Liouville's theorem and the problem of the increase of the entropy

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We show that it follows from the BBGKY hierarchy and the Gibbs definition of the entropy of a closed isolated system that the local entropy can increase, in full agreement with the second law of thermodynamics, and that this does not contradict the Liouville theorem. © *1995 American Institute of Physics.*

1. INTRODUCTION

The problem of a statistical justification of the second law of thermodynamics arose at the same time as the formulation of the law itself, i.e., in the middle of the last century. For equilibrium systems the determination of entropy was given by Gibbs, but for nonequilibrium systems it still remains unknown up to now. The reason for this is that it is not clear how to reconcile the condition that the statistical entropy must be constant, as follows from Liouville's theorem, with the increase of the thermodynamic entropy. It has not been possible to remove this contradiction, although during the last hundred years there has been great interest in the problem of the increase of the entropy.

It is well known that the increase δS in the entropy in thermodynamic is determined by the relation

$$\theta \frac{\delta S}{k_B} = \delta Q, \tag{1}$$

in which δQ is the amount of heat received by the system, $\theta = k_B T$ is the temperature, and k_B is Boltzmann's constant. Since this definition presupposes an exchange of heat with the surrounding medium, in this case we are dealing with an open system. On the other hand, Gibbs defined the entropy of a closed isolated system consisting of N particles and occupying a volume V as the logarithm of the phase volume Γ:

$$\frac{S}{k_B} = \ln \frac{\Gamma}{\Gamma_{\min}}, \tag{2}$$

where $\Gamma_{\min}$ is the minimum phase volume occupied by the system at the absolute zero of the temperature, $\theta = 0$. It is not clear to me how one can show that these two definitions are identical. Nonetheless they are most likely identical, since in the case of thermodynamic equilibrium they lead to the same expression for the first law of thermodynamics:

$$\theta \frac{\delta S}{k_B} = \delta E + P\,\delta V \tag{3}$$

(here E is the energy of the system and P the pressure). However, when the equilibrium is broken it looks as if their identity disappears since it follows from (1) that for nonequilibrium systems the equal sign in (3) must in accordance with the second law of thermodynamics be replaced by an inequality sign

$$\theta \frac{\delta S}{k_B} > \delta E + P\,\delta V, \tag{4}$$

whereas according to Liouville's theorem the statistical entropy S defined by Eq. (2) must remain the same as in equilibrium. Apparently the reason for this is that in the first case we are dealing with an open system and in the second case with a closed one. We shall try to prove that in nonequilibrium systems in the thermodynamic limit,

$$N, V \to \infty, \quad n_0 = \frac{N}{V} = \text{const.}, \tag{5}$$

the local entropy of a physically infinitesimal volume which forms an open system must change with time; the problem of whether it increases or decreases in this case remains open, since an answer to that question can be obtained only after one has developed a method for solving the BBGKY hierarchy.

The proof assumes a certain broadening of the base on which the Gibbs theory is constructed. On the basis of the latter we have the concept of a global description of the system by means of an N-particle distribution function $\mathscr{G}_{(N)}$. In the case of equilibrium this approach is fully justified, since the spatial homogeneity of equilibrium systems implies that one can always change from global to local quantities simply by splitting off the first of the total number N of particles in the system (e.g., for the local entropy we have $s = S/N$).

The global approach becomes inadequate in nonequilibrium systems, because one and the same value of the global characteristics may correspond to an infinite variety of local nonequilibrium states. In this case it is necessary to change to a local description of the system which, by the way, has always been done in the thermodynamics of nonequilibrium processes and in the macroscopic theory of transport processes. However, in the framework of the Gibbs theory it is impossible to carry out such a change. The step to resolve this dilemma was taken by Bogolyubov, Born, Green, Kirkwood, and Yvon, who introduced into the argument the l-particle distribution functions $\mathscr{G}_{(l)}$, $1 \leq l \leq N$ and constructed a set of equations to determine them (the so-called BBGKY hierarchy). In accordance with their scheme one must also analyze the concept of the global Gibbs entropy (2), which automatically splits into a sum of l-particle entropies after one makes the change to the l-particle distribution functions $\mathscr{G}_{(l)}$:

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$$S=\sum_{l=1}^{N} S^{(l)}.$$

It is then found that in nonequilibrium systems entropy can pass from one correlation to another which, however, does not mix the global entropy: $S=\Sigma_{l=1}^{N}S^{(l)}$ remains constant completely in agreement with Liouville's theorem (see Ref. 1). This result already shows that a more detailed description of the system through the l-particle distribution functions enables us to discover motion there where the Gibbs global approach predicts no time dependence.

The main idea of our paper is thus a replacement of the global description of the system by means of an N-particle distribution function by a more detailed local description through l-particle distribution functions $\mathscr{G}_{(l)}$, $1\leqslant l\leqslant N$. As a final result it led to the creation of an up-to-date theory of liquids by means of which it has been possible to calculate very different material parameters with high precision (see Ref. 1). However, the author is not aware that this idea has been applied so far to the problem of the increase in entropy. I am therefore unable to refer here to work by any predecessors.

The paper consists of seven sections. In the second one we formulate the basic equations of the theory (i.e., the BBGKY hierarchy), in the third one we consider the conservation law for the global entropy of the whole system, in the fourth one we introduce the concept of a local entropy and formulate its balance equation, in the fifth one we analyze the consequences of taking the thermodynamic limit and show that in that limit the global characteristics (the entropy S, the energy E, and so on) become infinite and lose their physical meaning; the only parameters which determine the state of the system turn out to be the local values of the entropy, the density, the energy, and so on. Finally, in the sixth section we discuss the problem of the increase of the local entropy and in the last, the seventh, section we give a general discussion of the results obtained.

