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Nonequilibrium statistical mechanics, transport equations, and the second law of thermodynamics

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Contents

Abstract. A first-principle statistical theory of nonequilibrium processes is attempted based on the assumption of quasiclassical particle motions. This assumption leads to the BBGKY hierarchy which, in addition to physically reasonable solutions, contains solutions contradicting the causality principle. In order to eliminate them, all the distribution functions involved must be expanded as series in the small parameter $\varepsilon = \sigma/L$, where σ is the particle diameter and L is a characteristic macroscopic length. To zeroth order in ε, the BBGKY hierarchy yields the Gibbs distribution, the first law of thermodynamics, and the equations of the theory of liquids, thus enabling the thermodynamical parameters of a substance to be calculated. To the first order, one obtains (a) a system of five transport equations for five hydrodynamic variables (mass, three velocity components, and temperature), (b) a set of equations for the first-principles calculation of transport coefficients, and (c) the second law of thermodynamics. The possibility of an entropy increase without Liouville's theorem being violated is demonstrated.

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1. Introduction

Undoubtedly, statistical mechanics belongs to fundamental sciences. And all fundamental physical theories are constructed according to one and the same scheme: first the initial equations of the theory are postulated on the basis of analysis of a few typical experiments, and then these equa-

tions fall into the hands of mathematicians or theoretical physicists who seek their solutions. In statistical mechanics, however, the situation is different: the Newtonian equations which form its basis can be written out in the first pages of any textbook — in fact, in the very first paragraph on the first page. But nobody knows what next is to be done. The fact is that the set involves about 10^{23} equations (according to the number of atoms and molecules in macroscopic bodies), and mathematicians are not able to tackle such sets. Because of this, statistical mechanics from its start in mid-nineteenth century faced — and is still facing — a major problem: how to convert a virtually infinite set of equations of classical mechanics into something that could be used for solving practical tasks. What is more, this has to be done without any additional postulates or simplifying hypotheses, since a fundamental theory must only derive from first principles — any simplifying assumption immediately makes the theory approximate rather than fundamental.

So far the problem of construction of statistical mechanics has always been solved by trial and error: an approximation was suggested, its results checked, and only then the linkage established with equations of motion of classical mechanics. An example is the theory of equilibrium phenomena. It was formulated by Gibbs as early as 1902 on the basis of brilliant insight, while its linkage with the Bogolyubov – Born – Green – Kirkwood – Yvon (BBGKY) hierarchy was only proved seventy years later by Suchov and Gurevich [1].

If we now turn to the theory of nonequilibrium processes, we find that there are numerous approaches and approximations, ranging from purely macroscopic ones based on solving the transport equations or equations of nonequilibrium thermodynamics to profoundly 'microscopic' theories like the kinetic theory of gases, theory of linear response, method of autocorrelation functions, method of projection operators, etc. In a sense, this diversity of approaches reflects the diversity of nonequilibrium processes themselves. At the same time, it is also a consequence of the fact that the most plausible theories among the nonequilibrium ones have not yet been selected. In other words, we are not able to argue that 'in this particular case this approach is the most rigorous because it follows from the initial Newtonian equations expanded in such-and-such small parameter'.

As I mentioned, the Newtonian equations in statistical mechanics form an infinite set. The number of mathematical manipulations that can be applied to such set is also infinitely large. Keeping within the framework of pure mathematics, one can easily get lost. To find one's bearings, one needs a clear-cut guiding principle. Such principle can only be derived from comprehensive analysis of the *physical* foundations of the theory. It is this analysis that the present paper is devoted to.

I am going to present the material in the following manner: Fig. 1 shows the scheme of construction of statistical mechanics as I see it. We shall discuss this scheme moving from one box to another, from top to bottom. Whenever possible, our discussion will proceed without formulas, on fingertips, since it is sometimes hard to trace the physical essence of things behind the algebraic thicket. The first sections are written in an especially simple manner — so simple in fact as to seem out of place in a respectable physical journal. I would ask the reader, however, not to jump at the conclusions. As a matter of fact, it is in these sections that the most profound problem of the theory are discussed. Had everything been so obvious as it might seem at first sight, the problem of reversibility would not have given rise to so many heated arguments, and no-one would attempt to attack frontally the Liouville equation, shoving aside the BBGKY hierarchy. Rather than that, the BBGKY hierarchy would

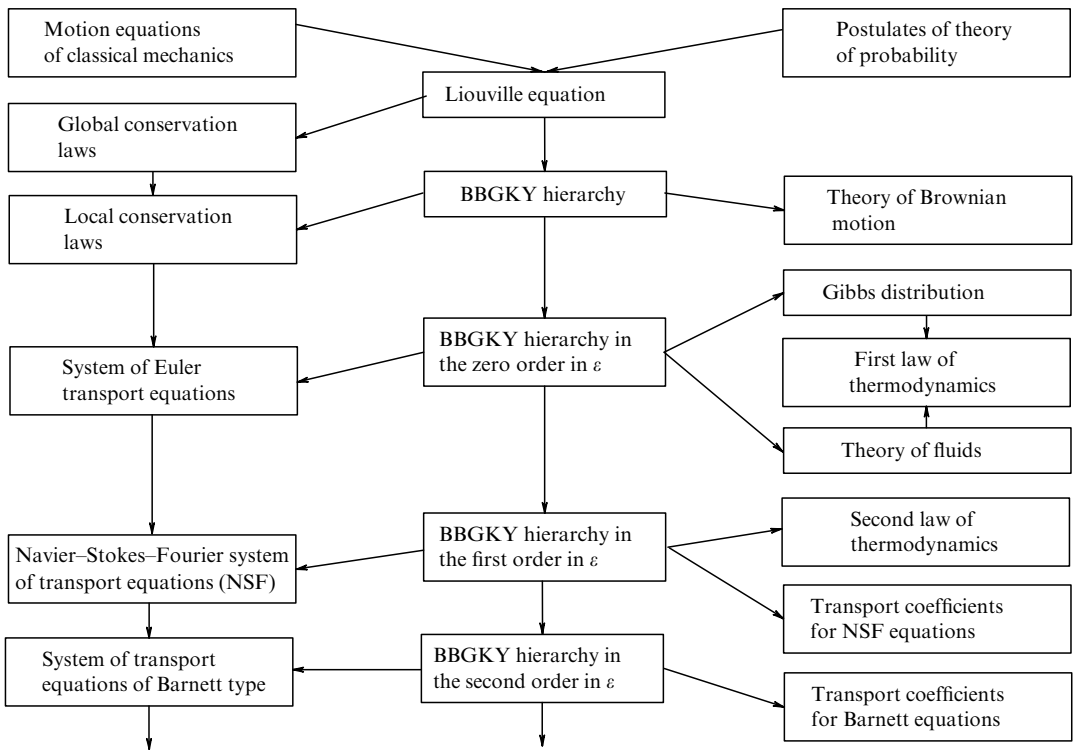

Figure 1. The scheme of construction of statistical mechanics.

have long won the honourable title of 'fundamental equations of statistical mechanics' (sadly, today this hierarchy is almost forgotten by all). Moreover, I would ask the reader to pay special attention to the first sections of the paper, since the principles set forth in these sections are in fact the only lodestar which highlights the general direction of development of the theory.

