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Phase-Space Description of Non-Uniform Systems

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1. – Introduction.

I shall describe here some work whose connecting link is its orientation towards the development of a Gibbsian statistical mechanics of non-equilibrium processes [1-7]. Essentially we try to find Γ-space ensembles that will represent systems not in equilibrium in the same way that the canonical ensembles represent systems in equilibrium. All the physically interesting equilibrium properties of a given macroscopic system, *i.e.*, one with a given Hamiltonian, are completely specified, through the use of the canonical ensemble, by one parameter, the temperature. It would be very desirable to find analogous ensembles which would give the properties of non-equilibrium systems in terms of a certain set of a few parameters characterizing the state of the system. Clearly such a description cannot hold for completely arbitrary non-equilibrium situations and, therefore, our main interest lies in those systems which, though not in equilibrium, are yet in a steady or quasi-steady state. A steady state can be realized, for example, by systems whose ends are kept in contact with heat reservoirs at constant but different temperatures. In such systems there can flow a stationary heat current. The quasi-state systems we have in mind are primarily those which are experimentally characterized by the local hydrodynamic quantities evolving in accordance with the Navier-Stokes equations. Since experimentally the behavior of these systems appears to be determined, to a large extent, by these hydrodynamic variables we hope that there exist general Gibbsian ensembles, depending only on these parameters and on the Hamiltonian, from which the properties of these systems may be directly deduced.

What we want for these quasi-steady-state systems is a Γ-space ensemble which is analogous to the Chapman-Enskog normal distributions in the kinetic

theory of gases [8]. There, the one particle distributions function $f(\boldsymbol{r}, \boldsymbol{v})$ is assumed to be determined by the values of the hydrodynamical variables. One can, of course, weaken this requirement and permit the ensemble to depend also on additional sets of variables (cf. Grad's thirteen moment method in the theory of gases [9]) including perhaps also the lower order distribution functions (cf. Bogoljubov's theory [10]) but we shall not consider here any more detailed knowledge of the system's state than that contained in the five hydrodynamic variables.

In practice it is not usually necessary to know the detailed Γ-space distribution of a system in order to find its macroscopic properties. These are mostly expressible in terms of the reduced single particle and two particle distribution functions. However, even aside from the theoretical importance of the Gibbs ensemble it might happen that, as in equilibrium, it will be more convenient to first find the N-particle distribution and then by integration the lower order distributions [11].

2. – Open systems.

We shall describe here our work on steady-state systems. In order for a system to be in a steady non-equilibrium state, it cannot be isolated but must be in contact with inexhaustable reservoirs. These reservoirs are the statistical mechanical analogue of hydrodynamic « temperature baths ». We hope that the detailed nature of the reservoirs will not significantly affect the steady-state of the system and we, therefore, construct idealized model reservoirs which have the following properties: 1) they consist of an infinite number of identical non-interacting components, 2) each component may interact with our system but once, 3) this interaction is impulsive. These idealizations permit us to describe the time evolution of the Gibbs-ensemble representing our system if we know the stochastic kernel $K(x, x')$. $K(x, x') \, \mathrm{d}x \, \mathrm{d}t$ is the conditional probability of a system located at the point x' in its Γ-space at time t to have a collision with a reservoir component, causing it to make a transition to the volume element $(x, x+\mathrm{d}x)$, in the time interval $(t, t+\mathrm{d}t)$.

The equation governing the time evolution of the ensemble density $\mu(x, t)$ is a generalization of the Liouville equation for isolated systems, taking account of changes in μ due to collisions with reservoir components. It has the form

$$(2.1) \qquad \frac{\partial \mu(x, t)}{\partial t} + (\mu, H) = \int_{\Gamma} [K(x, x') \mu(x', t) - K(x', x) \mu(x, t)] \, \mathrm{d}x' \,,$$

$$K(x, x') = \sum_{\alpha} K_{\alpha}(x, x') \,,$$

where K_α represents the effect of the α-th reservoir which, in the cases we have considered, is some kind of temperature bath at temperature T_α.

Our model, and eq. (2.1), can be generalized to include systems which can exchange both energy and particles with the reservoirs [2]. Each of these reservoirs is characterized by a temperature T_α, and chemical potential μ_x. They play the role of thermodynamic « temperature and chemical potential baths ». Almost all the results described here can be suitably generalized to include systems open with respect to particle exchange and we shall not give any more detailed consideration to it here.

It is also possible to use this type of model in quantum systems. This has been done for some problems by us [4] as well as by others. In attempting to do it, however, in a general manner, i.e., to derive an equation similar to eq. (2.1), one encounters certain difficulties. These are due to the fact that only the diagonal elements of the density matrix (which plays the role of the distribution function in quantum systems) correspond to probabilities. The quantum analogue of eq. (2.1) is, therefore, not known to us.

2'1. *Approach to stationary states.* – Eq. (2.1) unlike the Liouville equation can lead to true irreversible behavior of the ensemble density $\mu(x, t)$. We have been able to prove explicitly the following sufficiency theorems concerning $\mu(x, t)$.

1) If $K(x, x') < Mv(H(x))$, where M is a positive constant and v is an integrable function, then $\mu(x, t)$ will approach some time independent distribution as $t \to \infty$. The convergence is uniformly exponentially fast. (The proof is via a theorem due to Doeblin.)