2. BASIC RELATIONS

It is well known that the BBGKY hierarchy is simply another way to write down the equations of motion of classical mechanics. It determines the l-particle distribution functions (see Ref. 1)

$$\mathscr{G}_{1,\dots,l}\equiv\mathscr{G}_{(l)}(\mathbf{r}_1,\dots,\mathbf{r}_l,\mathbf{p}_1,\dots,\mathbf{p}_l,t) \tag{6}$$

through an infinite set of equations which are coupled with one another:

$$\frac{\partial\mathscr{G}_{1,\dots,l}}{\partial t}=\sum_{i=1}^{l}\left\{-\frac{\mathbf{p}_i}{m}\frac{\partial\mathscr{G}_{1,\dots l}}{\partial\mathbf{r}_i}+\frac{\partial U_{1,\dots,l}}{\partial\mathbf{r}_i}\frac{\partial\mathscr{G}_{1,\dots,l}}{\partial\mathbf{p}_i}\right.$$
$$\left.+\frac{n_0}{\mathscr{P}^3}\int\frac{\partial\Phi_{i,l+1}}{\partial\mathbf{r}_i}\frac{\partial\mathscr{G}_{1,\dots,l+1}}{\partial\mathbf{p}_i}\,d(l+1)\right\}. \tag{7}$$

Here t is the time, $\mathbf{r}_i$ and $\mathbf{p}_i$ are the coordinate and momentum of the ith particle, m is its mass, $n_0=N/V$ is the mean density in the system, $\mathscr{P}=\sqrt{2\pi m\theta}$ is a normalization momentum, $d(l+1)=d^3r_{l+1}d^3p_{l+1}$,

$$U_{1,\dots,l}\equiv U_{(l)}(\mathbf{r}_1,\dots,\mathbf{r}_l)=\sum_{1\leqslant i<j\leqslant l}\Phi_{ij} \tag{8}$$

is the configurational energy of a group of l particles, $\Phi_{ij}=\Phi(r_{ij})$ is the potential energy of the pair interaction of the particles i and j, and $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$. For the sake of simplicity we have put the energy of the particles in the external field equal to zero.

As is done in Refs. 1 and 2,[1)] in (7) it is convenient to change from the distribution functions $\mathscr{G}_{(l)}$ to the thermal potential $\omega_{(l)}$, putting

$$\tilde{\Omega}_{1,\dots,l}=\ln\mathscr{G}_{1,\dots,l}=\sum_{i=1}^{l}\omega_i+\sum_{i\,j}\omega_{ij}+\dots+\omega_{1,\dots,l}. \tag{9}$$

[In Ref. 2 (see also footnote 1)] we worked with potentials $\Omega_{(l)}$ which are connected with the potential $\tilde{\Omega}_{(l)}$ through the simple relation

$$\tilde{\Omega}_{1,\dots,l}=\sum_{i=1}^{l}\omega_i+\Omega_{1,\dots,l}.$$

3. GLOBAL ENTROPY

Here and henceforth we shall consider closed isolated systems of N particles occupying a fixed volume V. One can characterize the state of such systems by global quantities which determine the state of the complete system as a whole (its total energy E, total entropy S, and so on) and by local quantities which determine the state of the matter at a given point $\mathbf{r}$ of the system (e.g., the energy density e in that point, the entropy density s, and so on). We start with a discussion of the global entropy.

Gibbs has shown (see, e.g., Ref. 3) that the definition (2) of the global entropy implies that it can be written in the form

$$S=-\frac{k_B}{(V\mathscr{P}^3)^N}\int\tilde{\Omega}_{1,\dots,N}\mathscr{G}_{1,\dots,N}\,d(1)\dots d(N), \tag{10}$$

where the N-particle distribution function $\mathscr{G}_{(N)}$ is defined by Eq. 9 with $l=N$. As the entropy has the meaning of a logarithm of the phase volume which, according to Liouville's theorem, must always be constant, Eq. (10) must determine a value of S independent of the time t. We show using the BBGKY hierarchy that this is, in fact, the case (as far as the author is aware such a proof cannot be found in the literature).

Substituting in (10) for $\tilde{\Omega}_{(N)}$ its value from (9) we get after some simple transformations

$$S=\sum_{l=1}^{N}S^{(l)}(t), \tag{11}$$

where the global correlation entropy is

$$S^{(l)}(t)=-k_B\frac{N(N-1)\dots[N-(l+1)]}{l!(V\mathscr{P}^3)^l}$$
$$\times\int\omega_{1,\dots,l}\mathscr{G}_{1,\dots,l}\,d(1)\dots d(l). \tag{12}$$

Consider the derivative

$$\frac{dS}{dt}\sim\int\left[\frac{\partial\tilde{\Omega}_{1,\dots,N}}{\partial t}\mathcal{G}_{1,\dots,N}+\tilde{\Omega}_{1,\dots,N}\frac{\partial\mathcal{G}_{1,\dots,N}}{\partial t}\right]d(1)\dots d(l). \tag{13}$$

