Stationary nonequilibrium distributions

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We discuss a model to describe distributions of nonequilibrium uniform stationary states. We propose to use as a measure of the deviation from equilibrium the ratio of the nonequilibrium heat capacity of the system to its equilibrium value. When going over to the equilibrium state the distributions obtained degenerate into the standard Gibbs distributions. The thermodynamics based upon the distributions obtained contains a new independent thermodynamic variable which leads to a number of differences from the equilibrium theory: both the distribution and the entropy contain terms describing universal properties of nonequilibrium states which are not connected with the physics of the actual system considered. The quantity C_v taken normally as the heat capacity at constant volume may have singularities as in phase transitions.

1. INTRODUCTION

Nonequilibrium stationary states occupy a special place in nonequilibrium statistical physics.[1–5] On the one hand, the definition of such states does not cause any difficulties, as a rule, and they are defined as stationary solutions of transport-like equations but, on the other hand, the complexity of the equations[1,2] makes it usually impossible to obtain these states and, even more, to obtain distributions over these states. As one exception we may note the theory of Zubarev's Nonequilibrium Statistical Operator[3,4] which enables us to describe a distribution of spatially nonuniform stationary states. However, in the spatially uniform case these distributions become the usual equilibrium Gibbs distributions.

In this paper we wish to draw attention to nonequilibrium spatially uniform stationary states and their possible distributions. The best known example of such states is uniform stationary turbulence.

Before we turn to a description of the model we formulate our concept of nonequilibrium spatially uniform stationary states. We assume uniformity in some macroscopic volume which enables us to ascribe to the whole "box" a single characteristic and the time independence implies that the average characteristics do not change in time. We assume that we can characterize our states by the same parameters, such as temperature or pressure, as in equilibrium theory. For the present, leaving the problem of the determination of these parameters out of our discussion, we note that as soon as they are given we can speak of the corresponding equations of state, the partition function, and other potentials which determine the statistical properties of our model.

Since we intend to consider states different from equilibrium ones it is natural to expect that the equations of state, the partition function, and so on, will also differ from the equilibrium ones. In particular, the heat capacity of the state must differ from its equilibrium value for the same temperature, pressure, and so on. This allows us to estimate the degree of departure from equilibrium i.e., its difference from equilibrium state, by the magnitude of the deviation of the nonequilibrium heat C_N from its equilibrium value C_E when all other parameters are the same.

We propose to use for the derivation of stationary distributions an analog of the Heat Bath which is applied when one derives the equilibrium Gibbs distribution. There exist many different methods for obtaining the Gibbs distribution without necessarily using a Heat Bath[1,2,6,7] but we prefer this approach, postponing a comparison of various methods to a future date.

2. BASIC MODEL

The usual methods for defining nonequilibrium states of a system described by a Hamiltonian H consist in considering the effect of various external actions on the system.[1–4] In that case the actual form of the external forces, the dissipative currents, and so on, are given. We propose to describe nonequilibrium uniform stationary states and the corresponding distributions by using the concept of a Nonequilibrium Heat Bath in the same way as is done in equilibrium theory. We explain what we have in mind.

By a Nonequilibrium Heat Bath we shall understand a large system which is in a nonequilibrium uniform stationary state under the action of external influences. We shall here not be interested in the actual form of the external forces or currents which act on the Heat Bath. We assume that by virtue of the time independence and uniformity we can ascribe a constant average energy E to the whole of the Heat Bath. We shall characterize the degree of departure from equilibrium of the Heat Bath by the ratio of the heat capacity C_{TN} of the Heat Bath to its equilibrium heat capacity C_{TE}, i.e., by the quantity

$$t=\frac{C_{TN}}{C_{TE}}. \qquad (1)$$

Indeed, as soon as we intend to describe nonequilibrium stationary uniform states (the best known example is uniform stationary turbulence) we must at least introduce a

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parameter which would describe the differences between those states and the equilibrium state and between one another. Moreover, we are interested in describing internal statistical properties characteristic for a given system and hence they must not depend on what kind of external actions the system is subject to in a given nonequilibrium state. Assuming that such states can be characterized by, among others, the usual thermodynamic parameters such as the temperature, the pressure, and so on, it is natural to expect the equation of state or the corresponding partition function which describes the distribution of such states to differ from the corresponding equilibrium ones. This enables us to suggest as one of the characteristic parameters describing the model the value of the heat capacity of the Heat Bath or of the system. We discuss details of such a choice in what follows.

We assume that our system is in contact with a Nonequilibrium Heat Bath and is part of it. We thus bring the system into a nonequilibrium uniform stationary state without considering the structure of the external actions to which the system is subject in such a state.

