Irreversible Gibbsian Ensembles

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In this paper we continue the investigation of a model for the description of irreversible processes which we had proposed in an earlier publication. This model permits the construction of Gibbs-type ensembles for open systems not in equilibrium. The internal dynamics of the system that is engaged in a nonequilibrium process is assumed to be described fully by its Hamiltonian. Its interaction with its surroundings, i.e., the driving reservoirs, is described in terms of impulsive interactions (collisions). The reservoirs themselves possess definite temperatures, are inexhaustible, and are free of internal gradients (i.e., they are temperature baths). The ensemble obeys an integro-differential equation in F-space, containing both the terms of the Liouville equation and a stochastic integral term that describes the collisions with the reservoirs. It is shown in this paper that, under very general assumptions, all distributions approach each other in the course of time. If there exists a stationary solution, it will be unique and will be approached asymptotically by every time-dependent solution. In general the stationary state does not represent thermodynamic equilibrium; the ensemble remains unchanged only because its surroundings maintain temperature gradients inside the thermodynamic system. Only if these surroundings are all at one temperature, i.e., if the system is in contact with but one reservoir, then the stationary state will correspond to the canonical distribution. As a result, the stochastic integral kernel that describes the effect of collisions with the reservoir will satisfy certain symmetry conditions. A detailed investigation of our micro-model shows that these conditions are indeed satisfied if the reservoir components are themselves in a canonical distribution prior to collision. In the presence of several reservoirs at slightly different temperatures, the Onsager reciprocal relations are satisfied by the stationary distribution. In our model the Onsager relations are thus obtained without an appeal to fluctuation theory, and without the assumption that detailed balancing holds for the elementary stochastic processes, i.e., for the interactions between system and reservoir. In the latter part of the paper, finally, we consider reservoirs that maintain thermodynamic potentials in addition to the temperature, including chemical potentials. It turns out that our principal results are unaffected by this generalization.

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1. INTRODUCTION

In a previous paper (1), we have proposed a statistical-mechanical model for nonequilibrium processes which permits the use of Gibbs-type ensembles for open systems not in equilibrium. We consider a system, with canonical variables $x = (q_1, \cdots q_N; p_1, \cdots p_N)$, in contact with inexhaustible reservoirs, "temperature baths." These reservoirs maintain temperature gradients within the system. Because of the infinite size of the reservoirs, the $\Gamma$-space ensemble representing the system can approach in the course of time (and remain in) a stationary nonequilibrium state. In order to eliminate the infinite-dimensional phase space of the reservoir from the description of the system, we let the reservoir consist of an infinite number of independent, identical components, each of which is to interact with the system but once. We further assume an impulsive interaction between system and reservoir component. Thus at the beginning of an interaction the state of the reservoir component is independent of the previous history of the system. Subsequent to the collision, such a dependence exists but is to be disregarded, because by assumption there is no further interaction. Hence, the effect of the reservoir on the system can be completely described if we specify the time-independent distribution of the reservoir components in the $\mu$-space of the reservoir before collision; we never have to deal with the total phase space of the reservoir. We shall call the phase space of one reservoir component $\Gamma_x$ (this is the $\mu$-space of the reservoir).

Each collision results in the discontinuous transition of the system and a reservoir component from some initial state $(x', y')$ to a final state $(x, y)$. The over-all motion of the system in its own phase space $\Gamma_x$ will be continuous most of the time and determined by its own Hamiltonian $H(x)$; this continuous motion will be interrupted from time to time by jumps corresponding to collisions with the reservoir. These jumps are not uniquely determined by the position of the system in $\Gamma_x$ but depend also on the position of the reservoir component in $\Gamma_x$ prior to collision. Hence from the point of view of the system we can only specify a contingent probability $K(x', x) \, dx' \, dt$. This expression represents the probability that the representative point of the system, known to be at the location $x$ in $\Gamma_x$, will be thrown into the volume element $dx'$ within the time interval $dt$ as the result of a collision with some reservoir component.

This contingent probability is the result of averaging over the initial (pre-collision) states $y'$ and of summing over the final states $y$ of the reservoir component. Because of the nature of our reservoir the stochastic kernel $K(x, x')$ is independent of time $t$.

The ensemble density of systems at some point $x$ in $\Gamma_x$, $\mu(x)$, will change because of the natural motion of the system and because of collisions with the reservoir. The equation for $\mu$ will have the form

$$\frac{d\mu(x, t)}{dt} + (\mu(x, t), H(x)) = \int dx' \left[ K(x, x') \mu(x', t) - K(x', x) \mu(x, t) \right] \, dx' \quad (1.1)$$
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The Poisson-bracket on the left side represents the effect of the natural motion, whereas the right side describes the effect of collisions. When the system is isolated there are no collisions, \( K = 0 \), and Eq. (1.1) reduces to the usual Liouville equation. In I it had been assumed that the distribution of reservoir components prior to collision was canonical and corresponded to some definite temperature. Such a distribution has the form

\[
\mu(x') = (1/Z)e^{-\beta H(x')}, \quad \beta = 1/kT
\]  

(1.2)

On the grounds of microreversibility it was claimed in I that, for a system in contact with a reservoir of this kind, the kernel \( K(x, x') \) should have the symmetry property

\[
K(x', x) = \exp[\beta(H(x) - H(x'))] K(x, x'); \quad H(x) = H(\hat{\hat{x}})
\]  

(1.3)

where \( \hat{x} \) is that point in \( \Gamma_x \) which corresponds to \( x \) under time reversal, i.e. it has the same coordinates and the opposite momenta as \( x \). The “time-reversed symmetry” condition (1.3) was found to be insufficient to insure that the ensemble density \( \mu(x, t) \) approach the canonical distribution in the course of time, a result to be desired, because in the Gibbs formalism the canonical ensemble represents the equilibrium state of a system in contact with a temperature bath. Hence, if our model was to represent a physical situation it had to lead to canonical equilibrium in the course of time, i.e. \( K(x, x') \) must have properties such that under Eq. (1.1)

\[
\mu(x) = \lim_{t \to \infty} \mu(x, t) = (1/Z)e^{-\beta H(x)}
\]

for any initial conditions. Accordingly we went a step further and assumed that microreversibility, i.e. equality of cross sections, holds not only as regards the transition \( x \to x' \) and the “time-reversed” transition \( \hat{x}' \to \hat{x} \), but also for the “directly reversed” transitions \( x \to \hat{x}' \) and \( x' \to \hat{x} \). This assumption implies the “direct symmetry relation”

\[
K(x', x) = \exp[\beta(H(x) - H(x'))] K(x, x')
\]  

(1.4)

This additional assumption was shown to assure the monotonic decrease of the Helmholtz potential of the system in contact with a single temperature reservoir until the ensemble density becomes canonical. The “direct symmetry” condition (1.4) is equivalent to detailed balancing in the canonical ensemble as regards stochastic transitions: As many systems pass from \( x' \) to \( x \) as make the reverse transition from \( x \) to \( x' \). In I we were unable to decide whether the assumption of “direct reversibility” (1.4) is necessary (as well as sufficient) for our results to hold, and whether it can be justified in terms of our micro-model.

