sum_r f_r\{(\beta_r-\beta)\,\mathrm{Ts}[H,V_r]X_r\\-(\beta_r\mu_r-\beta\mu)\,\mathrm{Ts}[n,V_r]X_r\},\end{aligned}$$

or, putting $f_r=f_0$ in lowest order,

$$h=\textstyle\sum_r[(\beta-\beta_r)q_r-(\beta\mu-\beta_r\mu_r)j_r],$$

where

$$q_r=\frac{1}{i\hbar}\,\mathrm{Ts}[H,V_r]X_r,\quad j_r=\frac{1}{i\hbar}\,\mathrm{Ts}[n,V_r]X_r.$$

Finally consider the interaction with an external mechanical device. In the classical treatment we characterized such devices by the equation

$$\partial F_i/\partial p_i=0,$$

which, on taking into account Eq. (9), may be written

$$\int d\psi\{X,V\}=0, \tag{31}$$

where

$$X=(1+\chi)g.$$

The quantum mechanical analog of Eq. (31) is

$$\mathrm{Ts}[X,V]=0.$$

The contribution to h of a mechanical device is then

$$h=-(1/i\hbar f_0)\,\mathrm{Ts}[f_0,V]X.$$

Assuming n to be a constant of the motion in the presence of the mechanical device, and further assuming the flux $[H,V]/i\hbar$ to commute with H, we find

$$h=-\beta W,$$

where W is the rate at which work is done by the system,

$$W=-(1/i\hbar)\,\mathrm{Ts}[H,V]X.$$

In the presence of both reservoirs and mechanical devices

$$h=\textstyle\sum_r[(\beta-\beta_r)q_r-(\beta\mu-\beta_r\mu_r)j_r]-\beta W.$$

The derivation of the linear relations between fluxes and forces now proceeds as before.

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[14] J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, Princeton, New Jersey, 1955).

[15] N. G. van Kampen, Physica **20**, 603 (1954).