Our aim will be to find the form of the statistical distribution of a system which is in contact with such a Heat Bath, i.e., the analogs of the well known Canonical and Grand Canonical distributions.

To obtain the distribution we must propose a physical mechanism determining the change in the heat capacity in a nonequilibrium state.

We start from the following: we consider the Heat Bath as a large system which has, however, a finite number of degrees of freedom. We assume that if H_T is the Hamiltonian of the Heat Bath and H the Hamiltonian of the system the dimensionality of the phase space of the Heat Bath is N and the dimensionality of the phase space of the system is n, which is much smaller than N. We put here the dimensionality of a (p,q)-space, where p and q are conjugate variables, equal to unity. For instance, we understand the phase space of a free particle in three-dimensional space, which is described by the Hamiltonian

$$H=\frac{p^2}{2}+V(q)$$

to be three-dimensional.

It is well known from equilibrium theory[2,3,7] that the equilibrium heat capacity of a system is proportional to the number of degrees of freedom which in our terms corresponds to the dimensionality of the phase space. For instance, the specific heat of a perfect gas at constant volume is

$$C_V=\tfrac{1}{2}n,$$

where n is the dimensionality of the phase space of a single particle in three-dimensional space. For a given physical system the number of degrees of freedom, or rather the average number of degrees of freedom, may depend on the temperature, the pressure, and so on. However, for given thermodynamic parameters it is just the number (or the average number) of degrees of freedom which determines the heat capacity of the system.

We assume that the external nonequilibrium actions do not change the physics of the system, i.e., do not change the form of the initial Hamiltonian H (a liquid does not become a crystal, or a monatomic gas a molecular array). We assume that the only statistical effect of the external actions on the system can be a change in the average number of degrees of freedom—which at once affects the heat capacity.

The dimensionality of the phase space F_T of the initial Hamiltonian H_T of the Heat Bath is by assumption a large, but finite quantity N. For each $M\leqslant N$ there exists a set of subspaces $F(M)$ of the phase space F_T, each of which has the dimensionality M. These subspaces correspond to cases where different phase variables of the space F_T are the same. For instance, if F_T has the form

$$F_T=\{x_1,x_2,\dots,x_N\},\quad x_j=(p_j,q_j),$$

there exist for $M=N-2$ phase subspaces

$$F_1=\{x_1=x_2=x_3,x_4,\dots,x_N\},$$

$$F_2=\{x_1=x_2,x_3=x_4,x_5,\dots,x_N\}.$$

$x_1=x_2$ means $p_1=p_2$, $q_1=q_2$.

Since we measure the departure from equilibrium of the Heat Bath as the ratio of the heat capacities, by virtue of our hypothesis about the cause of the change in the heat capacity we find that (1) characterizes the ratio of the average dimensionality of the Heat Bath M to its maximum dimensionality N.

We now turn our attention to the evolution of the states of the Heat Bath (or of the system) in the phase subspaces. The evolution in the total phase space F_T is, of course, given by the initial Hamiltonian H_T. This means that we are able to describe the evolution in any phase subspace F using H_T, but it will not be a Hamiltonian description in the subspace F. We are, however, interested in the possibility of a Hamiltonian description in each of the phase subspaces. This means that we must reduce the initial Hamiltonian to the phase subspace and renormalize it in a well defined manner. As the simplest example of the fact that a single reduction is insufficient we consider the Hamiltonian

$$H^*=\frac{p_1^2}{2m}+\frac{p_2^2}{2m}$$

of two free particles of mass m in one-dimensional space. After reduction to the subspace $x_1=x_2$ ($q_1=q_2$; $p_1=p_2$) it takes the form:

$$H=\frac{p^2}{m}.$$

It is clear, however, that the correct Hamiltonian in such a subspace must have the form

$$H=\frac{p^2}{2(2m)}$$

simply because the mass of the moving point is doubled in the subspace. If, however, H^* describes the motion of a single particle of mass m in two-dimensional space, the correct form will be

$$H=\frac{p^2}{2m}.$$

Thus, one needs to renormalize the initial Hamiltonian as well as reduce it. The prescription for the renormalization must, of course, be chosen separately for each physical system.

The main reason why we have paid so much attention to this problem is to emphasize a rather unexpected statement: to describe fully a given physical system, which has a phase space dimensionality N much larger than unity, in a Hamiltonian form in all possible phase subspaces for all M smaller than N we must give, apart from the initial Hamiltonian to which one usually restricts oneself, a set of Hamiltonians describing the evolution in each of the phase subspaces. These Hamiltonians can be obtained by reduction of the initial Hamiltonian to the subspace and its subsequent renormalization.