When the system is in contact with several reservoirs, each with its own temperature and its own peculiar coupling to the system, then the kernel of Eq.
will be the sum of individual kernels
\[ K(x, x') = \sum_i K_i(x, x') \]  
(1.5)
each representing the effects of one (the ith) reservoir. The symmetry properties (1.3) or (1.4), respectively, now will apply to each \( K_i \) with its own temperature \( T_i = (k \beta_i)^{-1} \). In the stationary state (which is not an equilibrium state) there will be heat currents \( J_i \) flowing from each reservoir to the system. It was shown in I on the basis of (1.4), that the dependence of these currents on the temperatures of the different reservoirs satisfies Onsager's reciprocal relations
\[ \left( \frac{\partial J_i(\beta_i)}{\partial \beta_j} \right)_{\beta_i=\beta} = \left( \frac{\partial J_j(\beta_i)}{\partial \beta_i} \right)_{\beta_i=\beta} \]  
(1.6)
In this paper we shall demonstrate that the assumption of “direct symmetry” of \( K \) is not required for the approach to equilibrium, but may be replaced by a weaker requirement, which will be derived explicitly. Our argument will be based on a general theorem which states that, regardless of any symmetry assumptions on \( K, (1.1) \) possesses at most one stationary solution, and that this state is approached by the ensemble in the course of time (Section 2). Section 3 will be devoted to the investigation of the weaker condition to be obeyed by \( K(x, x') \), which is both necessary and sufficient for asymptotic approach to canonicity, and the proof of the Onsager relations under these conditions when there is more than one reservoir. In Section 4 we shall return to our physical model of impulsive interactions between the system and its surroundings and “derive” Eq. (1.1). Thus we shall construct the kernels directly from the physical model. We shall ascertain there the necessary properties which the reservoir and the laws of collision must possess for the different symmetry conditions on \( K \) to hold.

The remainder of this paper will be devoted to extending our formalism to more general types of reservoirs than “temperature baths.” In Section 5 we shall treat the case of a reservoir whose components prior to collision are distributed in a generalized canonical ensemble. Finally, in Section 6 we shall treat systems that can exchange particles with a reservoir.

2. APPROACH TO THE STATIONARY STATE

In I it was shown that if the kernel \( K(x, x') \) satisfies the condition
\[ K(x, x') < M v(H), \quad \int v(H) \, dx = 1, \quad M < \infty \]
and
\[ \int_{t_0}^{t} \int_{t_0}^{t'} K[x, x'(t')] \, dx \, dt' \geq \alpha(t - t_0) \]
then the distribution \( u(x, t) \) defined in Eq. (1.1) (with \( \delta H/\delta t = 0 \)) will approach
asymptotically some stationary distribution $\mu_\ast(x)$. Our proof was based on a theorem by Doeblin, which applies to general Markovian processes. In this section we shall prove under considerably weaker assumptions that an integrodifferential equation of the form (1.1) possesses solutions whose form for large values of $t$ becomes asymptotically independent of the initial distribution function $\mu(x)$ at some time $t_0$. For time-independent kernel $K$ and Hamiltonian $H$ this result implies: If there exists any stationary solution, then it is the only stationary solution, and it is approached for large values of $t$ by every nonstationary solution; if $K$ is time-independent and $H$ periodic in time, then if there exists any periodic solution it will also be unique and will serve as an asymptotic limit for all solutions. The assumptions under which our general result holds are: (1) that the stochastic kernel $K$ does not induce “run-away” conditions, in the sense that the system does not increase its mean energy indefinitely and without upper limit; (2) that the combination of deterministic and stochastic motion enables a system to get eventually from every part of its phase space to every other part. This latter condition we shall call the indecomposability of phase space, in close analogy to the terminology customary in ergodic theory.

For our proof we shall introduce a functional $W$ of two solutions of Eq. (1.1), $\mu_1$ and $\mu_2$, which is positive definite and which equals zero only if the two solutions coincide. We shall then show that the functional $W$ decreases monotonically in the course of time, so that its value must approach a lower limit. With the two assumptions made above, we shall show that this lower limit is zero.

We shall define the functional $W$ as the integral
\[
W = \int_{\Gamma} \mu_1 \ln \left( \mu_1 / \mu_2 \right) \, dx = \int_{\Gamma} (\mu_1 \ln \mu_1 - \mu_1 \ln \mu_2 - \mu_1 + \mu_2) \, dx
\]
\[
= \int_{\Gamma} \mu_2 (\phi \ln \phi - \phi + 1) \, dx, \quad \phi \equiv \mu_1 / \mu_2
\]

Its derivative is
\[
\frac{dW}{dt} = \int_{\Gamma} \left[ \ln \phi \frac{\partial \mu_1}{\partial t} - \phi \frac{\partial \mu_2}{\partial t} \right] \, dx = \int_{\Gamma} \ln \phi (H, \mu_1) - \phi (H, \mu_2) \right) \, dx
\]
\[
- \int_{\Gamma} \int K(x, x') \mu_2(x') \phi(x) \left[ \frac{\phi(x')}{\phi(x)} \ln \frac{\phi(x')}{\phi(x)} - \phi(x') / \phi(x) + 1 \right] \, dx \, dx'
\]
\[
= \int (\ln \phi (H, \mu_1) - \phi (H, \mu_2)) \, dx - \int K \mu_2 \phi \ln \phi - \phi' + 1 \right) \, dx \, dx'
\]

\[\text{According to Stueckelberg (8), W. Pauli first called his attention to the inequality}
\]
\[
\phi \ln \phi - \phi + 1 = \int_{t=1}^\phi \ln \xi d\xi \geq 0
\]
The last integral represents a self-explanatory abbreviating notation. Parenthetically, it should be noted that in this calculation no assumption concerning the time dependence of either \( H \) or \( K \) is involved. Of the two integrals on the right of Eq. (2.2) the second one is non-negative, because of the Stueckelberg-Pauli inequality. The first one can be shown to vanish, because the integrand may be converted into a series of complete Poisson brackets, whose integrals are zero because of Gauss's theorem. In fact, we have

\[
\int [\ln \phi(H, \mu_1) - \phi(H, \mu_2)] \, dx = \int (H, \mu_2) [\phi \ln \phi - \phi + 1] \, dx \tag{2.3}
\]

Hence \( dW/dt \) is negative. The integrand of the last integral in Eq. (2.2) will vanish for any two arguments \( x, x' \) only where \( K(x, x') \) vanishes, where \( \mu_2^{-1} \mu_1 \mu_2 \) vanishes, or where \( \phi = \phi' \). We shall now consider these possibilities. If \( \phi = \phi' \) throughout phase space, then \( \mu_1 \) is proportional to \( \mu_2 \); hence, because both distributions are normalized, they must equal each other. In that case, the two solutions are identical, and we have nothing further to prove. Or, we may have the situation in which, for large values of \( t \), \( \mu_2^{-1} \mu_1 \mu_2 \) tends to zero, a contingency we have called a run-away condition and have explicitly excluded. Such a run-away condition may be brought about by the choice of a kernel \( K \) which permits the system to pick up energy from the reservoir systematically and without limit, so that the high-energy domains become available for a progressive dilution of our ensemble. Finally, it is possible that the factor \( K \) vanishes wherever the square bracket fails to tend to zero. To examine this possibility further, we shall introduce new canonical coordinates, so-called co-moving coordinates, in terms of which the Hamiltonian vanishes and all representative points remain at rest except for the stochastic motion. In terms of these new coordinates, Eq. (1.1) is simplified in that the Poisson bracket term vanishes. \( K \) will in general become explicitly time-dependent, but this circumstance has no effect on the validity of Eq. (2.2). The argument that follows is to be understood in terms of these co-moving coordinates.