Since we have

$$\frac{\partial\tilde{\Omega}_{(N)}}{\partial t}\mathcal{G}_{(N)}=\frac{\partial\mathcal{G}_{(N)}}{\partial t},$$

the first integral on the right-hand side of (13) vanishes because of the normalization condition

$$\int\mathcal{G}_{1,\dots,N}d(1)\dots d(N)=\text{const.}$$

Using (9) to replace $\tilde{\Omega}_{(N)}$ in the second integral by $\omega_{(l)}$ we find

$$\frac{dS}{dt}=\sum_{l=1}^{N}\frac{dS^{(l)}}{dt}\sim\sum_{l=1}^{N}\int\omega_{1,\dots,l}\frac{\partial\mathcal{G}_{1,\dots,l}}{\partial t}d(1)\dots d(l) \tag{14}$$

and substituting for $\partial\mathcal{G}_{(l)}/\partial t$ from the BBGKY hierarchy we are led after some simple transformations to the balance equation for the global correlational entropy (see Ref. 1)

$$\frac{dS^{(l)}}{dt}=J^{(l-1)}(t)-J^{(l)}(t). \tag{15}$$

Here

$$J^{(l)}(t)=\frac{k_BN\dots(N-l)}{(l-1)!(V\mathcal{P}^3)^{l+1}}\times\int\frac{\partial\Phi_{1,l+1}}{\partial\mathbf{r}_1}\frac{\partial\omega_{1,\dots,l+1}}{\partial\mathbf{p}_1}\mathcal{G}_{1,\dots,l+1}d(1)\dots d(l+1) \tag{16}$$

is the flow of entropy from the group of l particles to the group of $l+1$ particles, averaged over the whole system. It propagates through the hierarchy: from the single-particle to the two-particle correlation, from the two-particle to the three-particle correlation, and so on.

It follows from (11) and (15) that

$$\frac{dS}{dt}=\sum_{l=1}^{N}\frac{dS^{(l)}}{dt}=(J^{(0)}-J^{(1)})+(J^{(1)}-J^{(2)})+\dots+(J^{(N-1)}-J^{(N)})=J^{(0)}-J^{(N)}. \tag{17}$$

However, $J^{(0)}=0$ holds since we have under the integral sign

$$\frac{\partial\omega_1}{\partial\mathbf{p}_1}\mathcal{G}_1=\frac{\partial\mathcal{G}_1}{\partial\mathbf{p}_1}.$$

The quantity $J^{(N)}$ is also zero because it is defined by Eq. (16) in which the correlation $\omega_{1,\dots N+1}$ stands in the position of the $N+1$ st particle, and this vanishes because the system consists of only N particles. As a result (17) reduces to

$$\frac{dS}{dt}=0,\quad S=\sum_{l=1}^{N}S^{(l)}(t)=\text{const.} \tag{18}$$

which is in complete agreement with the requirement of mechanics. However, it does in no way follow from (18) that the correlation entropies $S^{(l)}$ as well as the global entropy of the systems must be constant. In nonequilibrium systems they can change but, of course, in such a way that their sum remains constant. And this clearly does not contradict the Liouville theorem.

4. LOCAL ENTROPY

We define the local entropy using the obvious relations

$$S(t)=\int_V n(\mathbf{r},t)s(\mathbf{r},t)d^3r,$$

$$S^{(l)}(t)=\int_V n(\mathbf{r},t)s^{(l)}(\mathbf{r},t)d^3r,$$

$$s(\mathbf{r},t)=\sum_{l=1}^{N}s^{(l)}(\mathbf{r},t), \tag{19}$$

where in accordance with (12) the local correlation entropy is

$$s^{(l)}(\mathbf{r},t)=-k_B\frac{N(N-1)\dots[N-(l+1)]}{l!(V\mathcal{P}^3)^l}\times\int\omega_{1,\dots,l}\mathcal{G}_{1,\dots,l}d^3p_1d(2)\dots d(l). \tag{20}$$

We find the derivative

$$\frac{\partial(ns^{(l)})}{\partial t}\sim\int_{-\infty}^{+\infty}\frac{d^3p_1}{\mathcal{P}^3}\int\left[\frac{\partial\omega_{1,\dots,l}}{\partial t}\mathcal{G}_{1,\dots,l}+\omega_{1,\dots,l}\frac{\partial\mathcal{G}_{1,\dots,l}}{\partial t}\right]d(2)\dots d(l). \tag{21}$$

We can use Eqs. (7) of the BBGKY hierarchy to transform the expression within the square brackets appears in the integrand. It then follows from those for $l=1$ that

$$\frac{\partial\mathcal{G}_1}{\partial t}=-\frac{\mathbf{p}_1}{m}\frac{\partial\mathcal{G}_1}{\partial\mathbf{r}_1}+n_0\int\frac{\partial\Phi_{12}}{\partial\mathbf{r}_1}\frac{\partial\mathcal{G}_{12}}{\partial\mathbf{p}_1}d^3r_2\frac{d\mathbf{p}_2}{\mathcal{P}^3},$$

$$\frac{\partial\omega_1}{\partial t}=-\frac{\mathbf{p}_1}{m}\frac{\partial\omega_1}{\partial\mathbf{r}_1}+\frac{1}{\mathcal{G}_1}n_0\int\frac{\partial\Phi_{12}}{\partial\mathbf{r}_1}\frac{\partial\mathcal{G}_{12}}{\partial\mathbf{p}_1}d^3r_2\frac{d\mathbf{p}_2}{\mathcal{P}^3}. \tag{22}$$