So, the main purpose of this paper is the analysis of the general structure of statistical mechanics on the basis of simple physical reasoning and initial theoretical assumptions. Of course, it would be impossible to avoid considering its mathematical methods altogether. However, this will be reduced to a minimum required for understanding the essence of the theory. The interested reader will find detailed calculations and proofs in my monograph *Classical Statistical Mechanics* **[2].**

2. Equations of motion and probability

As seen from the scheme in Fig. 1, statistical mechanics is based on the equations of motion of classical mechanics (Newtonian equations), and on the postulates of theory of probability. It is sometimes argued that the symbiosis of these seemingly so different theories is only necessary because there are too many particles: had they been fewer, we could have solved the corresponding set of equations, compute the paths of all particles, and calculate all the parameters of interest exactly (the currently popular method of molecular dynamics is based on this philosophy). To find out whether this is actually the case, we begin our tour of the scheme in Fig. 1 with the analysis of such well-known concepts as probability and Newtonian equations.

2.1 Stable and unstable systems

We start with the simplest physical experiment. Imagine a display on which a digit lights up at $t = 0$, followed by a second digit a minute later, and so on. For simplicity we assume that there are just two digits, zero and one. Now the question is which digit is going to appear on the display at t_k, $k > 0$. Since, by assumption, the law which governs the generation of numbers is not known, this question cannot be answered *a priori*. We can wait, however, until there are many enough (say, $\mathcal{N}$) digits on the display, and then analyse the sequence. If we find any kind of regularity in the sequence of digits (for instance, 010101...), we can with some confidence predict that at $t = t_k$ the digit that appears on the screen will be one (or zero). One must bear in mind, however, that this confidence is based on the assumption that the law according to which the numbers are generated remains unchanged up to the time t_k, $k > \mathcal{N}$. Obviously, the longer the sequence of digits (the larger the accumulated experience), the stronger the confidence, and at $\mathcal{N} = \infty$ the confidence will become certainty. Systems which permit predicting the future by analysing the past under assumption that the experimental conditions remain unchanged are referred to as ordered systems, and their behaviour is called deterministic (that is, predictable).

Now what if we cannot find any regularity, or if it does not exist at all? In this case we shall not be able to predict which digit will light up on the display at t_k. Nevertheless, we can always count how many zeros and ones are among those digits which have already appeared on the screen. Then, if we are sure that the rules of the game are not going to change, we may assume that there will be approximately the same number of zeros and, respectively, ones in the next sequence on $\mathcal{N}$ digits. In other words, we may hope that the probability of occurrence of zero $\mathcal{P} = v/\mathcal{N}$ remains the same (here v is the number of zeros in the series of $\mathcal{N}$ digits). Systems for which the accumulated experience does not allow making unambiguous predictions for the future are called chaotic, and the process of realisation of unpredictable events is referred to as a random process.

Among other distinctions, there is one important difference between deterministic and chaotic systems: while in the former the present instant is not distinguished in any way, in the latter there is a clear-cut distinction between the past and the future. Indeed, the regularity established in deterministic systems works in the past, present and future. In those systems where chaos reigns, however, the future can never be predicted for sure. Therefore, for the future we always have $\mathcal{P} < 1$. The present and the past are always certain: Napoleon was born on August 15, 1769, and there is no power in the world to change this fact. Accordingly, for the past we always have $\mathcal{P} = 1$. This implies that a reduction in the probability distribution occurs at the time of observation t: the probability changes abruptly from $\mathcal{P} < 1$ to $\mathcal{P} = 1$. Knowing the past, we can reproduce it as accurately as required. This, however, does not take us anywhere: the future in chaotic systems remains as unpredictable as it has been, no matter how often we recollect the memory of the past.

Consider now a system whose behaviour is governed by the Newtonian equation

$$\frac{\mathrm{d}\mathbf{p}}{\mathrm{d}t} = \mathbf{F} \tag{1}$$

where $\mathbf{p} = m\,\mathbf{v}$ is the momentum of the body having mass m and velocity $\mathbf{v} = \mathrm{d}\mathbf{r}/\mathrm{d}t$, $\mathbf{F}$ is the force. Solving the Cauchy problem for Eqn (1) with initial conditions

$$\mathbf{r}(0) = \mathbf{r}_0, \qquad \mathbf{p}(0) = \mathbf{p}_0\,, \tag{2}$$

we can calculate the path of the body

$$\mathbf{r} = \mathbf{r}(t), \qquad \mathbf{p} = \mathbf{p}(t)\,, \tag{3}$$

that is, determine its position and velocity at any time $t > 0$. From the uniqueness theorem, the solution found in this way is unique. Obviously, the movement along the path is predictable, and the system described by Eqn (3) is deterministic. This statement, however, applies not to the system as such, but rather to the mathematical model which we ascribe to this particular body. As a matter of fact, there is one very important distinction between the mathematical model and the real body: the model assumes that the initial condition $\delta\mathbf{X}_0$ is defined with zero error, whereas the accuracy of a physical experiment is always finite. Because of this, the transition to the mathematical model is a certain idealisation which is far from being always justified. If the properties of the system under investigation are such that the smaller the initial inaccuracy $\delta\mathbf{X}_0$, the smaller the deviation of the real path $\mathbf{X}(t) = \{\mathbf{r}(t),\ \mathbf{p}(t)\}$ form the calculated path $\mathbf{X}^*(t)$ — that is, if

$$\delta\mathbf{X}(t) = \mathbf{X}(t) - \mathbf{X}^*(t) \to 0 \quad \text{at} \quad \delta\mathbf{X}_0 \to 0\,, \tag{4}$$

then we can go over to the limit $\delta\mathbf{X}_0 = 0$ and assume that, even though the real body does not precisely follow the calculated path (if only because the condition $\delta\mathbf{X}_0 = 0$ can never be realised in practice), the deviations are small enough to be neglected. An example of such system is a bobsleigh

pilot who steers his sleigh along the bottom of an ice trough. Any deviation from the calculated path laid along the bottom of the trough gives rise to a gravity component which forces the sleigh back, and does this the faster, the steeper the walls of the trough and the greater the deviation (Fig. 2a). Such systems are referred to as stable.