To enumerate all possible phase subspaces and the corresponding Hamiltonians in them we define a vector $\mathbf{a}=\{a_1,a_2,...\}$. Each of the phase subspaces is formed by merging two or more phase coordinates of the initial phase space. The vector $\mathbf{a}$ enumerates all possible subspaces: of the components of the vector a_1 indicates the number of unpaired coordinates, a_2 the number of coordinates formed letting two coordinates be the same, a_j the number of coordinates formed by the coincidence of j initial coordinates. Therefore, if the dimensionality of the full phase space is N, the vector $\mathbf{a}$, for which

$$|\mathbf{a}|=\sum_{k=1}^{\infty} a_k=\mathbf{M},\quad \|\mathbf{a}\|=\sum_{k=1}^{\infty} ka_k=N \tag{2}$$

describes a phase subspace of dimensionality M. We shall denote the Hamiltonian in this phase subspace by $H(\mathbf{a})$, while the initial Hamiltonian is H.

Let now H_T be the initial Hamiltonian of the Heat Bath and A_T the set of Hamiltonians $H_T(\mathbf{a})$ describing the Heat Bath in all phase subspaces F of dimensionality M of the phase space F_T of dimensionality N: $|\mathbf{a}|=M\leqslant N$. Let H be the initial Hamiltonian of a system with a phase space Φ of dimensionality n much smaller than N and B the set of Hamiltonians $H(\mathbf{b})$, $\mathbf{b}=\{b_1,b_2,...\}$ describing the system in all phase subspaces $\Phi(\mathbf{b})$ of the space Φ.

We assume, as is done in equilibrium theory,[2] that the following decomposition is permissible:

$$H_T=H_R+H,$$

where H_R is sometimes called the Hamiltonian of the reservoir. Moreover we assume that a similar decomposition is permissible for all Hamiltonians of the set A_T, i.e., for all $H_T(\mathbf{a})$:

$$H_T(\mathbf{a})=H_R(\mathbf{c})+H(\mathbf{b}); \tag{3}$$

here $H_R(\mathbf{c})$ describes the reservoir in the corresponding phase subspace and the following equations hold:

$$\mathbf{a}=\mathbf{b}+\mathbf{c};\quad a_k=b_k+c_k. \tag{4}$$

As always in the derivation of statistical distributions we assume that we have $b_k\ll a_k$.

We consider a stationary state of the Heat Bath which differs from equilibrium and which is characterized by (1); by virtue of our assumption about the mechanism for changing the heat capacity we put

$$t=\frac{C_{TN}}{C_{TE}}=\frac{M}{N},\quad 0\leqslant t\leqslant 1. \tag{5}$$

Below we discuss the relation between (5) and what can be measured experimentally. For the present we fix (5) and consider possible consequences of this model.

Equation (5) means that the Heat Bath is on average realized in phase subspaces of dimensionality $M=tN$ and has an energy E by virtue of the time in dependence of the state.

We can now use almost word for word the standard procedure for deriving the distribution analogous to the Canonical distribution.

Let $\Omega(E,M)$ be the number of states of the Heat Bath in the phase subspace of dimensionality M on the energy surface E, and let $G(N,M)$ be the number of different phase subspaces of dimensionality M of the phase space of dimensionality N. The total number of states of the Heat Bath on the energy surface E in all phase subspaces of dimensionality M will then be

$$\omega(E,N,M)=G(N,M)\cdot\Omega(E,M). \tag{6}$$

We assume that only the average value of the dimensionality is realized. Boltzmann's Principle about the equal probability of states on a surface of fixed energy E then means in our model that all states (6) are equally probable.

We explain this important point in some more detail. In equilibrium theory one always considers a Heat Bath in the complete phase space and Boltzmann's Principle leads to equal probabilities for all states of the Heat Bath of energy E. A consequence of this is zero probability for the states in the subspaces. We want to emphasize that the generally accepted statement of the equilibrium theory that the probability for states of the system in phase subspaces (for singular states) in which one or several particles have the same phase coordinates vanishes because of the original assumption that the Heat Bath is realized in the complete phase space. This means that it is, at least, *a priori* impossible to state that the probability for the realization of the Heat Bath itself in phase subspaces is equal to zero.

We note also that Eq. (6) enumerates all equally probable states of the Heat Bath of energy E in all phase subspaces of dimensionality M and this means that the description of the evolution of the Heat Bath in different phase subspaces is accomplished by different Hamiltonians.

Considering the analog of the Canonical distribution we assume that our system is a small part of the Heat Bath and that it has a constant number of particles n, i.e., a fixed value of the dimensionality of the total phase space. We assume that Eqs. (3) and (4) are satisfied and that the system in the phase subspace **b** is described by a Hamiltonian $H(\mathbf{b})$ with an energy $H(\mathbf{b}) = \varepsilon(\mathbf{b}) < E_T$.