This theorem, though very powerful, has the unfortunate disadvantage that the physically reasonable kernels K do not satisfy its stringent requirements. We have, therefore, proven a weaker but much more general type of H-theorem of the following nature:

2) If there exists a stationary ensemble satisfying eq. (2.1) then it will be approached asymptotically in time by an arbitrary initial distribution. The proof of this theorem is quite simple. Let $\mu_s(x)$ be the stationary distribution satisfying (2.1),

$$(2.2) \qquad (\mu_s, H) = \int [K(x, x') \mu_s(x') - K(x', x) \mu_s(x)] \, \mathrm{d}x' \, .$$

Define the function $w(t)$ as

$$(2.3) \qquad W(t) = \int \mu(x, t) \ln \varphi(x, t) \, \mathrm{d}x; \qquad \varphi(x, t) = \frac{\mu(x, t)}{\mu_s(x)} \, ,$$

then:

$$(2.4) \quad (a) \qquad\qquad\qquad W(t) \geqslant 0$$

the equality holding only for $\mu = \mu_s$ and

$$(2.5) \quad (b) \quad \frac{\mathrm{d}W}{\mathrm{d}t} = -\iint K(x, x')\, \mu(x', t) \left[\ln\left(\frac{\varphi(x', t)}{\varphi(x, t)} \right) + \frac{\varphi(x, t)}{\varphi(x', t)} - 1 \right] \mathrm{d}x\, \mathrm{d}x' \leqslant 0 \;.$$

The integrand in (2.5) will be zero only for those pairs of points x, x', for which either $K(x, x')$ vanishes or $\varphi(x) = \varphi(x')$. This implies that W will continue to decrease towards its minimum value until φ is constant, or $\mu(x, t)$ is proportional to $\mu_s(x)$, inside those regions A_i of Γ-space where $K(x, x') \neq 0$ for x, x' both in the same A_i. This by itself is insufficient to show an over-all asymptotic approach of $\mu(x, t)$ towards $\mu_s(x)$ when, as is often the case, the sets A_i are of a much lower dimensionality then the whole Γ-space (*i.e.*, of measure zero). It was therefore shown separately that W (or a function very similar to it) will continue to decrease until φ is constant inside all regions B_i, defined by the property that a system starting at a point in some B_i can reach any other point in the same B_i region under the *combined action* of its natural motion and collisions with reservoir components. The same type of consideration applies also to the first theorem.

The second theorem can be generalized somewhat further to show, without assuming the existence of a stationary solution μ_s, that any two distributions $\mu_1(x, t)$ and $\mu_2(x, t)$ will approach each other. This, therefore, shows that when there exists a final solution which is periodic in time, as would be the case when the Hamiltonian is periodic, then it will be approached by arbitrary initial distributions. More generally by taking $\mu_1(x, t) = \mu(x, t_1)$, $\mu_2(x, t) = \mu(x, t_2)$ we show that the initial information is gradually wiped away.

Bergmann and Morris [12] have also shown that one can construct a functional F of the distribution μ.

$$(2.6) \qquad F[\mu] = \int \frac{1}{\mu} \left[(H, \mu) + \int [K(x, x')\, \mu(x') - K(x', x)\, \mu(x)]\, \mathrm{d}x' \right]^2 \mathrm{d}x$$

is positive definite, is zero only for the stationary distribution and decrease monotonically with time. The functional F is a measure of the closeness to stationarity of any given distribution. It has the additional property that as time progresses the distribution becomes «better» by this measure. F can thus serve as a variational principle for finding the stationary distribution.

2·2. *Approach to equilibrium states.* – When the stationary state of the system is that of equilibrium, as would be the case when the system is in contact with only one reservoir, $W(t)$ assumes an easily recognizable form. This quantity which now measures the deviation of the ensemble from its equilibrium value and decreases steadily as time progresses becomes now,

$$(2.7) \qquad W(t) = \int \mu(x, t) [\ln \mu(x, t) - \ln \exp\left[(F_0 - H)\right]/kT]\,\mathrm{d}x =$$

$$= -\frac{S}{K} + \frac{U}{kT} - \frac{F_0}{kT} = [(U - TS) - F_0]/kT .$$

Here S is the ensemble entropy,

$$(2.8) \qquad\qquad S = -k \int \mu \ln \mu \, \mathrm{d}x ,$$

U is the average energy,

$$(2.9) \qquad\qquad U = \int \mu H \, \mathrm{d}x ,$$

T is the temperature of the reservoir with which the system is in contact and F_0 is the Helmholtz free energy of the system after it has come to equilibrium at this temperature. This suggests that we think of kTW as the derivation of the system's free energy from its equilibrium value. (When the equilibrium ensemble of the system is a grand canonical or an isobaric-isothermal one, corresponding to the system being also in particle and mechanical contact with its surroundings, then the role of the Helmholtz free energy in eq. (2.7) is taken over by the grand canonical or Gibbs potential respectively.)

There is, however, some difficulty with this interpretation of W in eq. (2.7). While the entropy S and internal energy U are defined by eqs. (2.8), (2.9) for an arbitrary ensemble the temperature T is only defined generally for the reservoir. It only becomes a characteristic parameter of the system when the system is close to equilibrium. The rate of change of W, however, has always a well defined meaning. According to (2.7) it has the value

$$(2.10) \qquad\qquad \dot{W} = -\frac{1}{k}\left[\dot{S} - \frac{\dot{U}}{T}\right] = -\frac{1}{k}\sigma \leqslant 0 .$$

Here σ is the sum of the rate of entropy production in the system S, and in the reservoir, $-\dot{U}/T$. The latter follows from the fact that $\dot{U}$ is the rate of

heat flow into the reservoir and T its temperature which remains unchanged. We may thus interpret W as the sum of the system's and reservoir's entropy referred to an appropriate reference level.