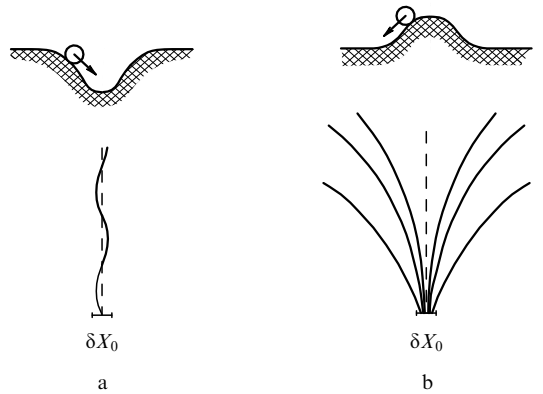

Figure 2. Calculated (dashed lines) and real (solid lines) trajectories of sleigh.

Along with the stable systems, there also are unstable systems for which

$$\delta\mathbf{X}(t) \to \infty \tag{5}$$

for any arbitrarily small but finite $\delta\mathbf{X}_0$.

An example is the same bobsleigh pilot who this time decides to take a ride downhill along the top of an ice ridge, which essentially is the same trough turned inside out (Fig. 2b). In case of a slightest deviation from the calculated path laid along the top of the ridge, the gravity component will force the sleigh astray rather than back. As a result, if at $t = 0$ the sleigh was slightly off the top to the right, it will slide to the right, and the sooner, the greater the initial (uncontrollable) deviation; or to the left if it started a little left from the top. In both cases the deviation from the calculated path $\delta\mathbf{X}(t)$ will increase unlimitedly with the time, according to a law which is impossible to predict. Indeed, let us assume that we have managed to calculate all paths which pass at $t = 0$ across the region of initial inaccuracy $\delta\mathbf{X}_0$ (which actually cannot be done since the number of these paths is infinitely large, and they all fan out to both sides). Even this would not help us to define the position of the sleigh at any $t > 0$, because we do not know which path will be taken by the sleigh (recall that $\delta\mathbf{X}_0$ is the accuracy of our measurements, and we cannot distinguish anything that is less than $\delta\mathbf{X}_0$). This example shows that in the case of unstable systems the calculation of paths becomes meaningless, since we can say nothing about the behaviour of the system in the future even if we know the paths. This does not imply, however, that there is nothing at all that we can say about the behaviour of the system 'bobsleigh pilot on ice ridge'.

If the sportsman has enough patience to do this exercise time and time again, we shall soon find that, say, in 70 cases out of 100 he slides to the right of the ridge, and in 30 cases to the left. This allows us to hope that the result will be approximately the same in the next hundred of rides. In other words, we can determine the probability of the events 'the pilot right of the ridge' and 'the pilot left of the ridge'. Of course, on the basis of this knowledge we cannot tell whether in his, say, 27th ride the pilot will end to the right or to the left of the ridge. This does not mean that in his 27th ride the sleigh ran downhill without any path: the traces it left on the ice prove that this is not the case. Moreover, we can use the traces and the Newtonian equation to calculate the path and the velocity of the downhill ride. This, however, can only be done post factum; we cannot predict the path of the sleigh. In other words, a predictable path (that is, such as can be calculated before carrying out the experiment) has turned into an unpredictable, random one. Simultaneously, the 'time arrow' comes forward: the past (traces on the ice) is certain, the future (the outcome of the next ride downhill) is unpredictable. The distinction between the past and the future makes the unstable systems unpredictable. This seems to conflict with the fact that the Newtonian equation is invariant with respect to the transformation

$$t \to -t', \qquad \mathbf{p} \to -\mathbf{p}' \tag{6}$$

(transformation (6) implies that the process develops like in a movie run backwards: scattered fragments reassemble into a cup which jumps on the table). The equation by itself, however, does not yet define the path: it must be supplemented by the initial conditions. As we have seen, even a slight inaccuracy in defining the latter makes the trajectory of motion unpredictable. The same will occur at the turnpoint (at the time when we implement transformation (6)): because of a small inaccuracy in defining t' and $\mathbf{p}'$ the sleigh may end up anywhere else but at the starting point. In order to get back to the starting point, the sleigh must be placed with absolute precision on the path which brought it to the turnpoint. This, however, is not possible since the path is a line without thickness. This is the reason why the path of the sleigh after the turnpoint is unpredictable future.

Formally, these arguments only apply to unstable systems, and do not apply to stable ones. Actually, however, this is not exactly the case. Recall that absolute stability, which is achieved through transition to the limit $\delta\mathbf{X}_0 = 0$, is a mathematical abstraction; in real experiments the initial inaccuracy is always non-zero. Transition to the ideal model with $\delta\mathbf{X}_0 = 0$ is far from being always worthwhile even in the case of stable systems. If $\delta\mathbf{X}_0$ could actually be made equal to zero, bobsleigh championships would make no sense, with all pilots crossing the finishing line at one and the same time (which follows from the uniqueness theorem). It is the unpredictability of paths followed by real sportsmen that adds the spirit of challenge to a sporting event.

So far we have been considering a macroscopic system 'bobsleigh pilot on the hill' with a purpose in mind: we wanted to make a point that the arising problems are not peculiar to microcosm. In the case of our bobsleigh pilot we can still hope that he will almost precisely follow the calculated path downhill if we position him on the top of the hill with the accuracy of, say, 1 cm (which, of course, is never done in practice). When we deal with microcosm this is hoping against hope. To prove this, let us make a simple estimate.