Multiplying the first of these equations by ω_1 and the second one by $\mathcal{G}_1$, adding the two expressions thus obtained, and integrating them over $\mathbf{p}_1$ we get

$$n\frac{ds_1^{(1)}}{dt}=-\frac{\partial\mathbf{J}_1^{(s^{(1)})}}{\partial\mathbf{r}_1}-k_Bn_0^2\int_V\frac{\partial\Phi_{12}}{\partial\mathbf{r}_1}d^3r_2\int_{-\infty}^{+\infty}\omega_1\frac{\partial\mathcal{G}_{12}}{\partial\mathbf{p}_1}\frac{d\mathbf{p}_1d\mathbf{p}_2}{\mathcal{P}^6}, \tag{23}$$

where the total time derivative is

$$n\frac{ds^{(1)}}{dt}\equiv n\left(\frac{\partial s^{(1)}}{\partial t}+\mathbf{c}\frac{\partial s^{(1)}}{\partial\mathbf{r}}\right)=\frac{\partial(ns^{(1)})}{\partial t}+\frac{\partial(ns^{(1)}\mathbf{c})}{\partial\mathbf{r}} \tag{24}$$

(in writing down the last Eq. (24) we have used the continuity equation) and the single-particle entropy flux is

$$\mathbf{J}^{(s^{(1)})}(\mathbf{r}_1,t)=-k_Bn_0\int_{-\infty}^{+\infty}\frac{\mathbf{p}_1}{m}\omega_1\mathscr{G}_1\frac{d\mathbf{p}_1}{\mathscr{P}^3},\quad \hat{\mathbf{p}}_1=\mathbf{p}_1-m\mathbf{c}. \tag{25}$$

We transform the interior integral on the right-hand side of (23) as follows:

$$\begin{aligned}\int_{-\infty}^{+\infty}\omega_1\frac{\partial\mathscr{G}_{12}}{\partial\mathbf{p}_1}\frac{d\mathbf{p}_1}{\mathscr{P}^3}&=\int_{-\infty}^{+\infty}\left\{\frac{\partial(\omega_1\mathscr{G}_{12})}{\partial\mathbf{p}_1}-\frac{\partial\omega_1}{\partial\mathbf{p}_1}\mathscr{G}_{12}\right\}\frac{d\mathbf{p}_1}{\mathscr{P}^3}\\&=-\int_{-\infty}^{+\infty}\frac{\partial}{\partial\mathbf{p}_1}[(\omega_1+\omega_2+\omega_{12})\\&\quad-\omega_{12}]\mathscr{G}_{12}\frac{d\mathbf{p}_1}{\mathscr{P}^3}\\&=\int_{-\infty}^{+\infty}\frac{\partial\omega_{12}}{\partial\mathbf{p}_1}\mathscr{G}_{12}\frac{d\mathbf{p}_1}{\mathscr{P}^3}\end{aligned}$$

(bear in mind that thanks to the condition $\mathscr{G}_{12}|_{p=\pm\infty}=0$ we have

$$\int_{-\infty}^{+\infty}\frac{\partial(\tilde{\Omega}_{12}\mathscr{G}_{12})}{\partial\mathbf{p}_1}d\mathbf{p}_1=0$$

and by definition $\tilde{\Omega}_{12}=(\omega_1+\omega_2+\omega_{12})$. Putting

$$w^{(1)}(\mathbf{r}_1,t)=-k_Bn_0^2\int_V\frac{\partial\Phi_{12}}{\partial\mathbf{r}_1}d\mathbf{r}_2\int_{-\infty}^{+\infty}\frac{\partial\omega_{12}}{\partial\mathbf{p}_1}\mathscr{G}_{12}\frac{d\mathbf{p}_1d\mathbf{p}_2}{\mathscr{P}^6}, \tag{26}$$

we can write down the conservation equation for the local single-particle entropy in the form

$$n\frac{ds^{(1)}}{dt}=-\frac{\partial\mathbf{J}^{(s^{(1)})}}{\partial\mathbf{r}}+w^{(1)}. \tag{27}$$

Using the second equation of the BBGKY hierarchy we similarly get for the local two-particle correlational entropy (see Appendix)

$$n\frac{ds^{(2)}}{dt}=-\frac{\partial\mathbf{J}^{(s^{(2)})}}{\partial\mathbf{r}}+w^{(2)}, \tag{28}$$

where the flux of the two-particle entropy is

$$\mathbf{J}^{(s^{(2)})}(\mathbf{r}_{1,t})=-\frac{1}{2}k_Bn_0^2\int_{-\infty}^{+\infty}\frac{\mathbf{p}_1}{m}\omega_{12}\mathscr{G}_{12}\frac{d\mathbf{p}_1}{\mathscr{P}^3}\frac{d(2)}{\mathscr{P}^3}, \tag{29}$$

and the power of its source is

$$\begin{aligned}w^{(2)}(\mathbf{r}_1,t)=-\frac{1}{2}k_Bn_0^3\int\Bigg[&\frac{\partial\Phi_{13}}{\partial\mathbf{r}_1}\frac{\partial\omega_{12}}{\partial\mathbf{p}_1}\\&\times(1-e^{\omega_{23}+\omega_{123}})e^{\omega_{13}}+\frac{\partial\Phi_{23}}{\partial\mathbf{r}_2}\frac{\partial\omega_{12}}{\partial\mathbf{p}_2}\\&\times(1-e^{\omega_{13}+\omega_{123}})e^{\omega_{23}}\Bigg]\mathscr{G}_3\mathscr{G}_{12}\frac{d\mathbf{p}_1}{\mathscr{P}^3}\frac{d(2)d(3)}{\mathscr{P}^6}.\end{aligned} \tag{30}$$