2`3. *Properties of the stochastic kernels and Onsager relations.* – The detailed form of the kernels $K(x, x')$ will depend for a given system on the nature of the reservoir components and on their distribution prior to a collision with the system. It was shown in reference [2] that when the components of a particular reservoir are in a Maxwellian distribution in their own μ-space at a temperature T_α, then quite generally the kernel K_α, representing the collision with that reservoir, has the « time reversed » symmetry property,

$$(2.11) \qquad K_\alpha(x', x) = \exp\left[\beta_\alpha[H(x) - H(x')]\right] K_\alpha(\bar{x}, \overline{x'}), \qquad \beta_\alpha = (kT_\alpha)^{-1}.$$

where $\bar{x}$ is that point in phase space which corresponds to x under time reversal, *i.e.*, it has the same co-ordinates and the opposite momenta as x. Further K_α will generally satisfy the « integral condition »,

$$(2.12) \qquad \int K_\alpha(x, x') \exp\left[-\beta_\alpha H(x')\right] \mathrm{d}x' = \int K_\alpha(x', x) \exp\left[-\beta_\alpha H(x)\right] \mathrm{d}x' .$$

This condition is clearly necessary, and according to the last section also sufficient, to make a system coupled only to this reservoir come to equilibrium at a temperature T_α.

When the system is coupled to several reservoirs whose temperatures are close to each other, then the final steady state of the system will deviate only slightly from equilibrium. The Onsager symmetry relations [13] for the matrix relating « fluxes » to « forces » are now valid. These can be proven in our model without an appeal to fluctuation theory and without the assumption that detailed balancing holds for the interactions between the system and reservoirs. All that is needed is the validity of eqs. (2.11), (2.12). The fluxes in our model are the rate of energy flows from the reservoirs to the system

$$(2.13) \qquad J_l = \int \mathrm{d}x \, \mu(x) \int \mathrm{d}x' \, K_l(x', x)\left[H(x') - H(x)\right] .$$

The rate of change of entropy in the l-th reservoir is σ_l,

$$(2.14) \qquad \sigma_l = - J_l/T_l$$

and the total entropy production at any time is

$$(2.15) \qquad \sigma = \dot{S} - \sum J_l/T_l .$$

In the steady state $\dot{S} = 0$ as well as

(2.16)
$$\dot{U} = \sum J_i = 0 .$$

Therefore in this state

(2.17)
$$\sigma = \sum k(\beta_i - \beta)J_i = \sum \gamma_i J_i ,$$

where β is the reference temperature. This equation shows that the J_i and γ_i are the fluxes and forces of the Onsager theory.

We can now prove from the definition of the J's that when μ in eq. (2.13) is a solution of the time-independent part of eq. (2.1) and the K_i satisfy eqs. (2.11), (2.12) that

(2.18)
$$A_{ij}^{(\beta)} \equiv \frac{\partial J_i}{\partial \gamma_j|_{\gamma_i=0}} = \frac{\partial J_j}{\partial \gamma_i|_{\gamma_i=0}} \equiv A_{ji}^{(\beta)} .$$

These are the Onsager relations.

3. – Examples.

In this section I shall describe briefly some examples to which our formalism has been applied. First we shall consider the case of a Knudsen gas [3] in a container whose walls are maintained at different temperatures. Then we shall specify our general model further by considering explicitly a particular type of reservoir. This will permit us to find exact solutions for some simple systems and to discuss approximate solutions for general systems.

3'1. *Knudsen gas.* – We wish to describe the time evolution of a gas so rarified that collisions between the molecules composing it may be neglected. The only forces acting on a molecule arise at the walls of the container holding this Knudsen gas. As stated previously, the interaction between a molecule and a wall which here acts as our temperature reservoir is impulsive. The state of a molecule (system) after a collision with the wall will be determined both by its own state and that of the wall at the «beginning» of the collision. We can only specify a certain probability that the walls are in some particular state prior to collision. In turn this implies that for any initial state of the molecule there will be many final states (after the collision) corresponding to different initial states of the wall. In short, in view of the nature of the reservoirs there will exist a stochastic kernel $K(v; v')$ such that if the velocity of the system prior to collision is v', then $K(v, v')$ is the probability that the system will have a velocity in the range $(v, v+dv)$ after the collision.

We may consider our container to be a right cylinder whose axis is the x axis of unit length, *i.e.*, $0 \leqslant x \leqslant 1$. We assume that molecules are perfectly reflected except from the normal bounding walls at $x = 1$ and $x = 0$. This reduces our problem to that of a one-dimensional gas.

Let N be the total number of molecules in our gas, v the x component of their velocity. The probability of finding a particle in the interval $(x, x+dx)$ having its velocity in the range $(v, v+dv)$ at time t we denote by $f(x, v; t)\, dx\, dv$. The one particle distribution function is normalized, *i.e.*,

$$(3.1) \qquad \int_{-\infty}^{\infty} dv \int f(x, v; t)\, dx = 1 \ .$$

At any time there will be two non-interacting streams of molecules; one going to the right with $v > 0$ and one to the left with $v < 0$. Because there are no collisions between the molecules, $f(x, v; t)$ may be discontinuous at $v = 0$, not only near the walls but also in the interior. The mean free path is the length of the cylinder. We therefore break up $f(x, v; t)$ into two parts, one for each stream,

$$(3.2) \qquad \begin{cases} f(x, v; t) = f_+(x, v; t) & \text{for } v > 0 \, , \\ \qquad\quad\ \ = f_-(x, v; t) & \text{for } v < 0 \, . \end{cases}$$

Since no forces are acting in the interior of the cylinder, we can write

$$(3.3) \qquad \frac{\partial f_+}{\partial t} + v \frac{\partial f_+}{\partial x} = 0 \, , \qquad \frac{\partial f_-}{\partial t} - v \frac{\partial f_-}{\partial x} = 0$$

in $0 < x < 1$, $v \geqslant 0$. The stochastic boundary conditions on f are

$$(3.4) \qquad \begin{cases} v f_+(0, v; t) = \displaystyle\int_0^{\infty} K_0(v; v')\, v' f_-(0, v'; t)\, dv' \, , \\[3ex] v f_-(1, v; t) = \displaystyle\int_0^{\infty} K_1(v; v')\, v' f_+(1, v'; t)\, dv' \, , \end{cases}$$

with $K_0(v; v')$ and $K_1(v; v')$ the stochastic kernels for the walls $x = 0$ and $x = 1$. The specification of initial data for f_+ and f_- completely prescribes with (3.3) and (3.4) the temporal evolution of the distribution of the system.