As \( W \) is bounded from below, the integral over \( dW/dt \) taken from \( t \) to \( t + \tau \) must tend to 0 for any fixed finite value of \( \tau \) as we let \( t \) go to \( \infty \). But according to Eq. (2.2) such an integral over \( dW/dt \) cannot tend to zero unless the stochastic flux of representative points from any region about \( x \) (of nonzero measure) to any similar region about \( x' \) with nonequal values of \( \mu_1/\mu_2 \) likewise tends to zero when integrated over a time interval \( \tau \). Thus we conclude that for any domain of nonzero measure the value of this ratio, \( \mu_1/\mu_2 = \phi \), must tend to a limiting value. We can now divide all of phase space into a (finite or infinite) set of domains each of which corresponds to a different value of \( \phi \). There can be no flux of representative points from one such domain to another that does not tend to zero. Hence, within any such domain the total number of representative
points belonging to either of our two solutions must remain constant. Thus we have divided up phase space into a set of domains between which there is no communication whatsoever. The nonexistence of such domains is the precise formulation of our assumption of indecomposability above.

This assumption is very much weaker than the assumption that \( K(x, x') \) be different from zero for all pairs of arguments; the latter would exclude from consideration all physically interesting situations. (For instance, a collision will not take a representative point from \( x \) to \( x' \) if the configuration coordinates of these two locations in phase space are different). The introduction of co-moving coordinates freezes the deterministic motion; our domains of equal \( \phi \) move about their respective energy surfaces in terms of stationary coordinates. Thus to get from \( x \) to \( x' \), a representative point is permitted to alternate between deterministic and stochastic motion an arbitrary number of times. We prohibit a situation in which in spite of this freedom of choice it cannot reach \( x' \).

If \( K \) is such as to satisfy our requirement of indecomposability and our prohibition of run-away solutions, then, except perhaps for a domain of zero measure, \( \mu_1 \) approaches \( \mu_2 \) asymptotically for large values of \( t \), and this regardless of any time dependence on the part of either \( H \) or \( K \). We are particularly interested in the case in which both of these functions are periodic in \( t \) with a period \( \tau_0 \) (in situations we have envisaged, \( K \) does not depend on the time \( t \) at all). In that event, we may in particular consider two solutions of Eq. (1.1) such that

\[
\mu_2(t) = \mu_1(t + n\tau_0)
\]  

(2.4)

where \( n \) is any integer. These two expressions approach each other, too; in other words, \( \mu \) will tend to be periodic for any fixed length of time \( T \). If there exists a strictly periodic solution, then \( \mu \) will approach that solution asymptotically. Hence, there cannot exist two different periodic solutions.

If both \( H \) and \( K \) are stationary, then there exists at most one stationary solution, toward which all other solutions tend in the course of time. In concluding this section, we should like to point out that the expression (2.1) for \( W \) is by no means the only functional that is non-negative, vanishes only if the two distributions considered are equal, and decreases monotonically with time. Our particular choice was motivated principally by the circumstance that for the case of single temperature bath and for the choice of the canonical distribution for \( \mu_2 \), the expression (2.1) is proportional to the excess of Helmholtz potential of the distribution \( \mu_1 \) over the equilibrium value, cf. Eq. (3.3). Even when the stationary solution \( \mu_s \) is not canonical, one can still give \( W_s \) a simple form. If we denote the negative logarithm of \( \mu_s \) by \( A \), \( \mu_s = e^{-A} \), then \( W_s \) is

\[
W_s = \langle A \rangle - kS
\]  

(2.5)
3. APPROACH TO EQUILIBRIUM AND THE ONSAGER RELATIONS

We shall now apply the results obtained in the previous section to those cases that interest us most: those of systems in contact with one or several temperature baths. Inasmuch as we require that in the presence of a single reservoir the ensemble density of a system approach canonicity as \( t \to \infty \), it is necessary that the canonical distribution be a solution of Eq. (1.1),

\[
(1/Z)(e^{-\beta H}, H) = (1/Z) \int [K(x', x)e^{-\beta H(x')} - K(x', x)e^{-\beta H(x)}] \, dx' = 0 \quad (3.1)
\]

since

\[
(e^{-\beta H}, H) = 0 \quad (3.2)
\]

Because of the theorem of Section 2, Eq. (3.1) is also a sufficient condition on \( K \) for the system to approach equilibrium. Equation (3.1) is obviously less restrictive than the "direct symmetry" condition (1.4): it implies only "circular balancing" in the canonical distribution.

The quantity \( W \), defined by (2.5), which decreases monotonically until equilibrium is reached, is in this case simply related to the Helmholtz free energy \( F \):

\[
W = -S/k + \beta U - \ln Z = \beta [U - T S - (1/\beta) \ln Z] = (1/kT)[F - F_0] \quad (3.3)
\]

where \( F_0 \) is the Helmholtz free energy at equilibrium.

It is to be noted that Eq. (3.1), which we might call the "integral condition" on \( K \), makes no reference to the "time reversed" symmetry condition (1.3). Though Eq. (1.3) will hold if the reservoir distribution is canonical, it neither implies nor is implied by (3.1). However, we can show that if the probability of a collision of the system with some reservoir component (total collision cross section) remains unchanged when all the momenta are reversed,

\[
1/\tau(x) = \int K(x', x) \, dx' = \int K(x', \bar{x}) \, dx' = 1/\tau(\bar{x}) \quad (3.4)
\]

then this equality, together with the "time reversed" symmetry of Eq. (1.3), implies (3.1) and through (3.1) the approach to the canonical distribution. For proof we combine (3.4) and (1.3)

\[
\int K(x', x) \, dx' = \int K(x', \bar{x}) \, dx' = \int K(x, \bar{x}') \exp [\beta[H(x) - H(x')]] \, dx' \quad (3.5)
\]

or

\[
\int K(x', x)e^{-\beta H(x')} \, dx' = \int K(x, \bar{x}')e^{-\beta H(x')} \, dx'
\]

which is just (3.1) since \( dx' = d\bar{x}' \). It can be shown similarly that the "integral
condition'' (3.1) combined with the “time-reversed symmetry” property (1.3) implies (3.4).

In the presence of a single reservoir, then, the kernel $K$ should satisfy the integral condition (3.1). When the system is in contact with $n$ reservoirs at temperatures $T_i = \frac{(k\beta_i)^{-1}}{n}$, $i = 1, \cdots n$, then as pointed out in Section 1 the kernel $K$ has the form

$$ K(x, x') = \sum_{i=1}^{n} K_i(x, x') $$

Each of the $K_i$ will satisfy (3.1) with its own $\beta_i$.

$$ \int K_i(x, x')e^{-\beta_i H(x')} dx' = \int K_i(x', x)e^{-\beta_i H(x)} dx' \quad (3.7) $$

The Onsager reciprocal relations, defined by Equation (1.6), which were derived in I on the basis of the assumption of the “direct symmetry” of the $K_i$, will now be shown to hold also on the basis of the less stringent “integral condition” of Eq. (3.7). However, unlike the approach to equilibrium, the validity of the Onsager relations (here as well as in I) depends on the “time-reversed symmetry” condition (1.3).