Extending this operation we are led to the conservation law for the l-particle entropy

$$n\frac{ds^{(l)}}{dt}=-\frac{\partial\mathbf{J}^{(s^{(l)})}}{\partial\mathbf{r}}+w^{(l)}. \tag{31}$$

Summing these expressions we get a formula for the local conservation law of the total entropy:

$$n\frac{ds}{dt}-\frac{d\mathbf{J}^{(s)}}{d\mathbf{r}}+w, \tag{32}$$

in which we clearly have

$$\mathbf{J}^{(s)}=\sum_{l=1}^{N}\mathbf{J}^{s^{(l)(s)}},\quad w=\sum_{l=1}^{N}w^{(l)}. \tag{33}$$

Equation (32) differs from the analogous conservation equation of, say, the internal energy (see footnote 1)

$$n\frac{de^{(\text{int})}}{dt}=-\frac{\partial\mathbf{J}^{(e^{(\text{int})})}}{\partial\mathbf{r}} \tag{34}$$

because it contains not only the flux term $\partial\mathbf{J}/\partial\mathbf{r}$ describing the redistribution of entropy in space but also the entropy source w characterizing the intensity of the local entropy production.

5. THERMODYNAMIC LIMIT

It follows from the definition (19) of the local entropy that it includes all l-particle entropies $s^{(l)}$ starting with number $l=1$ and ending with $l=N$. However, the correlation with number N is determined by the simultaneous contribution of all $N\simeq10^{23}$ particles of the system and hence it is not at all local. One can only remove this contradiction by assuming that only those $\mathscr{L}\simeq10^3$ particles which form the correlation sphere[2] with its center in a given point $\mathbf{r}_1$ make a real contribution to the sum $s=\sum_{l=1}^{N}s^{(l)}$, while the remaining $N-\mathscr{L}$ particles in the system essentially do not interact with particle 1 at the point $\mathbf{r}_1$, so that their contribution to any local quantity must be put equal to zero. The absence of particle correlations of order $l>\mathscr{L}$ means that for them we have

$$w_{(l)}=0\quad\text{when}\quad l>\mathscr{L}. \tag{35}$$

And since we have

$$s^{(l)}\sim\int\omega_{1,\ldots,l}\mathscr{G}_{1,\ldots,l}d(1)\ldots d(l)$$

[see (20)] it follows from (35) that

$$s^{(l)}=0,\quad\mathbf{J}^{(s^{(l)})}=0,\quad w^{(l)}=0\quad\text{when}\quad l>\mathscr{L}. \tag{36}$$

We can use (24) to write Eq. (31) for the l-particle local entropy in the form

$$\frac{\partial(ns^{(l)})}{\partial t}=-\frac{\partial(ns^{(l)}\mathbf{c}+\mathbf{J}^{(s^{(l)})})}{\partial\mathbf{r}}+w^{(l)}. \tag{37}$$

If we now integrate (37) over the volume V of the whole system the term with the divergence of the total entropy flux $\mathbf{J}^{(l)}=ns^{(l)}\mathbf{c}+\mathbf{J}^{(s^{(l)})}$ vanishes and we get

$$\frac{\partial S^{(l)}}{\partial t}=J^{(l-1)}-J^{(l)}=\int_V w^{(l)}(\mathbf{r},t)d^3r \tag{38}$$

Since we have $w^{(l)}=0$ for $l>\mathscr{L}$, the integral on the right-hand side of (38) will also vanish for the leading correlations. Hence, for them we have for the increase in the entropy satisfies $\partial S^{(l)}/\partial t=0$ and

$$S^{(l)}(t)=\text{const.}\quad \text{when}\quad l>\mathscr{L} \tag{39}$$

As a result of this the flux $J^{(l)}$ of the global entropy is no longer dependent on the number l since $J^{(l-1)}-J^{(l)}=0$ and

$$J=J^{(l-1)}=J^{(l)}\quad \text{when}\quad l>\mathscr{L}. \tag{40}$$

However, the condition $J^{(l-1)}-J^{(l)}=0$ can certainly not hold for $l=N$ since, on the one hand,[3] we have $J^{(N-1)}=J\neq 0$ and, on the other hand, we have $J^{(N)}=0$ because there is no thermal potential $\omega_{(l)}$ with number $l=N+1$ [see (16)]. The increase of the latter, the N-particle entropy, must therefore be nonvanishing:

$$\frac{\partial S^{(N)}}{\partial t}=J\neq 0. \tag{41}$$

In order to understand better the physical meaning of this statement we recall that the total global entropy of the system is

$$S=\sum_{l=1}^{N-1} S^{(l)}+S^{(N)}=\text{const.}.$$

Therefore we have

$$\frac{\partial S^{(N)}}{\partial t}=-\frac{\partial(\Sigma_{l=1}^{N-1}S^{(l)})}{\partial t}\approx-\frac{\partial(\Sigma_{i=1}^{\mathscr{L}}S^{(l)})}{\partial t}. \tag{42}$$

The N-particle correlation thus absorbs the whole entropy created for small correlations with $l<\mathscr{L}$. The source of the entropy (i.e., the correlations with small l) then is seen to be transferred from the sink (represented by the N-particle correlation) over a huge distance since $\mathscr{L}\lesssim 10^3$ and $N\simeq 10^{23}$. All intermediate correlations with orders satisfying $\mathscr{L}<l<N$ play the role of entropy conductors transferring it without loss from the source to the sink.