From the definition of the kernels it follows that

$$(3.5) \qquad P_i(v) = \int_0^\infty K_i(v'; v)\, dv' = 1 , \qquad\qquad i = 0, 1.$$

This insures that the normalization of f is preserved in time.

The explicit form of the kernels K_i will depend on the nature of the forces between the system and the wall and on the temperature of the wall. When both walls are at the same temperature $T_0 = T_1 = T$, we expect, as discussed earlier, that a stationary solution of (3.3) and (3.4), is the canonical distribution: $f_+(v) = f_-(v) = (1/Z) \exp\left[-\beta m v^2/2\right]$,

$$(3.6) \qquad \beta = (kT)^{-1} , \qquad Z = \int_{-\infty}^\infty \exp\left[-\beta m v^2/2\right] dv = (2\pi/\beta m)^{\frac{1}{2}} .$$

A necessary and sufficient condition for this to be the case is that the kernels should satisfy the «integral condition» of eq. (2.12).

$$(3.7) \qquad K_i(v; v') = R_i(v; v') \exp\left[\beta_i m v'^2/2\right]/v' ,$$

where

$$\int_0^\infty R_i(v; v')\, dv' = \int_0^\infty R_i(v'; v)\, dv', \qquad\qquad i = 0, 1.$$

Since our two walls act independently we may write in general (*i.e.*, when $T_1 \neq T_0$),

$$(3.8) \qquad \begin{cases} K_0(v; v') = R_0(v; v') \exp\left[+\beta_0 m v'^2/2\right]/v' , \\[2mm] K_1(v; v') = R_1(v; v') \exp\left[+\beta_1 m v'^2/2\right]/v' . \end{cases}$$

We consider now an explicit form of the kernels K. We will assume that at each wall a certain fraction of the incident molecules is specularly reflected while the remainder is diffusely reflected. The diffuse reflection is to be such as to lead to a redistribution of the velocities independent of the initial velocities of the molecules. This redistribution may be thought of as due to surface adsorption and subsequent release of the molecule at the wall. The kernels will have the form

$$(3.9) \qquad \begin{cases} K_0(v; v') = (1-\alpha_0)\, \delta(v-v') + \alpha_0 H_0(v) , \\[3mm] K_1(v; v') = (1-\alpha_1)\, \delta(v-v') + \alpha_1 H_1(v) ; \quad \int_0^\infty H_i(v)\, dv = 1 . \qquad i = 0, 1, \end{cases}$$

where the α_i are the thermal accomodation coefficients $(1 - \alpha_0)$ and $(1 - \alpha_1)$ being the fraction of molecules specularly reflected at the walls at $x = 0$ and $x = 1$, respectively. In order to satisfy eq. (3.7) we must choose $H_i(v)$, $i = 0, 1$ to be

$$(3.10) \qquad H_i(v) = v \exp\left[- \beta_i m v^2/2\right](\beta_i m) .$$

The stationary distribution corresponding to the kernels given by (3.9) and (3.10) can be found to be

$$(3.11) \quad \begin{cases} f_+(v) = \dfrac{\alpha_0 m \beta_0 \exp\left[- \beta_0 m v^2/2\right] + \alpha_1(1 - \alpha_0)m\beta_1 \exp\left[- \beta_1 m v^2/2\right]}{\frac{1}{2}\left[\alpha_0(2 - \alpha_1)(\pi m \beta_0/2)^{\frac{1}{2}} + \alpha_1(2 - \alpha_0)(\pi m \beta_1/2)\right]^{\frac{1}{2}}} , \\[3mm] f_-(v) = \dfrac{\alpha_1 m \beta_1 \exp\left[- \beta_1 m v^2/2\right] + \alpha_1(1 - \alpha_1)m\beta_0 \exp\left[- \beta_0 m v^2/2\right]}{\frac{1}{2}\left[\alpha_0(2 - \alpha_1)(\pi m \beta_0/2)^{\frac{1}{2}} + \alpha_1(2 - \alpha_0)(\pi m \beta_1/2)\right]^{\frac{1}{2}}} , \end{cases}$$

From (3.11) we can calculate the rate of heat transfer from the wall at $x = 0$ to that at $x = 1$, J_0. J_0 is the difference between the heat transfer by molecules with $v > 0$, J_+ and that by molecules with $v < 0$, J_-, i.e.,

$$(3.12) \qquad J_0 = J_+ - J_- .$$

We find that

$$(3.13) \quad J_0 = \frac{\left(\dfrac{\alpha_0 \alpha_1}{\alpha_0 + \alpha_1 - \alpha_0 \alpha_1}\right) Nk(T_0 - T_1)}{\left[\left(1 + \dfrac{\alpha_0 - \alpha_1}{\alpha_0 + \alpha_1 - \alpha_0 \alpha_1}\right)\left(\dfrac{\pi m}{2 k T_0}\right)^{\frac{1}{2}} + \left(1 + \dfrac{\alpha_1 - \alpha_0}{\alpha_0 - \alpha_1 - \alpha_0 \alpha_1}\right)\left(\dfrac{\pi m}{2 k T_1}\right)^{\frac{1}{2}}\right]} ,$$

which to terms $O(T_0 - T_1)^2$ reduces to

$$(3.14) \qquad J_0 = \frac{\alpha_0 \alpha_1}{\alpha_0 + \alpha_1 - \alpha_0 \alpha_1} \frac{Nk}{(2\pi m/kT_0)^{\frac{1}{2}}} (T_0 - T_1) .$$