We use the notation $\varepsilon(\mathbf{b})$ to emphasize an important point—different Hamiltonians $H(\mathbf{b})$ of the system may have different energy spectra.

Assuming the states to be nondegenerate we find, using (3), (4), and (6) and standard considerations[2,3] that the probability $p(\mathbf{b},\varepsilon(\mathbf{b}))$ for realizing the system in a phase subspace **b** of dimensionality $|\mathbf{b}| = m$ with an energy $\varepsilon(\mathbf{b})$ has the form

$$p[\mathbf{b},\varepsilon(\mathbf{b})] \propto \omega(E-\varepsilon(\mathbf{b}),M-m).$$

This leads directly to the expression

$$p[\mathbf{b},\varepsilon(\mathbf{b})] \propto \exp\{-\beta\varepsilon(\mathbf{b}) - \lambda m\} \tag{7}$$

with the standard definition of the reciprocal temperature

$$\beta = \frac{\partial \ln \omega}{\partial E} = \frac{\partial \ln \Omega(E,M)}{\partial E} \tag{8}$$

and the appearance of a new parameter λ:

$$\lambda = \frac{\partial \ln \omega}{\partial M} = \frac{\partial \ln \Omega(E,M)}{\partial M} + \frac{\partial \ln G(N,M)}{\partial M}. \tag{9}$$

We note that the distribution (7)–(9) reminds us of the Grand Canonical (GC) distribution, but it differs significantly from it in meaning: in contrast to the GC distribution which describes the probability for realizing systems with differing numbers of particles, i.e., fundamentally different systems, (7) describes the probability for the realization of a given system with a given number of particles—a given dimensionality n of the complete phase space—over different phase subspaces **b** with a dimensionality $|\mathbf{b}| = m \leqslant n$ with an energy $\varepsilon(\mathbf{b})$. Moreover, the analog of the "chemical activity" λ is only partially determined by the properties of the system itself—the first term on the right-hand side of (9). The main term in (9),

$$\frac{\partial \ln G(N,M)}{\partial M}$$

is combinatorial and clearly characterizes universal properties which are inherent to all nonequilibrium stationary states.

It is also completely obvious that we can obtain the analog of the GC distribution by taking into account a possible exchange of particles between the Heat Bath and the system. In our model this corresponds to a variable dimensionality of the complete phase space of the system and leads to the expression

$$p[n,\mathbf{b},\varepsilon(\mathbf{b})] \propto \exp\{-\beta\varepsilon(\mathbf{b}) - \lambda m - \gamma n\}, \tag{10}$$

$$\gamma = \frac{\partial \ln \omega}{\partial N} = \frac{\partial \ln G(N,M)}{\partial N}. \tag{11}$$

The parameter γ in (11) is for the distribution (10) already completely determined by the combinatorial term and must describe universal properties which are independent of the system considered.

We can write the partition function for (7) in the form

$$\begin{aligned} Z_C &= \sum_{m=1}^{n} \exp\{-\lambda m\} \sum_{|\mathbf{b}|=m} Z(\mathbf{b},\beta) \\ &= \sum_{m=1}^{n} \sum_{|\mathbf{b}|=m} \exp\{-\lambda m - \beta A(\mathbf{b},\beta)\} \\ &= \sum_{b_1=0}^{\infty} \cdots \sum_{b_2=0}^{\infty} \exp\left\{-\lambda \sum_{k=1}^{\infty} b_k - \beta A(\mathbf{b},\beta)\right\}\Bigg|_{\|\mathbf{b}\|=n} \\ &= \sum_{b_1=0}^{\infty} \exp(-\lambda b_1) \sum_{b_2=0}^{\infty} \exp(-\lambda b_2) \cdots \\ &\quad \times \sum_{b_k=0}^{\infty} \exp(-\lambda b_k) \cdots \exp\{-\beta A(\mathbf{b},\beta)\}\Bigg|_{\|\mathbf{b}\|=n} \end{aligned} \tag{12}$$

Here $Z(\mathbf{b},\beta)$ and $A(\mathbf{b},\beta)$ are the Canonical partition function and the Helmholtz free energy of our system in the phase subspace **b**:

$$\begin{aligned} Z(\mathbf{b},\beta) &= \frac{1}{C(\mathbf{b})} \sum_{\varepsilon(\mathbf{b})} \exp\{-\beta\varepsilon(\mathbf{b})\}, \\ \beta A(\mathbf{b},\beta) &= -\ln Z(\mathbf{b},\beta). \end{aligned} \tag{13}$$