Assume that two spherical molecules of a gas collide at an angle α, which is known to the accuracy of δ_0. We also assume that before and after collision the particles move by their own momentum, and at the time of collision their paths change according to the law 'the angle of incidence equals the angle of reflection' (both assumptions follow from the laws of classical mechanics). As seen from Fig. 3, after collision the inaccuracy in the definition of the angle increases to $\delta_1 > \delta_0$ because the

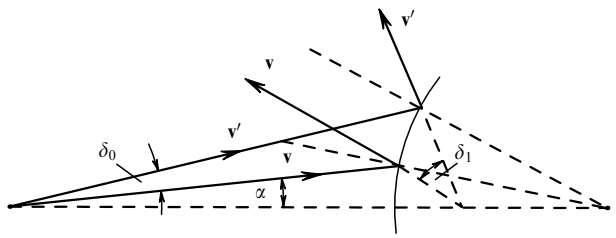

Figure 3. Change of inaccuracy angle δ at collision.

surface of the colliding particles is convex†. Obviously, after k collisions the inaccuracy becomes

$$\delta_k = \delta_0 \left(\frac{\delta_1}{\delta_0}\right)^k > \delta_0 \,.$$

Since $k \approx t/\tau$, where τ is the mean time between two successive collisions of the particles, we have

$$\delta(t) \simeq \delta_0 \left(\frac{\delta_1}{\delta_0}\right)^{t/\tau}$$

or

$$\delta(t) = \delta_0 \exp\left(\alpha \frac{t}{\tau}\right), \quad \text{where} \quad \alpha = \ln\frac{\delta_1}{\delta_0} \simeq 1 \,. \tag{7}$$

Assume now that we would like to monitor the path of one particle for one second. This attempt will only be successful if the error in the definition of the angle is not greater than π, because otherwise we cannot tell whether out particle is flying forward or backwards. Since for a gas under normal conditions we have $\tau \sim 10^{-10}$ s, Eqn (7) implies that the condition $\delta(t) < \pi$ can only be satisfied if we know δ_0 to a fantastic accuracy $\delta_0 = \exp(-10^{10})$, which is far beyond any reasonable limit.

From our example of the bobsleigh pilot it follows that there are two causes of unpredictability of the path of the sleigh: one internal, due to the instability of the system itself, and one external, which results from the lack of tools capable of reducing the initial inaccuracy δX_0 to zero. A chaotic system can be transformed into a stable one by eliminating at least one of these factors. We have already said that any ambiguity in the path of the sleigh can be eliminated by changing the profile of the hill. Observe that the same result can be achieved by reducing δX_0 to zero, since the value of $\delta X(t)$ will then also be zero (the uniqueness theorem). In macroscopic systems the uncertainty can be eliminated in both ways; in microscopic systems this is not possible. Indeed, we cannot transform 'convex' molecules into 'concave' ones. Neither can we eliminate the external uncertainty. The displacement $\delta X_0 = \exp(-10^{12})$ is so small that it could be caused by a butterfly flapping its wings a hundred miles away. This 'butterfly effect' cannot be eliminated: it is impossible to shield the system from external disturbances with such high precision. We should note from the start that this 'butterfly effect' has no macroscopic consequences, since the energy supplied to the system is negligibly small. Much greater energy is required to cause displacement of macroscopic masses to macroscopic distances.

†I hope that the rigorous reader will excuse my reference to 'convex and concave surfaces' of a molecule. In fact, we are talking about different types of the potential of interaction of molecules.

2.2 Comments

The main result of the above discussion is that the emergence of chaos is possible and even unavoidable in molecular systems whose particles obey the laws of classical mechanics. Because of this, such systems must be described with the methods of theory of probability. Of course, the latter does not mean that the particles are no longer moving along their paths. The paths still remain, but they have become unpredictable rather than predictable. Since the purpose of any physical theory is to predict the future, it is clear that statistical mechanics cannot be based on the analysis of unpredictable paths of particles. In other words, the concept of trajectory of a particle must be expelled from statistical mechanics. This makes the latter essentially different from ordinary mechanics, whose main task consists in the calculation of the paths.

3. Liouville equation

We see that even though atoms and molecules move according to the laws of classical mechanics, it is no use trying to calculate their paths. The only thing we can do is to find the probability of occurrence of a particle at a certain point in space. This requires using the concept of the Gibbs ensemble.

3.1 Gibbs ensembles

We saw that in order to find the probability of the event 'bobsleigh to the right of the ridge' we had to make the pilot take 100 rides down the hill. Alternatively, we can imagine that 100 different pilots rush down 100 different hills. If we now assume that all 100 sportsmen and all 100 hills are exactly alike, then in this 'gedanken experiment' the probability of the event 'bobsleigh to the right of the ridge' can be still defined as $\mathcal{P} = v/\mathcal{N}$; this time, however, $\mathcal{N}$ is not the number of rides taken by one and the same pilot, but the total number of copies of the pilot, and v is the number of pilot copies who slide to the right of the ridge. In statistical mechanics it is said that the copies of a given system constitute the Gibbs ensemble, and the probability of a given event is usually defined as the average over the ensemble.

When we say that all sportsmen and all hills are exact copies of each other, we do not mean that all sportsmen have the same complexion or are fond of reading detective stories; only those parameters should be the same which substantially affect the process in question. It is assumed that these definitive parameters can be given with the required accuracy; averaging is carried out over the uncontrollable degrees of freedom. All this fully applies to molecular systems composed of atoms and molecules.

Further on we shall only deal with closed systems, insulated from the environment with walls impenetrable by particles or heat. The state of such systems is characterised by their volume V, the shape of the vessel containing the fluid, the number of particles N, the potential of interaction between the particles $\Phi(r)$ (where r is the distance between the particles), and the total energy $E_{(N)}$ and total entropy $S_{(N)}$ (see Section 9). These parameters will be referred to as external. Obviously, all the copies of the system which constitute the Gibbs ensemble must have the same external parameters. This, however, is not yet sufficient, because the

same values of the external parameters may correspond to entirely different distributions of the local states of the system, characterised by the density of particles $n(\mathbf{r}, t)$, the mass velocity $\mathbf{c}(\mathbf{r}, t)$, the temperature $\Theta(\mathbf{r}, t)$, etc. The latter play a very important part in nonequilibrium systems, because the type of process which takes place in the system depends on the form of functions $n(\mathbf{r}, t)$, etc.