This result differs from that given by KENNARD [14] since we neglect the redistribution of kinetic energy in the y and z directions. For a truly one-dimensional gas the flux J given by KENNARD reduces precisely to the above expression.

3‘2. *Specific reservoirs.* – We consider an arbitrary physical system contained in a cylinder whose ends are closed by two movable pistons. The state of the inner system is specified by the variable $y = (\boldsymbol{r}_1, ..., \boldsymbol{r}_N, \boldsymbol{P}_1, ..., \boldsymbol{P}_N)$ that of the two pistons by (Q_1, P_1) and (Q_2, P_2) and the whole system by $x = (y, Q_1, P_1, Q_2, P_2)$, $Q_1 < Q_2$.

To the left of Q_1,
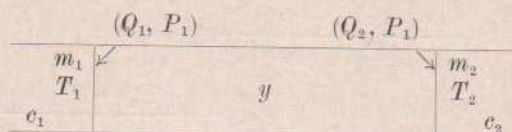
there is an ideal gas (heat reservoir) of particles having mass m_1, density c_1, and temperature T_1, while to the right of Q_2 there is a similar reservoir of particles having mass m_2, density c_2, and temperature T_2. It is clear that the only system variables which will change discontinuously during a collision with a component of reservoir one or reservoir two are P_1 and P_2 respectively. We shall thus have

$$K_1(x, x') = K_1(P_1, P_1')\, \delta(Q_1 - Q_1')\, \delta(y - y')\, \delta(Q_2 - Q_2')\, \delta(P_2 - P_2')$$

and a similar expression for $K_2(x, x')$. Hence our basis equation, eq. (1.1) will assume the form

$$(3.15) \qquad \frac{\partial \mu(x, t)}{\partial t} + (\mu, H) =$$

$$= \int [K_1(P_1, P_1')\, \mu(y, Q_1, P_1', Q_2, P_2, t) - K_1(P_1', P_1)\, \mu(x, t)]\, \mathrm{d}P_1' +$$

$$+ \int [K_2(P_2, P_2')\, \mu(y, Q_1, P_1, Q_2, P_2') - K_2(P_2', P_2)\, \mu(x, t)]\, \mathrm{d}P_2' ,$$

where

$$(3.16) \qquad H(x) = H_s(y) + U(r_1, r_N, Q_1, Q_2) + P_1^2/(2M_1) + P_2^2/(2M_2) .$$

We now assume that prior to collision the particles of each reservoir have a Maxwellian distribution of velocities with their respective temperature T_1 and T_2, and that the density of the particles is uniform everywhere outside the pistons. These assumptions are certainly not satisfied exactly by any real gas and neither is it possible to find a rigid piston, whose state is completely specified by its position and velocity, in nature. As was stated however in the introduction it is known experimentally, and we hope that it is possible also to prove mathematically for our model, that all the important features of the stationary state of a system conducting heat are independent of the details of the interaction with its surroundings.

Using the laws of conservation of energy and momentum during a col-

lision [25], we get

$$(3.17) \quad K(P_\alpha, P'_\alpha) = \frac{Ac_\alpha m_\alpha (M_\alpha + m_\alpha)^2}{(2\pi m_\alpha k T_\alpha)^{\frac{1}{2}}(2m_\alpha M_\alpha)^2} \, \varepsilon[(-1)^\alpha (P'_\alpha - P_\alpha)] \, |P_\alpha - P'_\alpha| \cdot$$

$$\cdot \exp\left[-\frac{[(P_\alpha - P'_\alpha) + m_\alpha/M_\alpha(P_\alpha + P'_\alpha)]^2}{8m_\alpha kT}\right],$$

where $\alpha = 1,2$, A is the area of the piston and h is the Heaviside unit function

$$\varepsilon(Z) = \begin{cases} 1, & Z > 0, \\ 0, & Z < 0. \end{cases}$$

The presence of the unit function is due to the fact that during a collision P_1 can only increase and P_2 decrease.

This model can be made much more realistic if we imagine each piston to consist of N parts which are held tightly together by strong forces but are not rigidly fixed. The state of the α-th piston would then be specified by $(\mathbf{Q}_\alpha, \mathbf{P}_\alpha) = (Q'_\alpha, ..., Q^N_\alpha, P'_\alpha, ..., P^N_\alpha, z)$, where z_α stands for all those variables not affected during collisions. The momentum of each part of the piston would now change independently during a collision with a reservoir component. The stochastic kernel $K_\alpha(\mathbf{P}_\alpha, \mathbf{P}'_\alpha)$ will now be a sum of N kernels $K^{(i)}_\alpha(P^{(i)}_\alpha, P'^{(i)}_\alpha)$. When the area a and mass m_w of each part of the pistons is held constant then the total area and mass A and M are proportional to N. Such a piston will approximate a physical wall when the structure of the wall molecules is unimportant in collisions with reservoir components. We shall however not consider this more complicated model in detail but shall sometimes indicate how our formulae are to be modified to apply to this model.