$C(\mathbf{b})$ is a normalizing factor for the Canonical ensemble of a system in the phase subspace **b** of our system. The symbol $\Sigma_{\varepsilon(\mathbf{b})}$ indicates summation over the energy spectrum of the Hamiltonian $H(\mathbf{b})$ in the phase subspace **b**. Altogether we get

$$p[\mathbf{b},\varepsilon(\mathbf{b})] = Z_C^{-1} C(\mathbf{b})^{-1} \exp\{-\beta\varepsilon(\mathbf{b}) - \lambda m\}.$$

The partition function for the distribution (10) has the form:

$$\begin{aligned} Z_{\mathrm{GC}} &= \sum_{n=1}^{\infty} \exp\{-\gamma n\} \sum_{m=1}^{n} \exp\{-\lambda m\} \sum_{|\mathbf{b}|=m} Z(\mathbf{b},\beta) \\ &= \sum_{b_1=0}^{\infty} \sum_{b_2=0}^{\infty} \cdots \exp\left\{- \sum_{k=1}^{\infty} (\gamma k + \lambda) b_k \right. \\ &\qquad \left. - \beta A(\mathbf{b},\beta) \right\}. \end{aligned} \tag{14}$$

Equations (7)–(9), (12), and (13) and (10), (11), (13), and (14) describe our generalizations of the Canonical and the Grand Canonical distributions for uniform stationary nonequilibrium states.

We shall consider the expressions obtained in some more detail.

3. TRANSITION TO EQUILIBRIUM DISTRIBUTIONS

The first thing we must obtain is the transition to the equilibrium description. In our model the equilibrium situation is defined by (1) for the value $t = 1$. This means that the Heat Bath is on average realized in its complete phase space which implies that the distributions (12) and (14) which we have obtained are exactly the same as the equilibrium expressions. We show that this result follows from the general expressions.

As an example we consider the limiting transition of Eq. (14) to the Grand Canonical distribution. We can write it in the form:

$$Z_{\mathrm{GC}}=\sum_{\substack{b_1=0\\(b_j=0,\,j>1)}}^{\infty}\exp\{-(\gamma+\lambda)b_1-\beta A(\mathbf{b},\beta)\}$$

$$+\sum_{b_1=0}^{\infty}\sum_{b_2=0}^{\infty}\cdots\sum_{b_j=1}^{\infty}\cdots$$

$$\times\exp\left\{-\sum(\gamma k+\lambda)b_k-\beta A(\mathbf{b},\beta)\right\}. \tag{15}$$

The first term on the right-hand side of (15) is exactly the same as the equilibrium GC partition function and the second one tends to zero as $t\to 0$. To show this it is necessary to consider the explicit form of the combinatorial term $G(N,M)$. For different physical systems these quantities may differ, depending on the structure of the phase space, whether pairing is allowed for all phase variables or not, and so on.

In the simplest case of a classical description of structureless particles in a phase space $F_T=\{x_1,x_2,\dots,x_N\}$, $x_j=p_j,\ q_j$ with dimensionality N, where pairing is allowed for all phase variables, the number of phase subspaces of dimensionality M is described[8] by Stirling numbers of the second kind σ_N^M—the number of ways of partitioning a set of N elements into M nonempty subsets. The number of ways of partitioning N elements into a given configuration $\mathbf{a}$,

$$|\mathbf{a}|=\sum a_k=M;\quad \|\mathbf{a}\|=\sum k a_k=N$$

is determined by the multinomial coefficients

$$(N,\mathbf{a})=N!\left[\prod_{k=1}^{\infty}(k!)^{a_k}a_k!\right]^{-1}.$$

We then have

$$\sum(N,\mathbf{a})=\sigma_N^M,$$

where the sum is taken over all configurations $|\mathbf{a}|=\Sigma a_k=M$.

For $N-M\ll M$, $N-M\simeq o(N^{1/2})$ the asymptotic form of σ_N^M is[8]

$$G(N,M)=\sigma_N^M\simeq\frac{N^{2(N-M)}}{2^{N-M}(N-M)!}.$$

This enables us to write the main term for $\ln G$ for $N-M\gg 1$ in the form

$$\ln G\simeq(N-M)\ln\frac{N^2}{2(N-M)}$$

and to obtain expressions for the parameters λ and γ:

$$\gamma=\frac{\partial\ln G}{\partial N}\simeq\ln\frac{N^2}{2(N-M)},$$

$$\lambda=\frac{\partial\ln\Omega}{\partial M}+\frac{\partial\ln G}{\partial N}\simeq\frac{\partial\ln\Omega}{\partial M}-\ln\frac{N^2}{2(N-M)}.$$

Hence it follows that as $t\to 1$

$$\gamma+\lambda=\frac{\partial\ln\Omega}{\partial N}\approx-\mu\beta;$$

$$k\gamma+\lambda=\frac{\partial\ln\Omega}{\partial N}+(k-1)\ln\frac{N^2}{2(N-M)}\to+\infty.$$

By virtue of this the first term in (15) is, indeed, the same as the GC partition function since we have $\lambda+\gamma=-\mu\beta$ (the usual definition of the chemical activity) and the second term becomes exponentially small compared to the first one, since there are always factors for b_k, $k>1$.