The entropy source and sink are different in nature: the power of the source is determined by local processes taking place in the system and the power of the sink by its global reactions. It is natural to assume that thermodynamics deals only with local effects. In this way we can remove the contradiction between the fact that the statistical entropy is constant, whereas the thermodynamic entropy increases. However, one can resort to a purely formal point of view.

The BBGKY hierarchy (like, by the way, the whole of statistical mechanics) is valid only in the thermodynamic limit (see Ref. 1)

$$N,V\rightarrow\infty,\quad n_0=\frac{N}{V}=\text{const.}. \tag{43}$$

In that limit the sink of the global entropy goes to infinity and vanishes. At the same time the global entropy itself increases without bound:

$$S=\int_V n(\mathbf{r},t)s(\mathbf{r},t)d^3r=\tilde{s}\int_V n(\mathbf{r},t)d^3r=N\tilde{s}\rightarrow\infty \tag{44}$$

and thereby loses its physical meaning (we used here in the transformations the theorem about averages). The local entropy therefore becomes the only entropic characteristic of the system. However, whereas the global entropy characterized the state of a closed isolated system, for which the Liouville theorem holds, the local entropy characterizes the state of an open system (the number of particles forming the correlation sphere is not fixed). However, for an open system the phase volume conservation law does not hold. Thus, the transition to the thermodynamic limit automatically removes the contradiction between mechanics and thermodynamics. However, in this treatment we are also led to the conclusion that only the local entropy has a physical meaning.

It is clear that taking the thermodynamic limit assumes replacing the sums which defined $s,\mathbf{J}^{(s)}$, and w by the series

$$s=\sum_{l=1}^{\infty} s^{(l)},\quad \mathbf{J}^{(s)}=\sum_{l=1}^{\infty}\mathbf{J}^{(s^{(l)})},\quad w=\sum_{l=1}^{\infty} w^{(l)}. \tag{45}$$

These series must necessarily converge; otherwise the whole theory loses its meaning. And if the series converge the conditions (35) and (36) which we postulated earlier on physical grounds are automatically satisfied.

In the thermodynamic limit Eq. (20) for the l-particle entropy takes the form

$$s^{(l)}(\mathbf{r},t)=-k_B\frac{n_0^l}{\mathscr{P}^{3l}}\int w_{1,\ldots,l}\mathscr{G}_{1,\ldots,l}d\mathbf{p}_1 d(2)\ldots d(l). \tag{46}$$

The integrals are here taken over the infinite volume V and over the momenta from $|\mathbf{p}|=-\infty$ to $|\mathbf{p}|=+\infty$. Since we have $d(k)=d^3r_kd^3p_k\sim r^2drp^2dp$, it is necessary that, in order that the local entropy have a finite value, all $\omega_{(l)}$ satisfy the inequalities

$$\frac{\text{const.}}{r_{12}^{\mu}\cdots r_{l-1,l}^{\mu}p_1^{\nu}\cdots p_l^{\nu}}>\omega_{1,\ldots,l}\quad \text{when}\quad r_{ij}\rightarrow\infty,\quad |\mathbf{p}_i|\rightarrow\pm\infty, \tag{47}$$

where $\mu,\nu>3$. The thermodynamic potentials

$$\Omega_{1,\ldots,l}=\sum_{i,j}\omega_{ij}+\sum_{ijk}\omega_{ijk}+\ldots+\omega_{1,\ldots,l} \tag{48}$$

must also satisfy the same inequalities; in Ref. 2 we assumed that these potentials are short-ranged. The inequalities (47) confirm this assumption.

The BBGKY hierarchy thus becomes free of internal contradictions only in the thermodynamic limit. And in this limit it determines the local entropy, the magnitude of which can change not only because it flows from neighboring regions but also due to internal processes leading to its generation. We also emphasize once again that now there is no contradiction whatever with the Liouville theorem.

6. INCREASE OF THE ENTROPY

We must still prove that in accordance with the second law of thermodynamics the entropy determined by the formulas obtained above necessarily increases. Since the increase in the global entropy is

$$\delta S \sim \int w(\mathbf{r},t)d^3r, \tag{49}$$

it is sufficient for a proof of the inequality $\delta S \geqslant 0$ that the condition

$$w(\mathbf{r},t) \geqslant 0 \tag{50}$$

is satisfied [we understand here by the global entropy the entropy produced by the correlations with low orders, $S = \Sigma_{l=1}^{\mathscr{S}} S^{(l)}(t)$]. The most direct way to check that $w \geqslant 0$ holds consists in evaluating it using Eqs. (26), (30), and so on. However, this requires developing methods for solving the BBGKY hierarchy, which up to now has not been done. We are therefore forced to restrict ourselves to qualitative discussions.

It follows from the definition (2) of the global entropy that it is always positive and that it vanishes only at the absolute zero of the temperature, $\theta = 0$, because there $\Gamma = \Gamma_{\min}$. For sufficiently low temperatures the entropy must therefore increase: the path in the opposite direction is forbidden for it. Correspondingly, at low temperatures w must be positive. We start now to increase the temperature and thereby change the quantity w. There are then two possibilities: either with increasing temperature w will as before remain positive (and, hence, as before the entropy will increase), or when reaching some value $\theta = \theta'$ the function w will become zero and after that change its sign. However, the vanishing of w means that at the temperature θ' the increase δS in the entropy will be equal to zero independent of the processes taking place in the system. This contradicts the first law of thermodynamics (3), according to which the quantity δS must be nonvanishing in any quasistatic process, provided this process is accompanied by a change in E or V. We now recall that Eq. (3) can be obtained from the Gibbs distribution and this distribution itself is a consequence of the BBGKY hierarchy (see Ref. 1). It is thus impossible for w to become equal to zero, since that would mean that there is an internal contradiction in the BBGKY hierarchy.