When the temperatures of the two reservoirs are equal, $T_1 = T_2 = T$, we expect the stationary state of the system to be one of true equilibrium. We can indeed find the stationary solution of eq. (2.2) for this case. It has the form

$$(3.18) \qquad \mu_s = (Z^{-1}) \exp\left[-\beta[H + \pi_2 AQ_2 - \pi_1 AQ_1]\right].$$

where $\pi_\alpha = c_\alpha kT$ is the pressure of the α-th reservoir and

$$(3.19) \qquad Z(T, \pi_1, \pi_2) = \int_\Gamma \exp\left[-\beta[H + \pi_2 AQ_2 - \pi_1 AQ_1]\right] \mathrm{d}x.$$

In order that Z be finite, i.e. μ_s normalizable, the system must be confined to a limited region of physical space. This is accomplished if there is some term in H which prevents Q_1, when $\pi_1 \leqslant \pi_2$, from assuming infinitely large

negative values. If piston two has no external forces acting on it then the pressure inside the system, π_1 equals π_2, and μ_s has the form

$$(3.20) \qquad \mu_s = (Z^{-1}) \exp\left[-\beta\left[H + \pi V + (\pi - \pi_1)AQ_1\right]\right],$$

where $V = A(Q_2 - Q_1)$ is the volume of the system.

When $\pi_2 = \pi_1$, or when Q_1 is held fixed, μ_s has the form usually assumed for an ensemble representing a system at fixed pressure [15]. It is gratifying that we get this ensemble, approached asymptotically in time for arbitrary initial conditions. The fact that only the temperature and pressure of the reservoirs enter into the description of the stationary state of the system lends strength to our belief that the details of the interaction between system and reservoir are not important for the final state.

It is interesting to note that the quantity W' which was shown in eq. (2.5) to be negative until the stationary state is reached is here too equal to the total entropy production in the system and reservoir

$$(3.21) \qquad \dot{W} = -\frac{1}{K}\left[\dot{S} - \frac{(\dot{U} + \pi\dot{V})}{T}\right] = -\frac{1}{K}\sigma \leqslant 0.$$

This is completely analogous to the case of a system whose stationary state is represented by a canonical ensemble, eq. (2.10) (*).

3`3. *Further simplification of the kernels.* – The solution of the time independent part of eq. (3.15) becomes much more difficult to find when the temperature of the two reservoirs is not the same. Even the form of the solution will now necessarily depend somewhat on H. To take a very extreme example; let the system consist of two separate parts, each interacting with but one reservoir, *i.e.*, $H = H_1(y_1, Q_1, P_1) + H_2(y_2, Q_2, P_2)$, $y = y_1, y_2$. The stationary ensemble would now be a product of two equilibrium ensembles,

$$\mu_s = (Z_1^{-1}) \exp\left[-\beta_1[_1H - \pi_1 Q_1 A)]\right] \cdot (Z_2^{-1}) \exp\left[-\beta_2[H_2 + \pi_2 Q_2 A]\right]$$

and no heat would be conducted across the system. This is of course not the kind of system we are interested in. To tackle the true non-equilibrium situation we simplify the structure of the right side of eq. (2.2). First we make the hypothesis that the mass of the pistons is much greater than the mass of

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(*) If the pistons are tied down to some equilibrium positions by very strong forces then our system would in effect have a constant volume and the stationary solution would be the canonical ensemble appropriate for such systems.

the reservoir particles, $\gamma'_\alpha = m_\alpha/M_\alpha \ll 1$. We now use the known result that the integral operator on the right of eq. (2.2) is equivalent to a differential operator of infinite order [16]. That is, for an arbitrary K,

$$(3.22) \quad \int [K(P, P')\mu(P') - K(P', P)\mu(P)]\,\mathrm{d}P' = \sum_{n=1}^{\infty} \frac{1}{n!} \frac{\mathrm{d}^n}{\mathrm{d}p^n} [Q^{(n)}(P)\mu(P)],$$

where

$$Q^{(n)}(P) = \int K(P', P)(P - P')^n\,\mathrm{d}P' .$$

The change from the integral to the differential operator can be made separately for each K_α. We have

$$Q^{(n)}(P) = \sum_\alpha Q^{(n)}_\alpha(P_\alpha) = \sum \int K_\alpha(P'_\alpha, P_\alpha)(P_\alpha - P'_\alpha)^n\,\mathrm{d}P'_\alpha$$

and for the kernels considered here

$$(3.23) \quad Q^{(n)}_\alpha(P_\alpha) = \frac{C_\alpha A \gamma_\alpha((n-1)/2)}{4(2\pi k T_\alpha M_\alpha)^{\frac{1}{2}}} \int_{-\infty}^{\infty} Z^n |Z| \varepsilon[(-1)^\alpha Z] \exp\left[-\frac{Z^2}{8 M_\alpha k T_\alpha}\right] \cdot$$

$$\cdot \left[1 + \frac{\sqrt{\gamma_\alpha}\, z P_\alpha}{2 M_\alpha k T_\alpha} + O(\gamma_\alpha)\right] \mathrm{d}z .$$

When only terms of $O(\sqrt{\gamma_\alpha})$ are kept in the differential operator (*) above then eq. (2.2) assumes the form

$$(3.24) \quad \frac{\partial \mu(x, t)}{\partial t} + (\mu, H) = -\pi_1 A \frac{\partial \mu}{\partial P_1} + \pi_2 A \frac{\partial \mu}{\partial P_2} + \sum_{\alpha=1,2} \left\{ \frac{\partial}{\partial P_\alpha}(\lambda_\alpha P_\alpha \mu) + \frac{\partial^2}{\partial P_\alpha}(D_\alpha \mu) \right\}$$

where

$$\lambda_\alpha = C_\alpha A (8 \gamma_\alpha k T_\alpha / \pi M_\alpha)^{\frac{1}{2}} \quad \text{and} \quad D_\alpha = \lambda_\alpha M_\alpha k T_\alpha .$$