Unlike the external parameters, the local parameters have the meaning of those averaged over the ensemble of copies. Assume, for example, that we are interested in the density of particles n. In order to find it we must count the number of copies ν_k in which at the time t the following event is realised: 'k particles occur with infinitesimal volume δV near point $\mathbf{r}$', where k runs from zero to infinity. Then we can find the probability $\mathcal{P}_k = \nu_k/\mathcal{N}$ of this event, and define

$$n(\mathbf{r}, t) = \sum_{k=0}^{\infty} k\,\mathcal{P}_k(\mathbf{r}, t)\,.$$

All other local variables are determined in a similar fashion.

Now let us define more exactly the concept of 'closed isolated system'. Permanently isolated systems are of no interest to us, since we are unable to act upon them. So we assume that at $t < 0$ the system is open, and we can apply external action to bring the system into a required initial state. Then, at $t = 0$, we 'close' the system, ceasing completely to interfere with its life, and start to monitor the spontaneous drift of the system towards thermodynamic equilibrium (this process can be monitored with instruments whose effect on the system is infinitesimally small).

The initial state we prepared at $t < 0$ has the meaning of the average over the ensemble of copies. This implies that out of all conceivable diversity of copies we selected only those whose average yields the required values of $n_0(\mathbf{r})$, $\mathbf{c}_0(\mathbf{r})$, etc. In other words, we carry out averaging with respect to only those configurations of molecules which are compatible with the given macroscopic state of the system. There is nothing new in this method of averaging. After all, when we deal with the equilibrium system we also carry out averaging with respect to only those configurations which are compatible with the given values of density $n_0 = \text{const}$ and temperature $\Theta_0 = \text{const}$. The equilibrium systems only differ from the nonequilibrium ones in that the initial parameters of the latter $n(\mathbf{r}, 0) = n_0(\mathbf{r})$, $\mathbf{c}(\mathbf{r}, 0) = \mathbf{c}_0(\mathbf{r})$, etc., are functions of the coordinates.

The number of local characteristics of the system is extremely large: pressure, compressibility, density, and so on, and so forth. Now the question is as follows: if we are to determine unambiguously the macroscopic evolution of the system, do we need to fix all the local macroscopic parameters, or it will suffice to fix only some of these? To answer this question we recall that in mechanics the properties of the system are determined by its Hamiltonian

$$H_{(N)} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_{(N)},$$

where $\mathbf{p}_i$ is the momentum of the ith particle, and $U_{(N)} = \sum_{i,j} \Phi(r_{ij})$ is the configuration energy of the system, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Accordingly, we may assume that the local macroscopic parameters which define the mean (over the ensemble) value of the Hamiltonian

$$E_{(N)} = \langle H_{(N)} \rangle = \int_V \mathrm{d}^3 r \left\{ n(\mathbf{r}, t)\,\frac{m\mathbf{c}^2(\mathbf{r}, t)}{2} + \frac{3}{2}\,n(\mathbf{r}, t)\Theta(\mathbf{r}, t) + \frac{1}{2}\langle \Phi \rangle \right\}, \quad (8)$$

at the same time define the mean values of other local parameters. The first term in braces in Eqn (8) has the meaning of the kinetic energy of ordered motion of particles and is determined by the density $n(\mathbf{r}, t)$ and the velocity $\mathbf{c}(\mathbf{r}, t)$. The second term, which relates to the kinetic energy of thermal chaotic motion of the particles, depends on the density and the temperature $\Theta(\mathbf{r}, t)$. The third term, which relates to the density of the potential energy of the particles, also depends on n and Θ. Thus, the mean value of the Hamiltonian of the system is uniquely determined by five hydrodynamic variables†:

$$n(\mathbf{r}, t), \quad c_\alpha(\mathbf{r}, t), \quad \text{where} \quad \alpha = x, y, z, \quad \text{and} \quad \Theta(\mathbf{r}, t); \quad (9)$$

whereas all other local parameters of the system are functions of hydrodynamic variables.

We have already said that the values of hydrodynamic variables are determined by transport equations. Given the initial conditions, the solution of the latter is unique (when the deviation from equilibrium is not too large). Therefore, the initial conditions imposed on the hydrodynamic variables unambiguously predetermine their time evolution. This in turn implies that at $t > 0$ the averaging over the ensemble must be performed for the preset values of $n(\mathbf{r}, t)$, $\mathbf{c}(\mathbf{r}, t)$ and $\Theta(\mathbf{r}, t)$.

The above definition of the Gibbs ensemble lies in the basis of the entire nonequilibrium statistical mechanics. It is interesting that, as a matter of fact, it also points to the main task of the theory. If averaging over the ensemble must always be carried out with the preset values of hydrodynamic variables, then the main task of the theory consists in the first-principle derivation of transport equations whose solution determines the time evolution of these variables. And since the transport equations, apart from the unknown hydrodynamic variables, involve also the transport coefficients, another — and no less important — task of the theory is the calculation of these coefficients from first principles.

3.2 Liouville equation

In order to characterise the microscopic state of the system, one must define the coordinates $\mathbf{r}_i$ and the momenta $\mathbf{p}_i$ of all N particles of the system. Alternatively, one can introduce the concept of $6N$-dimensional phase space, formed by $3N$ coordinates of particles $r_{i\alpha}$ and $3N$ momenta of particles $p_{i\alpha}$ ($\alpha = x, y, z$). In this case the state of each copy of the ensemble will be defined by the position of one point in the phase space (which is usually referred to as the 'portrayal point'). And since the number of copies in the ensemble‡ is $\mathcal{N} \gg 1$, the portrayal points of all copies fill the entire available phase space.

Now let us introduce the concept of N-particle distribution function $\mathscr{G}_{(N)}$ which has the meaning of the density of probability (defined as average over the ensemble) of the

†These variables are called hydrodynamic because their values are determined by equations of hydrodynamics. I believe, however, that the equations of hydrodynamics would be more correctly referred to as transport equations.