One can prove completely similarly that (12) goes over into the equilibrium Canonical partition function as $t\to 1$.

4. STATIONARY THERMODYNAMICS

In a single section it is impossible to describe with any degree of completeness the changes to which the stationary distributions which we have obtained may lead in thermodynamic problems. We try to indicate merely those features which we feel are the most interesting ones.

In our view the most important one is the appearance of yet another thermodynamic parameter: $\bar{m}$, the average dimensionality, which must be considered on equal footing with the other ones.

The standard definition of the entropy

$$S=\ln\omega=\ln\Omega+\ln G,\quad S=-\sum p\ln p$$

for stationary distributions leads to the appearance of a component $\ln G$ which describes the "disorder" in the set of all phase subspaces and thus to a significant extent is a universal component of the entropy. The analog of the Canonical distribution can be written in the form

$$p(\mathbf{b},\varepsilon)=\pi(\mathbf{b})\cdot p_b(\varepsilon),$$

$$p_b(\varepsilon)=Z^{-1}(\mathbf{b},\beta)C(\mathbf{b})^{-1}\exp\{-\beta\varepsilon(\mathbf{b})\}, \tag{16}$$

$$\pi(\mathbf{b})=Z^{-1}\exp\left\{-\lambda\sum b_k-\beta A(\mathbf{b})\right\},$$

where $A(\mathbf{b})$ and $Z(\mathbf{b},\beta)$ are given by (13) and Z by (12). In this case the entropy can be written in the form

$$S=-\sum p\ln p=\bar{S}_B+S_c,$$

$$\bar{S}_B=\sum S_B(\mathbf{b})\pi(\mathbf{b});\quad S_B(\mathbf{b})=-\sum p_b(\varepsilon)\ln p_b(\varepsilon), \tag{17}$$

$$S_c=-\sum\pi(\mathbf{b})\ln\pi(\mathbf{b}).$$

Here $\bar{S}_B$ is the Boltzmann entropy $S_B(\mathbf{b})$ of the system in the phase space $\mathbf{b}$ averaged with the weight $\pi(\mathbf{b})$. S_c is the combinatorial component of the entropy which is not present in equilibrium theory. It is clear that in the limit of an equilibrium state, $t\to 1$, we get $S_c\to 0$.

The pressure, defined in the usual way,

$$P=\frac{\partial}{\partial V}\frac{1}{\beta}\ln Z=\sum \pi(\mathbf{b})P(\mathbf{b}),$$
$$P(\mathbf{b})=\frac{\partial}{\partial V}\frac{1}{\beta}\ln Z(\mathbf{b},\beta) \tag{18}$$

is the usual pressure $P(\mathbf{b})$ in the phase subspace $\mathbf{b}$ averaged with the weight $\pi(\mathbf{b})$.

The appearance of yet another thermodynamic parameter $\bar{m}$, the average dimensionality, leads to an equation of state of the form

$$P=P(\rho,T,\bar{m}).$$

The new parameter significantly affects the heat capacity. New groups of independent variables appear:

$$(P,V,\bar{m})\leftrightarrow(T,V,\bar{m})\leftrightarrow(P,T,\bar{m})\leftrightarrow(P,V,T) \tag{19}$$

the variables (P,V,T) are not at all independent in equilibrium thermodynamics but in our model this is permissible. The relations (19) mean that one must distinguish three forms of the heat capacity: $C_{V\bar{m}}$, $C_{P\bar{m}}$, and C_{VP}, the heat capacity at constant volume and pressure:

$$C_{V\bar{m}}=\frac{\partial Q}{\partial T}\bigg|_{V=\text{const},\ \bar{m}=\text{const}},\quad C_{VP}=\frac{\partial Q}{\partial T}\bigg|_{V=\text{const},\ P=\text{const}},$$

$$C_{P\bar{m}}=\frac{\partial Q}{\partial T}\bigg|_{P=\text{const},\ \bar{m}=\text{const}}.$$

Measuring the heat capacity keeping only the volume constant leads, for instance, to the quantity

$$C_V=C_{V\bar{m}}+\frac{\partial Q}{\partial \bar{m}}\frac{d\bar{m}}{dT}=C_{VP}+\frac{\partial Q}{\partial P}\frac{dP}{dT}. \tag{20}$$