The right side of this equation has a structure similar to the usual Fokker-Planck equation where $\pi_1 A$ and $(-\pi_2 A)$ is the average force exerted by the reservoirs on pistons 1 and 2 and λ_α is the friction coefficient [17]. Note that if the α-th reservoir were on both sides of the α-th piston then the average force-term would vanish and the friction constant would be $2\lambda_\alpha$. The average

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(*) These are the lowest order terms which contain the essential features of the reservoirs.

forces can be included in the Liouville term by defining a new Hamiltonian H', $H' = H' + \pi_2 A Q_2 - \pi_1 A Q_1$. The fundamental equation whose stationary solution we want is then

$$(3.25) \quad \frac{\partial \mu}{\partial t} + (\mu, H') = \sum_{\alpha=1,2} \frac{\partial}{\partial P_\alpha} \left[D_\alpha \exp\left[-\frac{\beta_\alpha P_\alpha^2}{2 M_\alpha} \right] \frac{\partial}{\partial P_\alpha} \left(\exp\left[\frac{\beta_\alpha P_\alpha^2}{2 M_\alpha} \mu \right] \right) \right],$$

where use has been made, in the last expression, of the relation between γ and D. After this simplification of the kernels the total entropy production σ can be written down easily. The entropy produced in the first reservoir is $\sigma_1 = (- J_1'/T)$, where $J_1' = J_1 - \pi_1 A \, (\mathrm{d}\langle Q_1 \rangle / \mathrm{d}t)$ is the heat current flowing into the system from that reservoir; J_1 being the energy flux. Similarly for the second reservoir

$$\sigma_2 = -\frac{J_2'}{T_2} = -\left[J_2 + \pi_2 A \frac{\mathrm{d}\langle Q_2 \rangle}{\mathrm{d}t} \right] \quad \text{while} \quad \frac{\mathrm{d}\langle H \rangle}{\mathrm{d}t} = J_1 + J_2; \quad \frac{\mathrm{d}\langle H' \rangle}{\mathrm{d}t} = J_1' + J_2'.$$

The rate of entropy in the system is

$$(3.26) \quad \frac{\mathrm{d}S_s}{\mathrm{d}t} = -k \frac{\mathrm{d}}{\mathrm{d}t} \int \mu \ln \mu \, \mathrm{d}x = -k \int \frac{\partial \mu}{\partial t} \ln \mu \, \mathrm{d}x.$$

We find from eq. (3.4) that $J_\alpha' = \lambda_\alpha [kT_\alpha - \langle P_\alpha^2 \rangle / 2 M_\alpha]$

$$\sigma = \sigma_1 + \sigma_2 + \frac{\mathrm{d}S_s}{\mathrm{d}t} = k \sum_\alpha D_\alpha \int \exp\left[-\frac{\beta_\alpha P_\alpha^2}{2 M_\alpha} \right] (\mu)^{-1} \left[\frac{\partial}{\partial P_\alpha} \left(\exp\frac{\beta_\alpha P_\alpha^2}{2 M_\alpha} \mu \right) \right]^2 \mathrm{d}x \geqslant 0.$$

In the stationary state

$$(3.27) \quad \frac{\mathrm{d}S_s}{\mathrm{d}t} = 0; \quad \frac{\mathrm{d}\langle H' \rangle}{\mathrm{d}t} = J_1' + J_2' = 0; \quad J_\alpha = J_\alpha'$$

so that

$$(3.28) \quad 0 \leqslant \sigma = -\frac{J_1}{T_1} - \frac{J_2}{T_2} = \frac{J_1}{T_1 T_2} (T_1 - T_2)$$

and

$$(3.29) \quad J = J_1 = \lambda_1 (kT_1 - \langle P_1^2 \rangle / M_1) = \lambda_2 \left(\frac{\langle P_2^2 \rangle}{M_2} - kT_2 \right) \geqslant 0, \quad \text{if } T_1 > T_2$$

is the heat current in the stationary state. We expect the following relation to hold in general $T_1 \geqslant T_1^{(w)} \geqslant T_2^{(w)} \geqslant T_2$, where $\frac{1}{2} kT_\alpha^{(w)} = \frac{1}{2} \langle P_\alpha^2 \rangle / M_\alpha$ is the wall temperature. The physical meaning of the expression for J' is obvious. J_α' is proportional to the deviation of the mean kinetic energy of the α-th

piston from the equilibrium value it would have if it were only in contact with the α-th reservoir. It is a further consequence of eq. (3.9) that in the stationary state,

$$(3.30) \qquad \frac{\sum \lambda_\alpha T_\alpha^{(W)}}{\sum \lambda_\alpha} = \frac{\sum \lambda_\alpha T_\alpha}{\sum \lambda_\alpha} = \overline{T} \,,$$

where $\overline{T}$ is the weighted average temperature of the two reservoirs.

It also follows from the definition of λ that J and σ are proportional to the area of the piston so that a heat flux per unit area, j, can be defined. The quantity λ_α/A plays the role of a heat conductivity across the interface between piston and reservoir. In the more realistic case described after eq. (3.17) of a piston consisting of N parts, the mass of the piston M_α is replaced by $m_\alpha^{(w)}$ the mass of one segment of the piston, in the expression for the heat flux.