‡Do not confuse the number of copies in the ensemble $\mathcal{N}$ with the number of particles N in one copy.

following event: 'at time t particle 1 occurs at point $\mathbf{r}_1$ and its momentum is $\mathbf{p}_1$, particle 2 occurs at point $\mathbf{r}_2$ and its momentum is $\mathbf{p}_2$, and so on up to the last particle number N'. Since the probability by definition is always positive, $\mathscr{G}_{(N)}$ can be written as

$$\mathscr{G}_{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{p}_1, \ldots, \mathbf{p}_N; t) = \exp\{\Omega_{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{p}_1, \ldots, \mathbf{p}_N; t)\}. \tag{10}$$

Since the number of copies of the ensemble $\mathcal{N}$ (or, which is the same, the number of experiments repeated with one and the same systems) is fixed once and for ever, none of the portrayal points in the phase space can disappear — they only can move from one infinitesimal volume of phase space $\delta\Gamma_{(N)}$ to an adjacent one, or accumulate within $\delta\Gamma_{(N)}$. Accordingly, the equation of balance of the number of copies has the form

$$\frac{\partial \mathscr{G}_{(N)}}{\partial t} + \mathrm{div}_{6N}(\dot{\mathbf{X}}_{(N)} \mathscr{G}_{(N)}) = 0, \tag{11}$$

where the velocity vector $\dot{\mathbf{X}}_{(N)}$ of the displacement of the portrayal points in $6N$-dimensional has $6N$ components $\mathrm{d}\mathbf{r}_i/\mathrm{d}t$ and $\mathrm{d}\mathbf{p}_i/\mathrm{d}t$. Expressing the latter with the aid of the Newton equation, after some straightforward algebra we come to the Liouville equation

$$\frac{\partial \mathscr{G}_{(N)}}{\partial t} = \sum_{i=1}^{N} \left\{ \frac{\partial U_{(N)}}{\partial \mathbf{r}_i} \cdot \frac{\partial \mathscr{G}_{(N)}}{\partial \mathbf{p}_i} - \frac{\mathbf{p}_i}{m} \cdot \frac{\partial \mathscr{G}_{(N)}}{\partial \mathbf{r}_i} \right\}, \tag{12}$$

which can also be written in the form (see Eqn (10))

$$\frac{\partial \Omega_{(N)}}{\partial t} = \sum_{i=1}^{N} \left\{ \frac{\partial U_{(N)}}{\partial \mathbf{r}_i} \cdot \frac{\partial \Omega_{(N)}}{\partial \mathbf{p}_i} - \frac{\mathbf{p}_i}{m} \cdot \frac{\partial \Omega_{(N)}}{\partial \mathbf{r}_i} \right\}. \tag{13}$$

We derived Eqn (12) under assumption that the particles move without friction (condition required for the system to be a Hamiltonian one). This condition is very important because it ensures 'perpetual' motion of the particles.

Since the Liouville equation is a differential one, it must be supplemented by boundary and initial conditions. It is obvious that $\mathscr{G}_{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N, t) = 0$ when at least one particle is outside the volume of the system V, or when its momentum becomes infinite. For the initial condition we take

$$\mathscr{G}_{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{p}_1, \ldots, \mathbf{p}_N, 0) = \mathscr{G}^{(0)}_{(N)}(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{p}_1, \ldots, \mathbf{p}_N),$$

where $\mathscr{G}^{(0)}_{(N)}$ is a preset function. Later on (see Section 3.4) we shall discuss this condition in greater detail, and presently we are going to consider some corollaries of the Liouville equation.

3.3 Global conservation laws

Integrating Eqn (12) with respect to the coordinates $\mathbf{r}_i$ and the momenta $\mathbf{p}_i$ of all particles with due account for the boundary conditions, we get

$$\frac{\partial}{\partial t} \int_V \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \int_{-\infty}^{\infty} \mathscr{G}_{(N)} \, \mathrm{d}\mathbf{p}_1 \ldots \mathrm{d}\mathbf{p}_N = 0,$$

that is,

$$\int_V \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \int_{-\infty}^{\infty} \mathscr{G}_{(N)} \, \mathrm{d}\mathbf{p}_1 \ldots \mathrm{d}\mathbf{p}_N = \Gamma^{(0)}_{(N)}. \tag{14}$$

Setting the integration constant equal to

$$\Gamma^{(0)}_{(N)} = V^N \mathcal{P}^{3N}, \tag{15}$$

where V is the volume occupied by the system, and $\mathcal{P} = \sqrt{2\pi m \Theta}$ is the normalisation momentum, we rewrite Eqn (14) as the normalisation condition for the N-particle distribution function (the probability conservation law):

$$\frac{1}{V^N \mathcal{P}^{3N}} \int_V \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \int_{-\infty}^{\infty} \mathscr{G}_{(N)} \, \mathrm{d}\mathbf{p}_1 \ldots \mathrm{d}\mathbf{p}_N = 1. \tag{16}$$

Representing the Hamiltonian $H_{(N)}$ of the system in the form

$$H_{(N)} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U_{(N)}, \tag{17}$$

multiplying Eqn (12) by $H_{(N)}$, and integrating with respect to coordinates and momenta of all N particles, we get the energy conservation law

$$\frac{\partial E_{(N)}}{\partial t} = 0, \qquad E_{(N)} = \mathrm{const}, \tag{18}$$

where the total (global) energy of the system is

$$E_{(N)}(t) = \frac{1}{V^N \mathcal{P}^{3N}} \int_V \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \int_{-\infty}^{\infty} H_{(N)} \mathscr{G}_{(N)} \, \mathrm{d}\mathbf{p}_1 \ldots \mathrm{d}\mathbf{p}_N. \tag{19}$$

Finally, we multiply Eqn (12) by $\Omega_{(N)}$, Eqn (13) by $\mathscr{G}_{(N)}$, add together the resulting expressions and integrate again over all $\mathbf{r}_i$ and $\mathbf{p}_i$ to get the conservation law for the global entropy of the system:

$$\frac{\partial S_{(N)}}{\partial t} = 0, \qquad S_{(N)} = \mathrm{const}, \tag{20}$$

where

$$S_{(N)}(t) = -\frac{k_{\mathrm{B}}}{V^N \mathcal{P}^{3N}} \int_V \mathrm{d}\mathbf{r}_1 \ldots \mathrm{d}\mathbf{r}_N \times \int_{-\infty}^{\infty} \Omega_{(N)} \mathscr{G}_{(N)} \, \mathrm{d}\mathbf{p}_1 \ldots \mathrm{d}\mathbf{p}_N. \tag{21}$$

These three conservation laws are actually the mathematical definition of the physical concept of 'closed isolated system'.

3.4 Comments

The facts presented in this section are for the most part known well and long. The construction of the theory of nonequilibrium processes would be just not possible without the formulas presented above. This is the reason why I quote them here.