This is not surprising, for in contrast to the approach of a system to equilibrium which is unidirectional in time and happens, so to speak, in spite of the reversibility of the fundamental laws of nature, the Onsager relations are a direct consequence of micro-reversibility.

The heat current $J_x$ that flows from the $i$th reservoir to the system is given by Eq. 5.4 of I as

$$ J_x = \int \mu(x)K_i(x', x)[H(x') - H(x)] dx' dx \quad (3.8) $$

Although $K_i$ depends only on the temperature of the $i$th reservoir (or $\beta_i$), the current $J_x$ will depend on all the $\beta_i$, $i = 1, \cdots, n$, through $\mu$. When the system has reached a steady state, then

$$ \dot{U} = \sum_{i=1}^{n} J_i = 0 \quad (15.6) $$

The stationary distribution $\mu_i(x)$ satisfies the equation

$$ (\mu_i, H) = \sum_{i=1}^{n} \int [K_i(x, x')\mu_i(x') - K_i(x', x)\mu_i(x)] dx' \quad (3.9) $$

If all the $\beta_i$ are equal, $\beta_i = \beta$, then because of (3.7)

$$ \mu_i(x) |_{\beta=\beta} = Z^{-1}e^{-\beta H(x)} \quad (3.10) $$

and the steady state is that of equilibrium.
When only linear deviations from equilibrium are taken into account, then, according to the Onsager relations, the cross-derivatives of the flows with respect to the thermodynamic forces are, respectively, equal. It was shown in I (Section 5) that in our formalism the "forces" \( f_i \) are linear functions of the \( \beta_i \), \( f_i = k(\beta_i - \beta_0) \). Hence, we have to show that

\[
J_{lk} = \left( \frac{\partial J_k(\beta)}{\partial \beta_l} \right)_{\beta_i = \beta} = \left( \frac{\partial J_l(\beta)}{\partial \beta_k} \right)_{\beta_i = \beta} = J_{lk} \tag{3.11}
\]

Now

\[
J_{kl} = \iint \mu_l(x)K_k(x', x)[H(x') - H(x)] \, dx' \, dx, \quad k \neq l \tag{3.12}
\]

where

\[
\mu_l(x) = \left( \frac{\partial \mu_l}{\partial \beta_i} \right)_{\beta_i = \beta}, \quad K_k(x', x) = K_k(x', x) \big|_{\beta_i = \beta}
\]

Changing the variables of integration from \((x, x')\) to \((\bar{x}, \bar{x}')\) and then using (1.3) we get

\[
J_{kl} = \iint \mu_l(\bar{x})K_k(x, x') \exp \left[ \beta[H(x) - H(x')] \right] \left[ H(x') - H(x) \right] \, dx' \, dx \tag{3.13}
\]

From Equation (3.9)

\[
(\mu, H) = \int [\tilde{K}(x, x')\mu_k(x') - \tilde{K}(x', x)\mu_k(x)] \, dx' \tag{3.14}
\]

\[
+ Z^{-1} \int \tilde{K}(x, x')e^{-\beta H(x')} \left[ H(x') - H(x) \right] \, dx'
\]

where

\[
\tilde{K}(x, x') = \sum_{i=1}^{n} \tilde{K}_i(x, x')
\]

Multiplying (3.14) by \( e^{\beta H} \), and substituting the resulting expression for the second term on the right of (3.14) into (3.13), we find for the difference in the cross-derivatives

\[
J_{kl} - J_{lk} = Z \int dx' \partial_{\beta_k}[\mu_l(\bar{x})(\mu_k, H) - \mu_k(\bar{x})(\mu_l, H)]] - Z \int K(x, x') \exp \left[ \beta[H(\bar{x}) - H(\bar{x}')] \right] \, dx' \, dx \tag{3.15}
\]

\[
+ Z \int K(x', x) \exp \left[ \beta[H(\bar{x}) - H(\bar{x})] \right] \, dx' \, dx
\]
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The first and third term on the right of (3.15) will vanish, partly because the terms in the square brackets are odd functions of $x$, whereas the expressions by which they are multiplied are even functions of $x$, and partly because the integral of a complete Poisson bracket over all space vanishes. Similarly in the second term the part in the square bracket changes sign when $(x, x') \to (x', x)$ while the factor multiplying it remains unchanged because of (1.3). Hence, Eq. (3.11) has been proved.

4. CONSTRUCTION OF KERNE LTS

In the last two sections we have taken Eq. (1.1) as our starting point. This equation makes explicit use of the transition kernels $K$ to describe the effect of the reservoirs on the system. Our approach has been to find out what properties these kernels must possess so that Eq. (1.1) may lead to certain results which we believe to be true. We shall now return to our physical micro-model (as described in Section 1) and construct the kernels $K(x, x')$ directly from the assumed distribution of reservoir components prior to collision and from the laws of the collision. We shall then examine the symmetry properties of these kernels.

Let $\Gamma_x$ be the phase space of the system, $\Gamma_y$ the phase space of a reservoir component, and $\Gamma_z$ the composite phase space, $z = (x, y)$

$$x = (q_1, \cdots q_N; p_1, \cdots p_N), \quad y = (Q_1, \cdots Q_M; P_1, \cdots P_M)$$

The assumption of impulsive interaction between system and reservoir implies that except for some $2(N + M) - 1$ dimensional surfaces $S(z) = 0$, the system-reservoir combination moves along trajectories $z(t)$ determined by the Hamiltonian $H(z) = H_z(x) + H_y(y)$. Whenever the trajectory $z(t)$ reaches a point $z'$ on one of these singular hypersurfaces, $S(z') = 0$, the representative point jumps to another point $z$ on $S$, $z = T(z')$; thence it continues its motion along the trajectory passing through $z$. At each point on $S$ the vector $z$ will make an acute angle with the normal to one side of $S$, the "outgoing" side $S_o$, and an obtuse angle with the normal to the opposite side of $S$, the "incoming" side $S_i$. The combined system then approaches $S_i$ at $z'$ and leaves $S$ at $z$. The mapping is a completely deterministic transformation.

The joint distribution function $f(x, y) = f(z)$ will be discontinuous at $S$. Let us call the value of $f$ on $S_i$ (the incoming side), $f_i(x, y)$ and on $S_o$, $f_o(x, y)$. We can specify $f_i(x, y)$, the distribution before a collision, in advance. This and the collision transformation $z = T(z')$ will then determine $f_o(x, y)$.

Since $S$ has $2(N + M) - 1$ dimensions it can be described by the $2N$ system variables $x$ and $(2M - 1)$ parameters $u_i$, $i = 1, \cdots (2M - 1)$, so that on $S$

$$y_j = y^{(o)}_j(x, u); \quad j = 1, \cdots, 2M \quad S(x, y^{(o)}(x, u)) = 0$$

Let $dw'$ be a volume element on the incoming side of $S$ such that all the points contained in $dw'$ will reach $S_i$, in the range $dS'_i = dx'du'$ in the time
interval \( dt \). The collision transformation \( T \) will carry \( dS'_e = dx'du' \) into \( dS_e = dx du \). All the points leaving \( dS_e \) in a time interval \( dt \) will then form a volume element \( dw_e \).