7. DISCUSSION

We briefly summarize the results obtained above. Working with the BBGKY hierarchy and using a definition of the entropy given by Gibbs we have shown that, on the one hand, it follows from these assumptions that the global entropy of the system is constant, $S(t) = \text{const}$, and, on the other hand, that they define a local entropy $s(\mathbf{r},t)$ such that its change is described by the balance equation (32), which contains not only a flux term, $\partial \mathbf{J}^{(s)}/\partial \mathbf{r}$, characterizing the rate at which the entropy is redistributed over the volume of the system, but also an entropy source $w(\mathbf{r},t)$ which determines the rate at which it is produced at a given point $\mathbf{r}$ of the system at a given time t. Simple physical considerations then show that the function w most likely must be positive and, hence, classical mechanics shows that the entropy increases, but only the local and not the global entropy.

Equation (18) showing that the global entropy is constant and Eq. (32) for the local entropy were obtained for a finite-size system. If one then takes the thermodynamic limit (43)—and this step is necessary since the BBGKY hierarchy itself is valid only in the thermodynamic limit—the global entropy $S \propto N$ tends to infinity and loses its physical meaning. After this the only entropic characteristic of the system becomes the local entropy $s(\mathbf{r},t)$ which, clearly, must be identified with the thermodynamic entropy.

It would appear that the divergence of the global entropy in the thermodynamic limit implies the failure of Gibbs's theory. However, this is in fact not the case. One must introduce the concept of a local entropy $s = S/N$ only before taking the limit and afterwards let N and V tend to infinity. Of course, after that the global energy vanishes, but the local entropy retains its value. And it is important that from this follows as before the same formulation of the first law of thermodynamics as from Gibbs's global definition. Gibbs's formula, like the balance equation (32), therefore in fact determines the local entropy. In this respect there is no difference whatever between the equilibrium and the nonequilibrium theory; both are dealing only with the local entropy.

We have seen that the local entropy can increase. This dose not contradict Liouville's theorem at all, since the latter is valid only in the case of closed isolated systems. On the other hand, the local entropy characterizes the state of a physically infinitesimal volume of matter which can exchange particles, momentum, and energy with the surrounding medium. For such systems Liouville's theorem does not hold.

And, finally, a last remark. The balance equation (32) we have obtained for the local entropy has been well known for a long time in the thermodynamics of nonequilibrium systems (see Ref. 4). However, in that case it was simply postulated, whereas we have obtained it from first principles which made it possible better to elucidate its physical meaning.

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APPENDIX

Here we derive Eqs. (28)–(30). According to (21) the increase in the two-particle local entropy is equal to

$$\frac{\partial ns^{(2)}}{\partial t}=-\frac{1}{2}k_Bn_0^2\int_{-\infty}^{+\infty}\frac{d^3p_1}{\mathscr{P}^3}\int\left(\frac{\partial\omega_{12}}{\partial t}\mathscr{G}_{12}+\omega_{12}\frac{\partial\mathscr{G}_{12}}{\partial t}\right)\frac{d(2)}{\mathscr{P}^3}. \tag{A1}$$

To find the derivatives which here occur under the integral sign we use the second equation from the BBGKY hierarchy (7):

$$\frac{\partial\mathscr{G}_{12}}{\partial t}=-\left(\frac{p_{1\alpha}}{m}\frac{\partial\mathscr{G}_{12}}{\partial r_{1\alpha}}+\frac{p_{2\alpha}}{m}\frac{\partial\mathscr{G}_{12}}{\partial r_{2\alpha}}\right)+\left(\frac{\partial\Phi_{12}}{\partial r_{1\alpha}}\frac{\partial\mathscr{G}_{12}}{\partial p_{1\alpha}}+\frac{\partial\Phi_{12}}{\partial r_{2\alpha}}\frac{\partial\mathscr{G}_{12}}{\partial p_{2\alpha}}\right)+n_0\int\left(\frac{\partial\Phi_{13}}{\partial r_{1\alpha}}\frac{\partial\mathscr{G}_{123}}{\partial p_{1\alpha}}+\frac{\partial\Phi_{23}}{\partial p_{2\alpha}}\frac{\partial\mathscr{G}_{123}}{\partial p_{2\alpha}}\right)\frac{d(3)}{\mathscr{P}^3}. \tag{A2}$$