It is much less known, however, that the Liouville equation cannot be used for the straightforward definition of the global N-particle distribution function $\mathscr{G}_{(N)}$. The fact is that this is a differential equation, and the solution of any differential equation is unique only given the initial (and boundary) conditions. With this statement of the problem, the Liouville equation is precisely equivalent to the set of Newtonian equations, which also has a unique strictly deterministic solution when the initial conditions are set. We, however, are interested in the states of chaotic systems — states which are not described by such a solution. We have also seen that averaging over the Gibbs ensemble is always carried out for a fixed macroscopic state of the system (that is, with the preset values of hydrodynamic variables). In other

words, we must always perform averaging over all microscopic states of the system which are compatible with its given macroscopic state. Nobody knows how to accomplish this while remaining within the framework of the concept of N-particle distribution function $\mathscr{G}_{(N)}$. All this points to the fact that the Liouville equation must be regarded as a necessary first (but far not the last) step on the way to construction a logically consistent theory of nonequilibrium phenomena — and nothing more. As we shall see, the next step is the transition to the concept of l-particle distribution functions $\mathscr{G}_{(l)}$ with $l = 1, 2, \ldots, N$.

4. BBGKY hierarchy

All further theory is based on the concept of the correlation sphere, which will be our next starting point.

4.1 Correlation sphere

Assume that in the ocean of particles which constitute the system we have managed somehow to fix the coordinate and momentum of particle 1. Now we ask how the rest $N-1$ particles of the system are going to behave. To answer this question, imagine that we put an observer on particle 1 in each copy of the ensemble, ask them all to measure coordinates and particles of surrounding particles at the time t, and average the collected data over all copies of the ensemble. We shall find that if the distance to particle 1 is large enough (say, greater than R_c), then the behaviour of some particle 2, located at point $\mathbf{r}_2$, will be completely unpredictable: particle 2 may move with any velocity in any direction. Of course, this is because chaos reigns in the system. If, however, r_{12} is less than R_c, the result will be different: there will be a certain correlation in the behaviour of particles 1 and 2 due to interaction between the particles. The nature of this interaction may be diverse: it may be direct if particle 2 falls within the force field of particle 1, or indirect, when particle 1 acts upon some intermediate particle 3, which then acts upon particle 2. At present, however, this does not concern us. The main thing is that, as a result of such interactions, a kind of order emerges within *the correlation sphere* of radius R_c (the correlation radius), whereas absolute chaos reigns elsewhere. Of course, the correlation radius is a convention, because the transition from 'order' to 'disorder is always gradual and smooth. For qualitative analysis, however, it is convenient to assume that the transition from 'order' to 'disorder' occurs abruptly at $r_{12} = R_c$, and this is what we are going to do.

Correlation sphere is the key concept of the entire theory: if the orderly processes only take place within the correlation sphere, then all the laws formulated in statistical mechanics are based on the processes within the correlation sphere, whereas everything that occurs outside is irregular and haphazard from the microscopic standpoint, and cannot contribute to those effects which can be regularly reproduced time and time again. Without going into the details, I would like to emphasise that arguments developed above apply not only to gases and liquids, but also to crystals, because only those particles in crystals are engaged in direct interaction which fall within the correlation sphere.

Before we proceed further, I would like to make two remarks. Calculations for equilibrium thermodynamic systems indicate — and the experiments confirm this — that the value of R_c usually does not exceed a few diameters of particles σ (with the exception of critical phenomena). Since on the average all particles move with the thermal velocity v_0, the mean time spent by particle 2 within the correlation sphere of particle 1 is $\tau \simeq R_c/v_0$. And finally, because the volume of the correlation sphere is finite, we can introduce the concept of the maximum number M of particles found within the correlation sphere. The usual values are

$$R_c \lesssim (5-10)\sigma \simeq 10^{-7}\,\mathrm{cm}, \quad \tau \simeq \frac{R_c}{v_0} \simeq 10^{-12}\,\mathrm{s}, \quad M \lesssim 10^3\,. \tag{22}$$

In nonequilibrium systems these parameters have approximately the same values.

And the last point is as follows. Widely used in the kinetic theory of gases are such concepts as the mean free path length R_k and the mean free path time τ_k. To avoid confusion, it ought to be stated from the outset that these have no relation to the correlation radius R_c and the characteristic microscopic time τ. If anything, this follows from the fact that when the density of gas tends to zero, $n \to 0$, the quantities R_k and τ_k tend to infinity, while R_c and τ tend to zero. Indeed, the rarer the gas, the less correlated is the behaviour of its individual particles, and the longer the path of a particle between successive collisions. Free path length and free path time are the characteristics of paths of particles, and in statistical mechanics the concept of a 'path' is outlawed. Accordingly, there is no room for such concepts as free path length and free path time — they are replaced with the concept of correlation.

4.2 *l*-particle distribution functions

Consider the conditional probability† $\mathscr{G}_{1,\ldots,l/l+1,\ldots,N}$ of the event consisting in that particle 1 occurs at point $\mathbf{r}_1$, $\mathbf{p}_1, \ldots$, particle l occurs at point $\mathbf{r}_l$, $\mathbf{p}_l$ on condition that the rest $N-1$ particles of the system occur at points $\mathbf{r}_{l+1}$, $\mathbf{p}_{l+1}, \ldots$, $\mathbf{r}_N$, $\mathbf{p}_N$ (the numbering of particles may be arbitrary). By definition of conditional probability, we have

$$\mathscr{G}_{1,\ldots,N} = \mathscr{G}_{1,\ldots,l/l+1,\ldots,N}\mathscr{G}_{l+1,\ldots,N}\,, \tag{23}$$

where $\mathscr{G}_{1,\ldots,N}$ is the unconditional probability of distribution of particles $1, \ldots, N$ in $6N$-dimensional phase space, and $\mathscr{G}_{l+1,\ldots,N}$ is the same for particles $l+1, \ldots, N$. Since the position of the latter is of no interest to us, we integrate the right-hand and the left-hand sides of Eqn (23) over all possible position of particles $l+1, \ldots, N$. As a result, we get

$$\frac{1}{V^{N-l}\mathcal{P}^{3(N-l)}}\int_{\Gamma_{(N)}} \mathscr{G}_{1,\ldots,N}\,\mathrm{d}(l+1)\ldots\mathrm{d}(N)$$
$$= \frac{1}{V^{N-l}\mathcal{P}^{3(N-l)}}\int_{\Gamma_{(N)}} \mathscr{G}_{1,\ldots,l/l+1,\ldots,N}\mathscr{G}_{l+1,\ldots,N}\,\mathrm{d}(l+1)\ldots\mathrm{d}(N). \tag{24}$$