Then, because of Liouville's theorem, we must have

\[
f'(x', u') = f_e(x, u) \quad f(x', u') = f_e[x', y^{(e)}(x', u')], \text{ etc.} \quad (4.1)
\]

and

\[
dw'_e = dw_e. \quad (4.2)
\]

We may express this equality of volume elements by introducing as a new quantity the coefficient \( \sigma(x, u) \),

\[
dw = \sigma(x, u) \, dx \, du \, dt \quad (4.3)
\]

for both the incoming and the outgoing trajectory.

This coefficient may be interpreted as the Jacobian of a coordinate transformation in phase space \( \Gamma_e \). We may characterize every point \( P \) in \( \Gamma_e \), both on and off the surface \( S \), by means of the trajectory on which it is located, and identify the latter by means of the parameters \( x^{(e)}, u \) of the point \( P^{(e)} \) at which it intersects \( S \). To complete the identification of \( P \), we also introduce the time \( t \) which has passed since the trajectory traversed \( S \), positive for outgoing and negative for incoming trajectories. Thus \( x^{(e)}, u \) and \( t \) form a complete coordinate system, and \( \sigma \) is the Jacobian \( J(x/x^{(e)}, u, t) \), for \( t = 0 \), that is on \( S \). Accordingly we must have

\[
\sigma(x', u') \, dx' \, du' = \sigma(x, u) \, dx \, du \quad (4.4)
\]

As for the form of \( \sigma \), an evaluation of the Jacobian, whose details we shall omit, yields the expression

\[
\sigma = \left| \delta_{j,j'} \prod_{r=1}^{M} \frac{\partial y^{(j')}_{r}}{\partial u^{(j)}_{r}} \left( \frac{\partial y^{(j')}_{r}}{\partial x^{(e)}_{r}} \right) \right| \quad (4.5)
\]

In this expression, the symbol \( \delta_{j,j'} \) represents the (skew-symmetric) Levi-Civita symbol in the \((2M)\)-dimensional space \( \Gamma_y \), and the indices \( j, j' (= 1, \ldots, 2M) \) and the index \( i (= 1, \ldots, 2N) \) are summation indices. The velocity components \( \dot{y}, \dot{x} \) are those obtained from the Hamiltonian equations of motion.

Physically, \( \sigma \) represents the flux of representative points (per unit density) into (and out of) the hypersurface \( S \) in terms of the parameters on \( S, x^{(e)}, u \). (On the hypersurface \( S, x^{(e)} \) and \( x \) are, of course, identical).

We shall now consider the (fractional) number of systems that undergo collision during the time interval \( dt \) and in the region \( dx \) of the system phase space \( \Gamma_e \). This quantity is

\[
n^{(-)} \, dx \, dt = \int f_e(x, u) \sigma(x, u) \, dx \, du \, dt, \quad n^{(+)} = \int f_e(x, u) \sigma(x, u) \, du \quad (4.6)
\]
\( n_e^{(+)} \) is the fraction of systems lost from a given region of \( \Gamma_x \) per unit volume and per unit time because of collisions. Likewise, we define a similar quantity \( n_e^{(-)} \) that enters the same region of \( \Gamma_x \), as follows:

\[
n_e^{(+)} = \int_u f_\sigma(x, u) \sigma(x, u) \, du \tag{4.7}
\]

The net gain is represented by the difference between \( n_e^{(+)} \) and \( n_e^{(-)} \). Presumably, \( f_\sigma \) is given to us, whereas \( f_\sigma \) must be obtained from the Liouville relationship (4.1). For this purpose we shall introduce both the collision mapping leading from the incoming point \( z' \) on \( S \) to the corresponding point \( z \) on \( S \), and the inverse mapping, as follows:

\[
x = T_1(x', u'), \quad u = T_2(x', u') \tag{4.8}
\]

and

\[
x' = \hat{T}_1(x, u), \quad u' = \hat{T}_2(x, u) \tag{4.9}
\]

Accordingly, we may write the net change in \( \sigma(x) \) per unit time as a result of collisions in the form

\[
\frac{\partial \sigma}{\partial t} + \langle u, H \rangle = \int_u [f_\sigma(x, u) - f_\sigma(x, u)] \sigma(x, u) \, du
\]

\[
= \int_u [f_\sigma(x', u') - f_\sigma(x, u)] \sigma(x, u) \, du - \int_u \{ f_\sigma[x, \hat{T}_1(x, u), \hat{T}_2(x, u)] - f_\sigma(x, u) \} \sigma(x, u) \, du \tag{4.10}
\]

which must now be compared with Eq. (1.1).

To this end we write the incoming joint probability density \( f_\sigma \) in the form

\[
f_\sigma(x, y^{(S)}) = \mu(x)G(x, y^{(S)}) \tag{4.11}
\]

By this definition we have introduced a new function \( G \), which represents the (conditional) distribution of reservoir components and which is independent of the time \( t \). We then conclude that the positive term in the integral (4.10) is to be equated with the positive term in the integral (1.1), and that likewise the negative terms in the two integrals correspond to each other. Hence we shall equate

\[
\int_u \mu' \sigma \, du = \int_{x'} K(x, x') \mu' \, dx' \quad \text{and} \quad \int_u G \sigma \, du = \int_{x'} K(x', x) \, dx' = 1/\tau(x) \tag{4.12}
\]

The integrals, as they stand, are disparate in that the domains of integration on the left and on the right are not comparable. To remedy this defect we shall introduce on the left the primed and the unprimed variables as formally inde-
pendent and connect them again by the introduction of appropriate Dirac delta functions into the expanded integrals

$$\int_0^\mu G^\sigma \, du = \int_0^\mu \int_0^\mu G^\sigma \delta_{2N}[x', \hat{T}_1(x, u)] \delta_{2M-1}[u', \hat{T}_2(x, u)] \, du \, dx' \quad (4.13)$$

Substituting into the first Eq. (4.12), and omitting on both sides the integration over $x'$, we then obtain the following expression for $K(x, x')$

$$K(x, x') = \int_0^\mu G^\sigma \delta_{2N}[x', \hat{T}_1(x, u)] \delta_{2M-1}[u', \hat{T}_2(x, u)] \, du \, dx'$$

$$= \int_0^\mu G[x', y^\sigma(x', \hat{T}_2(x, u))] \sigma(x, u) \delta_{2N}[x', \hat{T}_1(x, u)] \, du \quad (4.14)$$

This expression automatically satisfies the second Eq. (4.12), because of the equality (4.4).