The main point is, as one should note at once, that C_V from (20) characterizes not only the state, like, for instance, $C_{V\bar{m}}$, but also the process: $\bar{m}=\bar{m}(T)$ under the condition $V=\text{const}$, or $P=P(T)$ under the condition $V=\text{const}$. Thus, if a process occurs with a rather fast change in $\bar{m}$ for a small change in T near a critical value T_c this may lead to a singularity in the quantity C_V in the point T_c. For instance, for

$$\bar{m}=\bar{m}(T)=\bar{m}_c+\text{sign}(T-T_c)\,|T-T_c|^{1-\alpha},$$
$$0\leqslant\alpha<1$$

we get for C_V in the vicinity of T_c a singularity of the form

$$C_V\simeq|T-T_c|^{-\alpha}.$$

Here we do not consider in detail the possible consequences of this, but it is impossible not to note that an abrupt change in the average dimensionality for a small change in the temperature in (20) may cause a singularity of the quantity C_V—very similar to what is observed in phase transitions.

To characterize the degree of departure of stationary states from equilibrium proposed by us it is natural to choose $C_{V\bar{m}}$ or $C_{P\bar{m}}$.

5. EXAMPLES

For simplicity we consider a one-dimensional perfect gas.

1. We take the analog of the canonical distribution (7), (12), and (13) for a one-dimensional model of three ideal particles described by the Hamiltonian:

$$H=\frac{p_1^2}{2m_0}+\frac{p_2^2}{2m_0}+\frac{p_3^2}{2m_0}.$$

There exist three phase subspaces of dimensionality two and one of dimensionality 1 with the Hamiltonians H_2 and H_1 in them:

$$H_2=\frac{p_1^2}{2(2m_0)}+\frac{p_2^2}{2m_0},\quad H_1=\frac{p_1^2}{2(3m_0)}.$$

The Boltzmann partition functions in the corresponding subspaces are equal to

$$Z_1=3^{1/2}(2\pi m_0T)^{1/2}L,\quad Z_2=2^{1/2}\frac{Z_1^2}{3},$$

$$Z_3=3^{-3/2}\frac{Z_1^3}{3!},$$

where L is the linear size of the region.

The total partition function corresponding to (12) is equal to

$$Z=\frac{B^3}{3!}+3\cdot 2^{1/2}B^2+3^{1/2}B,$$

$$B=e^{-\lambda}L(2\pi m_0T)^{1/2}.$$

There are two cases possible:

1) $t\to 1,\quad \lambda\to-\infty,\quad B\to\infty:\quad Z\to Z_3,$

2) $t\to 0,\quad \lambda\to\infty,\quad B\to 0:\quad Z\to Z_1.$

From the partition function we obtain the average dimensionality,

$$\bar{m}=-\frac{\partial\ln Z}{\partial\lambda};$$

1) $t\to 1,\quad \lambda\to-\infty,\quad B\to\infty:\quad \bar{m}\to 3,$

2) $t\to 0,\quad \lambda\to\infty,\quad B\to 0:\quad \bar{m}\to 1,$

and also the average energy

$$U=-\frac{\partial\ln Z}{\partial\beta}=\frac{T}{2}\bar{m}.$$

2. We consider the analog of the Grand Canonical distribution (10), (11), and (14) for a one-dimensional model of ideal particles described by the Hamiltonian:

$$H=\sum_{k=1}^{n}\frac{p_k^2}{2m_0},\quad n=0,1,\dots\ .$$

The Hamiltonian describing the dynamics in the phase subspace **b** is

$$H(\mathbf{b})=\sum_{k=1}^{\infty}\sum_{j=1}^{b_k}\frac{p_{k,j}^2}{2km_0},\quad b_k=0,1,\dots$$

and it can be seen from (14) that the corresponding partition function $Z(\mathbf{b})$ is

$$Z(\mathbf{b})=\left[\prod b_k!\right]^{-1}\int dq\,dp\exp[-\beta H(\mathbf{b})]$$
$$=\prod_{k=1}^{\infty}\frac{1}{b_k!}(2\pi k m_0 T)^{b_k/2}.$$

The total partition function of the kind (14) has the form

$$Z=\prod_{k=1}^{\infty}\sum_{b_k=0}^{\infty}\frac{1}{b_k!}\exp\{-(\lambda+k\gamma)b_k\}(2\pi k m_0T)^{b_k/2}$$
$$=\prod_{k=1}^{\infty}\exp\{B_k\}=e^{B},$$

$$\ln Z=B=\sum B_k,\quad B_k=(2\pi m_0T)^{1/2}e^{-\lambda}k^{1/2}e^{-\gamma k}.$$