3'4. *Simple stationary ensembles.* – We consider here some very simple systems for which exact stationary non equilibrium ensembles can be found. First we consider the case of one piston between two reservoirs. The position and momentum of this piston are designated by (Q, P), and its Hamiltonian is $h(Q, P) = P^2/2M + V(Q)$. Eq. (3.4) will now have the form

$$(3.31) \qquad \frac{\partial \mu(Q, P, t)}{\partial t} + (\mu, h') = \sum_\alpha \frac{\partial}{\partial P} \left[D_\alpha \exp\left[-\frac{\beta_\alpha P^2}{2M}\right] \frac{\partial}{\partial P} \left(\exp\left[\frac{\beta_\alpha P^2}{2M}\right] \mu \right) \right],$$

where $h' = h + (\pi_2 - \pi_1) AQ$.

Equation (3.31) has the time-independent solution

$$(3.32) \qquad \mu_s = \exp\left[-\overline{\beta} h'(Q, P)\right]/Z \,,$$

where

$$(3.33) \qquad \overline{\beta} = \frac{\sum D_\alpha \beta_\alpha}{\sum D_\alpha} = (k\overline{T})^{-1} : \overline{T} = \frac{c_1(m_1 T_1^3)^{\frac{1}{2}} + c_2(m_2 T_2^3)^{\frac{1}{2}}}{c_1(m_1 T_1)^{\frac{1}{2}} + c_2(m_2 T_2)^{\frac{1}{2}}} \,.$$

The stationary heat flux J and the entropy production σ are, (for $T_1 > T_2$)

$$(3.34) \qquad \begin{cases} J = \lambda_1 k(T_1 - \overline{T}) = \lambda_2 k(\overline{T} - T_2) = \left(\dfrac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}\right) k(T_1 - T_2) \,, \\[3mm] \sigma = \dfrac{J}{T_1 T_2}(T_1 - T_2) = \left(\dfrac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2}\right)\left(\dfrac{k}{T_1 T_2}\right)(T_1 - T_2)^2 \,. \end{cases}$$

From the expression for λ given in eq. (3.3) we get for the heat current per unit area

$$(3.35) \qquad \gamma = \frac{J}{A} = \left(\frac{8k^3}{\pi M^2}\right)^{\frac{1}{2}} \frac{c_1 c_2 (m_1 m_2 T_1 T_2)^{\frac{1}{2}}}{(c_1(m_1 T_1)^{\frac{1}{2}} + c_2(m_2 T_2)^{\frac{1}{2}}} \,.$$

The magnitude of J will be determined primarily by the reservoir with the lower value of λ. It is that reservoir which imposes the limit on the transport of heat.

The stationary non-equilibrium ensemble found here for a simple piston can be extended immediately to a piston consisting of N parts. The Hamiltonian of such a piston is

$$(3.36) \qquad \mathcal{H} = \sum_{i=1}^{N} \frac{P_i^2}{2m_i^{(w)}} + U(Q_1, \ldots, Q_N, z) ,$$

where z stands for all those pairs of canonically conjugate variables which do not change during a collision. The equation governing the time evolution of this system's ensemble is similar to eq. (4.1)

$$(3.37) \qquad \frac{\partial \mu(Q_1, \ldots, Q_N, P_1, \ldots, P_N, z)}{\partial t} +$$

$$+ (\mu, \mathcal{H}) = \sum_{\substack{i=1 \\ \alpha=1,2}}^{N} \frac{\partial}{\partial P_i} \left[D_\alpha \exp\left[\frac{\beta_\alpha P_\alpha^2}{2m_i^{(w)}} \right] \frac{\partial}{\partial P_i} \left(\exp\left[\frac{\beta_\alpha P_i^2}{2m_i^{(w)}} \right], \mu \right) \right] ,$$

where in order to get the right side of this equation we have to assume $m_\alpha \ll m_i^{(w)}$. Equation (4.7) again has the stationary solution

$$(3.8) \qquad \mu_s = (Z^{-1}) \exp\left[-\bar{\beta}\mathcal{H} \right] ,$$

with $\bar{\beta}$ given by eq. (4.3). This average temperature is the same for all parts of the piston being independent of the mass $m_i^{(w)}$ and the area a_i of each part.

The heat flux j across this piston will be proportional to $\sum_{i=1}^{N} a_i (m_i^{(w)})^{-2} / \sum a_i$ but will not depend otherwise on the structure of the piston.

4. – Some further comments.

The stationary ensembles found here for these simple systems may have some relevance to the kind of ensembles we may expect for a fluid between two temperature reservoirs. They suggest that, as a starting point, we might isolate (mentally) a narrow cylinder of fluid perpendicular to the temperature gradient and consider the fluid to the right and left of this cylinder as two temperature baths. The interaction among the particles inside each cylinder will set up an approximate equilibrium there which will not be too disturbed by the surroundings when the temperature is intermediate between those of the sides. Thus a kind of local equilibrium can exist in the fluid. Indeed the

Γ-space ensemble representing a system in local equilibrium has been taken as the starting point in recent investigations of transport processes in fluids [3, 18].

This local equilibrium is, however, continuously disturbed by the interaction among particles in adjacent layers. This gives rise to deviations from local equilibrium which are responsible for the dissipative behavior.

We have shown recently [6] that the low order distribution functions computed by first finding the Γ-space ensemble are similar to those found from the kinetic equations for these low order distributions. Furthermore the Γ-space distribution can be expressed in terms of a variational principle [6, 7]. The quantity whose maximum yields the non equilibrium distribution is a sum of the system's entropy and the time integral of the entropy production in the reservoirs. It is thus a generalization of the quantity W discussed in this paper.

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