We now divide (A2) by $\mathscr{G}_{12}=\exp(\omega_1+\omega_2+\omega_{12})$ and afterwards subtract from the expression obtained in that way the equations for $\partial\omega_1/\partial t$ and $\partial\omega_2/\partial t$ [see (22)]. As a result we get an equation for

$$\frac{\partial\omega_{12}}{\partial t}=-\left(\frac{p_{1\alpha}}{m}\frac{\partial\omega_{12}}{\partial r_{1\alpha}}+\frac{p_{2\alpha}}{m}\frac{\partial\omega_{12}}{\partial r_{2\alpha}}\right)+\left(\frac{\partial\Phi_{12}}{\partial r_{1\alpha}}\frac{\partial(\omega_1+\omega_{12})}{\partial p_{1\alpha}}+\frac{\partial\Phi_{12}}{\partial r_{2\alpha}}\frac{\partial(\omega_1+\omega_{12})}{\partial p_{2\alpha}}\right)+\frac{1}{\mathscr{G}_{12}}n_0\int\left(\frac{\partial\Phi_{13}}{\partial r_{1\alpha}}\frac{\partial\mathscr{G}_{123}}{\partial p_{1\alpha}}+\frac{\partial\Phi_{23}}{\partial r_{2\alpha}}\frac{\partial\mathscr{G}_{123}}{\partial p_{2\alpha}}\right)\frac{d(3)}{\mathscr{P}^3}-\frac{1}{\mathscr{G}_1}n_0\int\frac{\partial\Phi_{13}}{\partial r_{1\alpha}}\frac{\partial\mathscr{G}_{13}}{\partial p_{1\alpha}}\frac{d(3)}{\mathscr{P}^3}-\frac{1}{\mathscr{G}_2}n_0\int\frac{\partial\Phi_{23}}{\partial r_{2\alpha}}\frac{\partial\mathscr{G}_{23}}{\partial p_{2\alpha}}\frac{d(3)}{\mathscr{P}^3}. \tag{A3}$$

We then multiply (A2) by ω_{12} and (A3) by $\mathscr{G}_{12}$, integrate the expressions thus obtained over $d^3p_1d(2)$, and after that add them. This gives

$$\frac{\partial(ns^{(2)})}{\partial t}=-\frac{\partial}{\partial r_{1\alpha}}(ns^{(2)}c_\alpha+\mathscr{J}_{1\alpha}^{(s^{(2)})})+\frac{1}{2}k_Bn_0^3\int\left(\frac{\partial\Phi_{13}}{\partial r_{1\alpha}}\frac{\partial\omega_{12}}{\partial p_{1\alpha}}\mathscr{G}_{123}+\frac{\partial\Phi_{23}}{\partial r_{2\alpha}}\frac{\partial\omega_{12}}{\partial p_{2\alpha}}\mathscr{G}_{123}+\frac{\partial\Phi_{13}}{\partial r_{1\alpha}}\frac{\partial\mathscr{G}_{13}}{\partial p_{1\alpha}}\frac{\mathscr{G}_{12}}{\mathscr{G}_1}+\frac{\partial\Phi_{23}}{\partial r_{2\alpha}}\frac{\partial\mathscr{G}_{23}}{\partial p_{2\alpha}}\frac{\mathscr{G}_{12}}{\mathscr{G}_2}\right)\frac{d^3p_1}{\mathscr{P}^3}\frac{d(2)d(3)}{\mathscr{P}^6}, \tag{A4}$$

where the flux of the two-particle entropy is given by (29). Since

$$\frac{\mathscr{G}_{12}}{\mathscr{G}_1}=\exp(\omega_2+\omega_{12}),\quad \frac{\mathscr{G}_{12}}{\mathscr{G}_2}=\exp(\omega_1+\omega_{12}),$$

after integrating by parts the third integral on the right-hand side of (A4) takes the form

$$\int_{-\infty}^{+\infty}\frac{\partial\mathscr{G}_{13}}{\partial p_{1\alpha}}\frac{\mathscr{G}_{12}}{\mathscr{G}_1}d^3p_1=\int_{-\infty}^{+\infty}\left\{\frac{\partial}{\partial p_{1\alpha}}\left(\frac{\mathscr{G}_{12}\mathscr{G}_{13}}{\mathscr{G}_1}\right)-\mathscr{G}_{13}\mathscr{G}_2\frac{\partial(e^{\omega_{12}})}{\partial p_{1\alpha}}\right\}d^3p_1=\int_{-\infty}^{+\infty}\frac{\mathscr{G}_{13}\mathscr{G}_{12}}{\mathscr{G}_1}\frac{\partial\omega_{12}}{\partial p_{1\alpha}}d^3p_1=-\int_{-\infty}^{+\infty}\frac{\partial\omega_{12}}{\partial p_{1\alpha}}e^{(\omega_1+\omega_2+\omega_3+\omega_{12}+\omega_{13})}d^3p_1. \tag{A5}$$

Similarly we get for the fourth integral

$$\int_{-\infty}^{+\infty}\frac{\partial\mathscr{G}_{23}}{\partial p_{2\alpha}}\frac{\mathscr{G}_{12}}{\mathscr{G}}d^3p_2=-\int_{-\infty}^{+\infty}\frac{\partial\omega_{12}}{\partial p_{2\alpha}}\times e^{(\omega_1+\omega_2+\omega_3+\omega_{12}+\omega_{23})}d^3p_2. \tag{A6}$$

Substituting these expressions into (A4) we get Eq. (29) in which $w^{(2)}$ is given by Eq. (30).

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(1) See also G. A. Martynov, *Theory of Nonequilibrium Effects, Based on the BBGKY Hierarchy,* submitted for publication to Teor. Mat. Fiz.

(2) Data from Monte-Carlo calculations and molecular dynamics indicate a number of this order in the case of liquids. Theoretical estimates lead to the same values of $\mathscr{S}$ in the case of liquids (see Ref. 1); for gases we find $\mathscr{S}\rightarrow 0$ for a density for which $n\rightarrow 0$.

(3) An exception is the state of thermodynamic equilibrium for which all $J^{(l)}$ vanish (see Ref. 2). However, we are just now not interested in equilibrium states.

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