We shall now proceed to discuss the properties of the kernel $K$ in terms of the assumed incoming joint probability density $f_i$, Eq. (4.11). We shall begin with time reversal. If the collisions between the system and the components of the reservoir are subject to the laws of mechanics, including the law of (micro-) reversibility, then the transition $(x', u') \rightarrow (x, u)$ must have a counterpart, $(\bar{x}, \bar{u}) \rightarrow (\bar{x}', \bar{u}')$. In terms of the Dirac delta functions we must have

$$\delta_{2N}[x', \hat{T}_1(x, u)] \delta_{2M-1}[u', \hat{T}_2(x, u)] \, dx' \, du'$$

$$= \delta_{2N}[ar{x}, \bar{T}_1(\bar{x}', \bar{u}')] \delta_{2M-1}[\bar{u}, \bar{T}_2(\bar{x}', \bar{u}')] \, d\bar{x} \, d\bar{u}$$

regardless of the choice of coordinate system and parameters $u$. On the other hand, it will be understood that, for time-reversed points, coordinates and parameters have been chosen so that

$$dx = d\bar{x}, \quad du = d\bar{u}$$

With this choice, we have also

$$\sigma(x, u) = \sigma(\bar{x}, \bar{u})$$

and hence, because of Eq. (4.4),

$$\sigma \, d\bar{x} \, d\bar{u} = \bar{\sigma} \, dx' \, du' \quad (4.18)$$

By combining Eqs. (4.18) and Eq. (4.15), we obtain the equality

$$\delta_{2N}[x', \hat{T}_1(x, u)] \delta_{2M-1}[u', \hat{T}_2(x, u)] \sigma(x, u)$$

$$= \delta_{2N}[ar{x}, \bar{T}_1(\bar{x}', \bar{u}')] \delta_{2M-1}[\bar{u}, \bar{T}_2(\bar{x}', \bar{u}')] \sigma(\bar{x}', \bar{u}')$$

With its help, and by applying the expression for $K$, Eq. (4.14), we find for the
time-reversed kernel $K(x', x)$ the expression

$$K(x', x) = \int_u \int_{u'} G(\delta(x') \delta(x), \hat{T}_1(x, u) \delta_{x'} \delta_{u'} \hat{T}_2(x, u)) du \; du' \quad (4.20)$$

It differs from Eq. (4.14) only in that $G'$ is replaced by $\hat{G}$.

The strongest assumption we can make about the form of $G(x, y)$ is that it be independent of $x$ and a Boltzmann-type exponential in $H_1(y)$; this assumption yields the time-reversed symmetry condition (1.3) immediately when we utilize the principle of energy conservation

$$H_1 + H_2 = H_1' + H_1', \quad H_1 = H_1', \quad H_2 = H_2.$$ \hspace{1cm} (4.21)

However, Eq. (1.3) holds even under a much weaker assumption concerning $G$, to the effect that $G$ may be given the form

$$G(x, y) = e^{-\beta H_1(y)} g(x, y) \quad (4.22)$$

with

$$g(x', u') = g(x, u) \quad (4.23)$$

This weakened assumption is sometimes useful when we consider a reservoir whose configuration coordinates are constrained in a manner that depends on the value of configuration coordinates of the system. We may, for instance, wish to consider a system consisting of “hard” particles of finite extension. We should not want to be required to permit the penetration of these hard particles by the reservoir molecules. In such situations the factor $g$ depends only on configuration coordinates, which neither are affected by transition to the time-reversed situation nor suffer a jump in the event of a collision. Hence the assumption (4.23) still holds, and with it Eq. (1.3).

We next investigate the conditions for the validity of the integral condition (3.1), which is both necessary and sufficient for the canonical distribution to be a stationary solution of Eq. (1.1). We can do this best directly from Eq. (4.10). If we let $\mu$ there be the canonical distribution $\mu_\alpha$, then, using the definitions (4.11), (4.22) along with Eq. (4.21) we find that the integral condition requires that

$$\frac{\partial \mu}{\partial t} \bigg|_{\mu = \mu_\alpha} = Z^{-1} \int \exp \{-\beta [H_1(x) + H_2(y^{(x)})]\}$$

$$\left[ g(x', u') - g(x, u) \right] \sigma(x, u) \; du = 0 \quad (4.24)$$

This integral will of course vanish if

$$g(x', u') = g(x, u) \quad (4.25)$$
If the distribution of reservoir components prior to collision is independent of the state of the system and if it is canonical, then \( g(x, y^{(S)}) \) is constant, and both Eq.'s (4.21) and (4.23) are fulfilled. Hence a system in contact with one such reservoir will reach equilibrium in the course of time; in the presence of several such reservoirs the Onsager relations will hold in the stationary nonequilibrium state.

The time-reversed condition for \( g \), Eq. (4.23), together with Eq. (4.24) leads to

\[
\int \exp \left[ -\beta H(x, y^{(S)}) \right] g(\bar{x}, \bar{a}) \sigma(x, u) \, du \\
= \int \exp \left[ -\beta H(x, y^{(S)}) \right] g(x, u) \sigma(x, u) \, du
\]

(4.26)

According to the second Eq. (4.12), this equality implies the invariance of the total collision cross section with respect to time reversal, i.e. \( 1/\tau(x) = 1/\tau(\bar{x}) \), which had been obtained previously in Eq. (3.5) without reference to the micromodel.

The validity of the direct symmetry condition, Eq. (1.4), which implies detailed balance in equilibrium, would be assured, according to Eq. (4.14), by the following two properties of the micro-model: (a) Each transition \((x', u') \rightarrow (x, u)\) has an inverse \((x, u) \rightarrow (x', u')\),

\[
\delta_{x}(x', T_{1}(x, u)\delta_{x}^{-1}(x', T_{1}(x, u)) \, dx \, du = \delta_{x}(x', T_{1}(x', u')\delta_{x}^{-1}(x, T_{1}(x', u')) \, dx \, du
\]

(4.27)

and (b) the coefficient \( g \) satisfies the equality

\[
g(x', y^{(S)}) = g(x, y^{(S)})
\]

(4.25)

To illustrate the results of this section we shall work out a simple example of a micro-model in the Appendix, whose initial joint distribution satisfies the condition (4.23), but not the condition (4.24). The kernel \( K(x, x') \) will therefore satisfy the time-reversed symmetry condition (1.3), but the canonical distribution will not be a stationary solution.