The average dimensionality is equal to

$$\bar{m}=-\frac{\partial\ln Z}{\partial\lambda}=\ln Z.$$

The average number of particles is equal to

$$\bar{n}=-\frac{\partial\ln Z}{\partial\gamma}=(2\pi m_0T)^{1/2}e^{-\lambda}\sum_{k=0}^{\infty}k^{3/2}e^{-\gamma k}.$$

The average energy U of the whole system is

$$U=-\frac{\partial\ln Z}{\partial\beta}=\frac{T}{2}\bar{m}.$$

The average energy u per particle is

$$u=\frac{T}{2}\frac{\bar{m}}{\bar{n}},$$

$$1)\ t\to1,\quad \lambda\to-\infty,\quad \gamma\to\infty:\ \frac{\bar{m}}{\bar{n}}\to1,\quad u\to\frac{T}{2},$$

$$2)\ t\to0,\quad \lambda\to\infty,\quad \gamma\to0:\ \frac{\bar{m}}{\bar{n}}\to0,\quad u\to0.$$

Indeed, as $t\to0$, i.e., for $M=tN$, $M\geqslant1$, we have[8] $\sigma_N^M\simeq M^N/M!$ and

$$\lambda\simeq\frac{N}{M}\to\infty,\quad \gamma\simeq\ln M\to0\ \text{as}\ M\to1.$$

For the present we confine ourselves to these very simple examples.

6. DISCUSSION

We mentioned in the Introduction that many papers (see, e.g., Ref. 1 and the references given there) have been devoted to a study of various aspects of nonequilibrium stationary states (stability, fluctuations, thermodynamics). It is necessary to clarify the place of the stationary states proposed in our paper amongst those known already in the literature.

The stationary states proposed in our paper differ somewhat from those described in the literature.[1] The differences are not connected with the fact that the stationary states in our paper are at once in a form similar to the Gibbs distribution. This can be done in a similar form also for the stationary states obtained as the time-independent solutions of kinetic equations. In our view, a more important difference is the statistical functional behavior of the stationary distributions which is given, for instance, by Eqs. (7)–(9).

In the usual discussion (e.g., in Ref. 1) the kinetic equations describe the change in the density function in a fixed phase space under the action of given external actions and currents. The stationary state is therefore obtained also in the fixed subspace defined by the original model of the kinetic equation.

In contrast to those Eqs. (7)–(9) describe stationary distributions in a set of different phase subspaces **b** of the complete phase space of the system considered and in each of these phase subspaces, rather than in a well defined phase space. This means that in order to obtain the analogous stationary states, starting from kinetic equations, we need consider the density function and its equations in each of the phase subspaces and, moreover, we need a condition describing the evolution of the density function in the set of the phase subspaces themselves. This description corresponds most closely to what on p. 380 of Ref. 1 is called "dynamically uncoupled variables".

In our view stationary distributions such as Eqs. (7)–(9) may be of interest for a number of reasons.

Firstly, a "purely" equilibrium distribution is the limiting case $t\to1$ of a family of stationary distributions and therefore the results obtained for (7)–(9) for arbitrary t may be the same, as $t\to1$, as the equilibrium ones ($t=1$), but in a number of cases they may be different, i.e., there may be a dependence on the order in which the transition to the limit is taken; it would be interesting to clarify the cause of such a dependence.

Secondly, it is known that if H_{eff} is some effective Hamiltonian describing a state in the form of a "Gibbs distribution," in the vicinity of this state a density function ρ, different from a stationary distribution, is described by the Liouville equation generated by the Hamiltonian H_{eff} and by virtue of Liouville's theorem ρ is conserved, which leads to a constant entropy when ρ evolves. This means that even a density function which is close to a stationary distribution does not converge to it, strictly speaking. An interesting feature of the distributions (7)–(9) is that the evolution equation for the density function ρ in the vicinity of (7)–(9) must necessarily be described using the evolution of the states along each of the phase subspaces **b** which is determined by the Hamiltonian $H(\mathbf{b};p,q)$ and, moreover, it is necessary to take into account the possible evolution of the vector **b** itself. Since the evolution of **b** in no way can be determined by the Hamiltonians $H(\mathbf{b};p,q)$ there are no grounds whatever for requiring the conservation of the density function as in Liouville's theorem and it is possible without distorting the Hamiltonian nature of the evolution along the phase subspaces to use purely thermodynamic and thus dissipative relations to determine the evolution of the vector **b**. This may allow us to obtain an equation for the density function describing the convergence to a stationary distribution, increasing the entropy in the evolution, and so on, combining a Hamiltonian description along the phase subspaces with thermodynamic laws such as the law for the increase of the entropy to describe the evolution of the vector **b**.

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