5. GENERALIZED CANONICAL ENSEMBLES

In this section we shall extend some of our previous results, which we had derived on the assumption that the reservoirs were pure temperature baths, so that we needed to consider only the transfer of heat. We shall now examine systems interacting with more general types of reservoirs, whose components prior to collision form a "generalized canonical ensemble" (3). The joint distribu-
tion of system and reservoir components prior to collision will now have the form
\[ f(x', y^{(S)}) = \mu(x) \exp \left[ -\sum_{i=0}^{n} \alpha^i A_i^r(y^{(S)}) \right] g(x, y^{(S)}) \] (5.1)
where
\[ A_r^0 = H_r, \quad \alpha^0 = 1/kT \]
We are particularly interested in those cases where all the \( A_i^r \) are (a) additive,
\[ A_i^r(x, y) = A_i^r(x) + A_i^r(y), \quad A_s^0 = H_s \] (5.2)
(b) conserved by collisions,
\[ A_i^r(x') + A_i^r(y^{(S)}) = A_i^r(x) + A_i^r(y^{(S)}) \] (5.3)
and (c) conserved by the natural motion of the system
\[ (A_i^r, H_s) = 0 \] (5.4)
When all these conditions are satisfied, many of the theorems derived in the last section for temperature baths remain valid. Thus, in analogy to Eq. (4.24), the equality
\[ \int \exp \left[ -\sum \alpha^i [A_i^r(x) + A_i^r(y^{(S)})] \right] [g(x', u') - (g(x, u)]u(x, u)du = 0 \] (5.5)
implies that the generalized canonical ensemble \( \mu_{ge} \) is a stationary distribution for the system density,
\[ \mu_{ge} = \frac{1}{Z_0} \exp \left[ -\sum \alpha^i A_i^r(x) \right] \] (5.6)
In turn, if this distribution is to be stationary, then the kernel \( K \) representing the interaction of a system with one generalized canonical reservoir satisfies an integral condition of the form
\[ \int K(x', x) \exp \left[ \sum \alpha^i A_i^r(x') \right] dx' = \int K(x', x) \exp \left[ -\sum \alpha^i A_i^r(x) \right] dx \] (5.7)
The quantity \( W_c \) defined originally by Eq. (2.5), which decreases monotonically as long as the system is not in its stationary state, is here given by
\[ W_c = \int \mu [\ln \mu + \sum_{i=0}^{n} \alpha^i A_i^r - \ln Z_s] dx = \frac{1}{kT} [F - F_0] \] (5.8)
where \( F \) is a generalized thermodynamic potential,
\[ F = [U - ST + kT \sum_{i=1}^{n} \alpha^i(A_i^r)] \] (5.9)
6. GRAND ENSEMBLES

Up to now we have considered systems whose chemical composition was fixed, i.e. systems which did not exchange matter with their surroundings. Hence, the system was completely specified by a point in some fixed phase space $\Gamma_z$. We shall now consider systems that can exchange particles with their surroundings (chemical potential reservoirs). According to Gibbs, the treatment of such systems calls for the construction of grand ensembles.

For simplicity, let us deal with a system that contains but one type of particle; the generalization to several types of particles is straightforward. At any time $t$ the state of the system can be specified by a point $x_n$ in some phase space $\Gamma_{z_n}$ having $2nd$ dimensions; $n$ is the number of particles in the system at $t$ and $l$ is the number of degrees of freedom of one particle,

$$x_n = (\xi_1, \ldots, \xi_n)$$

$$\xi_i = (q_i^1, \ldots, q_i^l; p_i^1, \ldots, p_i^l)$$

Both $n$ and $x_n$ will vary in time. Although the variation in $x_n$ (for fixed $n$) results both from the natural motion of the system and from collisions with the reservoir, $n$ can change only as the result of interaction with the reservoir.

By assumption all the particles are identical. As a result, we have a choice of two descriptions of the state of the system. If two points $x_n'$ and $x_n''$, in $\Gamma_{z_n}$, differ only by a permutation of the $\xi_i$'s they may be considered to describe two different states of the system, or they may be considered as representing the same state. In the first case, according to Gibbs, one speaks of a specific phase; in the second case, the phase space obtained by the identification of all such points is called the generic phase space $\Gamma_{z_n}^g$.

For a system containing $n$ particles there are $n!$ specific phases for each generic phase. Hence, if $f(x_n)$ is a symmetric function of all the $\xi_i$'s then

$$\int_{\Gamma_{z_n}^g} f(x_n^g) \, dx_n^g = \frac{1}{n!} \int_{\Gamma_{z_n}} f(x_n^a) \, dx_n^a \quad (6.1)$$

We shall now construct an ensemble which contains member systems having different numbers of particles, a grand ensemble. For each ensemble we may define two ensemble densities, $\mu_n'(x_n)$ and $\mu_n''(x_n)$, as follows: $\mu_n'(\xi_1, \ldots, \xi_n) \, d\xi_1 \ldots d\xi_n$ is the probability that there are $n$ particles in the system and that particle 1 is in the range $(\xi_1, \xi_1 + d\xi_1)$, particle 2 in $(\xi_2, \xi_2 + d\xi_2)$, etc., whereas $\mu_n''(\xi_1, \ldots, \xi_n) \, d\xi_1 \ldots d\xi_n$ is the probability that there is one particle whose identity is not specified in the range $(\xi_1, \xi_1 + d\xi_1)$, one in $(\xi_2, \xi_2 + d\xi_2)$ etc. It is clear from these definitions that

$$\mu_n'(x_n) = \sum_p \mu_p(x_n)$$
Gibbs found that in order to make the entropy, defined as

$$ S = -k \sum_{n} \int \mu_n \ln \mu_n \, dx_n $$

(6.2)

additive, it was necessary to use the generic density in Eq. (6.2). In quantum mechanics, the specific phase of classical physics does not even have an analog. In our model, in which particles can enter and leave the system in the course of time, use of the specific phase space would be awkward. We shall work with the generic density $\mu_n(x_n, t)$ in the phase space $\Gamma_{x_n, t}$. Henceforth we shall omit the superscript $n$.

The equation which describes the time evolution of $\mu_n(x_n, t)$ is a generalization of Eq. (1.1); it includes the possibility that the system loses or gains particles. This generalized equation is

$$ \frac{\partial \mu_n(x_n, t)}{\partial t} + (\mu_n, H_n(x_n)) = \sum_{i=0}^{\infty} \int \int [K_{n, i}(x_n, x_i') \mu_i(x_i') - K_{i, n}(x_i', x_n) \mu_n(x_n)] \, dx_i' $$

(6.1)

where $K_{n, i}(x_n, x_i')$ is the probability per unit time that a system at $x_i'$ will make a transition to $x_n$. In such a transition the number of particles in the system changes by $(n - i)$.

The stationary grand ensemble which represents an open system in equilibrium with a reservoir that has a chemical potential $\nu$ and a temperature $T$ is the grand canonical ensemble whose density $\mu_n(x_n)$ is

$$ \mu_n(x_n) = \frac{1}{Z} \exp [-\beta H_n(x_n) + \gamma n] $$

(6.2)

where

$$ \gamma = \beta \nu = \nu / kT; \quad Z = \sum_{n=0}^{\infty} e^{\gamma n} \int_{\Gamma_{x_n}} \exp [-\beta H_n(x_n)] \, dx_n $$

The necessary and sufficient condition for the grand canonical ensemble to be a stationary solution of Eq. (6.1) is that

$$ \sum_{i=0}^{\infty} \int_{\Gamma_{x_i', x_n}} [K_{n, i}(x_n, x_i') \exp [-\beta H_i(x_i') + \gamma i] - K_{i, n}(x_i', x_n) \, dx_i' \exp [-\beta H_n(x_n) + \gamma n] = 0 $$

(6.3)

The role played by the Helmholtz free energy for a petit ensemble in contact with a temperature reservoir is assumed in a grand ensemble by the “grand canonical potential” $G$,

$$ G = U - TS - \nu \langle n \rangle $$

(6.4)
where

\[ U = \sum_{i=1}^{\infty} \int H_i(x_i) \mu_i(x_i) \, dx_i \]

\[ (n) = \sum_{i=1}^{\infty} n \int \mu_i(x_i) \, dx_i \]  

(6.5)

A theorem analogous to that of Section 2 shows that the stationary state is approached monotonically in a grand ensemble. The symmetry properties of the particle exchange kernels \( K_{n,m}(x_n, x'_m) \) that are analogous to the time-reversed symmetry condition (1.3) for the kernels \( K(x, x') \) are

\[ K_{n,m}(x_n, x'_m) = \frac{K_{m,n}(x'_m, x_n)}{\beta [H_m(x'_m) - H_n(x_n)] - (m - n) \gamma} \]  

(6.11)

When \( n = m \), i.e. when no particles are exchanged, Eq. (6.11) reduces to Eq. (1.3). The factor \( e^\gamma \) is the "fugacity" of the reservoir and so represents in some sense the probability of a particle leaving the reservoir and entering the system, while \( (e^\gamma)^k \) represents the same for \( k \) particles leaving the reservoir. Usually \( K_{n,n} \) is zero unless \( m = n, n \pm 1 \), as the number of particles in the system changes by one at a time. In analogy to Eq. (3.5) we can prove that if Eq. (6.11) is satisfied and if further

\[ 1/\tau_n(x_n) = \sum_{i} \int K_{i,n}(x'_i, x_n) \, dx'_i = 1/\tau_n(\hat{x}_n) \]  

(6.12)

then Eq. (6.3) also holds.

When the system is connected to two or more reservoirs having different temperatures and chemical potentials, then in the stationary state there will be both particle and heat current flowing through the system.

If we consider the heat flowing from the \( i \)th reservoir to the system, \( Q_i \), and the particle flux \( J_i \) as "currents" and \( \beta_i \) and \( \gamma \) as the corresponding "forces," then for systems not far from equilibrium these quantities satisfy Onsager relations.

7. CONCLUSION

In this paper we have considered the asymptotic independence of solutions of our basic integro-differential equation under more general assumptions than previously. We found that if there exists a stationary solution then it will be unique, and it will be approached by all other solutions in the course of time. The existence of a stationary solution under the Doeblin condition had been established previously, and we have added nothing to that result. We have re-examined the necessary symmetry conditions obeyed by the stochastic kernels, have found that our original requirement was stronger than necessary, and have
been able to derive the new and weaker conditions directly from the properties of the underlying micro-model.

As the principal lines of future investigation, we envisage the extension of our physical model to quantum physics, and the development of methods permitting the explicit construction of stationary solutions.

APPENDIX

We shall give here a simple illustration of the ideas developed in Section 4. We consider a system consisting of a one-dimensional particle with a Hamiltonian $H_z$,

$$H_x(x) = p^2/2M + V(q)$$  \hspace{1cm} (A.1)

The reservoir will likewise consist of an ideal one-dimensional gas each of whose components has a Hamiltonian $H_r(y)$,

$$H_r(y) = p^2/2M + U(Q)$$  \hspace{1cm} (A.2)

The three-dimensional surface $S(x)$ where collisions (elastic) between the system and reservoir components take place is defined by the relation,

$$S(x) = q - Q = 0$$  \hspace{1cm} (A.3)

A point on $S$ will be defined by the system variables $(q, p)$ and the parameter $u = P$, so that here

$$Q' = q; \quad P' = P$$  \hspace{1cm} (A.4)

The collision transformation $T$, which transforms the initial state $x'$ into the final state $x$, is

$$\begin{align*}
p &= \left(\frac{m - M}{m + M}\right)p' + \left(\frac{2m}{m + M}\right)P' \\
P &= \left(\frac{2M}{m + M}\right)p' + \left(\frac{M - M}{M + m}\right)P'
\end{align*}$$  \hspace{1cm} (A.5)

$$q = q'; \quad Q = Q' = q'$$  \hspace{1cm} (A.6)

This transformation satisfies Eq. (4.27).

Substituting (A.5) and (A.6) into Eq. (4.14) for the kernel $K$ we get

$$K(x, x') = \delta(q - q') \int dP'dP \left\{ \delta \left[ p' - \left(\frac{2m}{m + M}\right)P - \left(\frac{m - M}{m + M}\right)p \right] \right. \right. \right. \right.$$

$$\cdot \delta \left[ P' - \left(\frac{M - M}{m + M}\right)P - \left(\frac{2M}{M + m}\right)p \right] \exp \left\{ - \beta \left[ U(q') + \frac{P'^2}{2M} \right] \right\} \left. \right. \left. \right. \left. \right. (A.7) \right.$$ 

In order to perform the integration in (A.7) we need to know the form of $g$. 

We shall consider here two cases: (1) The distribution of reservoir components prior to collision is independent of the system, i.e. \( g \) is constant.

\[
g = n/Z_r ; \quad Z_r = \int_{-\infty}^{\infty} e^{-\beta \epsilon p'^2/2M} dP
\]  

(2) The reservoir components are always to the right of the system, \( g \leq Q \). Hence at the beginning of a collision \( p'/m \geq p'/M \), and \( g \) has the form

\[
g = (n/z_r) h(p'/m - P'/M)
\]

where

\[
h(\epsilon) = \begin{cases} 
1 & \text{for } \epsilon > 0 \\
0 & \text{for } \epsilon < 0 
\end{cases}
\]

In the first case Eq. (4.25) is satisfied in addition to Eqs. (4.27), so that \( K(x, x') \) has the direct symmetry property of Eq. (1.4). In fact, integration of Eq. (A.7) yields

\[
K_{(1)}(q, p; q', p') = \frac{n}{Z_r} \frac{(M + m)^2}{4mM} \delta(q - q') \exp \left\{ -\beta U(q') + \frac{\beta}{2M} \left[ \left( \frac{m + M}{2m} \right)^2 (p^2 + p'^2) + \frac{M^2 - m^2}{2m^2} pp' \right] \right\} L(q', p'; q', q) \exp [\beta H_s(q', p')]
\]

where

\[
L(q', p'; q, p) = L(q, p; q', p')
\]

In the second case \( g \) will not satisfy Eq. (4.25) or even Eq. (4.24). The canonical ensemble will therefore not be a stationary distribution when the system is in contact with this reservoir. However, since \( g \) satisfies Eq. (4.23), the kernel \( K \) will have the time-reversed symmetry property of Eq. (1.3). The actual form of \( K \) is

\[
K_{(2)}(q, p; q', p') = h(p' - p)K_{(1)}(q, p; q', p) + K_{(2)}(q, p; q', p') e^{-\beta H_s(q', p')} = K(q, -p'; q, -p') e^{-\beta H_s(p, p')}
\]

We can find the stationary solution of the integro-differential equation obeyed by the ensemble density \( \mu \)

\[
\frac{\partial \mu}{\partial t} + (\mu, H_s(q, p)) = \int \left[ K_{(1)}(q, p; q', p') \mu(q', p') - K_{(2)}(q', p', q, p) \mu(q, p) \right] dq' dp'
\]  

(A.12)
in the special case when the mass of the system equals the mass of a reservoir particle, \( m = M \), and \( U(Q) = 0 \). This solution turns out to be

\[
\mu_s(q, p) = C \exp \left\{ -\beta \left[ \frac{p^2}{2m} + V(q) + \frac{\eta}{\beta} q \right] \right\}
\]

(A.13)

The last term in the exponent produces a probability density gradient that is the same as would be caused by a constant force directed toward the left. We may think of this force as the unilateral pressure caused by the reservoir gas, which is constrained to be only on the right of our system particle. The value of this pressure is \( \eta/\beta \), in accordance with the equation of state of a perfect gas.

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**References**