Of course, the conditional probability $\mathscr{G}_{1,\ldots,l/l+1,\ldots,N}$ depends on the coordinates of particles $l+1, \ldots, N$. As we have seen, however, the positions of particles are only correlated at distances smaller than R_c. Accordingly, if we draw a sphere of radius R_c around each of l particles whose coordinates are fixed, the particles which fall outside of these spheres will not correlate with the fixed particles of the selected set. Let us now split the range of integration in Eqn (24) into V_l and $V - V_l$, where $V_l \lesssim lR_c^3$ is the volume of all correlation spheres drawn

†Here and further we shall represent any function $\psi_{(l)}$ of coordinates and momenta of particles (and of the time t) as $\psi_{(l)}(\mathbf{r}_1, \ldots, \mathbf{r}_l, \mathbf{p}_1, \ldots, \mathbf{p}_l, t) = \psi_{1,\ldots,l}$, and the differentials $\mathrm{d}\mathbf{r}_i\,\mathrm{d}\mathbf{p}_i$ will be denoted simply as $\mathrm{d}(i)$.

around the particles of the selected set. In the integral over the volume $V - V_l$, the conditional probability $\mathscr{G}_{1,\ldots,l/l+1,\ldots,N}$ can be factored out, since, by virtue of arguments developed above, it does not depend on the coordinates of particles $l+1,\ldots,N$. Naturally, this cannot be done in the integral over the volume V_l. If, however, we go over to the so-called thermodynamic limit

$$N,\ V \to \infty \quad \text{at} \quad n_0 = \frac{N}{V} = \text{const}\,, \tag{25}$$

we immediately find that, since $V \gg V_l$, the integral over V_l in Eqn (24) can be simply discarded. As a result, Eqn (24) becomes

$$\frac{1}{V^{N-l}\,\mathcal{P}^{3(N-l)}} \int_{\Gamma_{(N)}} \mathscr{G}_{1,\ldots,N}\,\mathrm{d}(l+1)\ldots\mathrm{d}(N)$$
$$= \mathscr{G}_{1,\ldots,l/l+1,\ldots,N}\,\frac{1}{V^{N-l}\,\mathcal{P}^{3(N-l)}} \int_{\Gamma_{(N)}} \mathscr{G}_{l+1,\ldots,N}\,\mathrm{d}(l+1)\ldots\mathrm{d}(N)\,.$$

Since any unconditional probability must satisfy the normalisation condition,

$$\frac{1}{V^{N-l}\,\mathcal{P}^{3(N-l)}} \int_{\Gamma_{(N)}} \mathscr{G}_{l+1,\ldots,N}\,\mathrm{d}(l+1)\ldots\mathrm{d}(N) = 1\,, \tag{26}$$

we finally get

$$\mathscr{G}_{1,\ldots,l} \equiv \mathscr{G}_{1,\ldots,l/l+1,\ldots,N}$$
$$= \frac{1}{V^{N-l}\,\mathcal{P}^{3(N-l)}} \int_{\Gamma_{(N)}} \mathscr{G}_{1,\ldots,N}\,\mathrm{d}(l+1)\ldots\mathrm{d}(N)\,. \tag{27}$$

Here in the function $\mathscr{G}_{1,\ldots,l/l+1,\ldots,N}$ we have dropped the subscripts $l+1,\ldots,N$, because there is no dependence on these particles in the volume $V - V_l$. The function $\mathscr{G}_{(l)}$ defined in this way is called the l-particle distribution function. Observe that it is rigorously defined only in the thermodynamic limit, since it is only then that we may neglect the integral over V_l.

4.3 Hierarchy of BBGKY equations

Now that we have defined the l-particle distribution functions, we must find the set of equations which will enable us to calculate them. With this purpose we integrate the Liouville equation (12) with respect to the coordinates of particles $l+1,\ldots,N$, and use Eqn (27). After some straightforward manipulations we get the infinite set of linked Bogolyubov–Born–Green–Kirkwood–Yvon equations (or, for short, the BBGKY hierarchy):

$$\frac{\partial \mathscr{G}_{1,\ldots,l}}{\partial t} = \sum_{i=1}^{l}\left\{-\frac{\mathbf{p}_i}{m}\cdot\frac{\partial \mathscr{G}_{1,\ldots,l}}{\partial \mathbf{r}_i} + \frac{\partial U_{1,\ldots,l}}{\partial \mathbf{r}_i}\cdot\frac{\partial \mathscr{G}_{1,\ldots,l}}{\partial \mathbf{p}_i} + \frac{n_0}{\mathcal{P}^3}\int_{\Gamma_{(N)}} \frac{\partial \Phi_{i,l+1}}{\partial \mathbf{r}_i}\cdot\frac{\partial \mathscr{G}_{1,\ldots,l+1}}{\partial \mathbf{p}_i}\,\mathrm{d}(l+1)\right\},$$
$$l = 1,\,2,\,\ldots,\,\infty \tag{28}$$

(these equations have been derived under assumption that

$$U_{1,\ldots,l} = \sum_{1\leqslant i<j\leqslant l} \Phi_{ij}\,,$$

where $\Phi_{ij} = \Phi(r_{ij})$ is the potential of pairwise interaction between particles i and j; the more complicated triple, quadruple, etc. interactions are neglected). The last, Nth equation in this hierarchy coincides with the initial Liouville equation. After transition to the thermodynamic limit $N = \infty$, however, this equation 'goes to infinity' and becomes meaningless.

Since the BBGKY hierarchy is a set of integro-differential equations, to make it to define uniquely the sought-for solution we must supplement it with the condition of attenuation of correlations

$$\mathscr{G}_{1,\ldots,l} \to \prod_{i=1}^{l} \mathscr{G}_i \quad \text{at} \quad r_{ij} \to \infty \tag{29}$$

for the functions with $l \geqslant 2$, and impose the normalisation condition on the one-particle function with $l = 1$:

$$\frac{1}{V\mathcal{P}^3}\int_V \mathrm{d}\mathbf{r}\int_{-\infty}^{\infty} \mathscr{G}_{(1)}(\mathbf{r},\,\mathbf{p},\,t)\,\mathrm{d}\mathbf{p} = 1\,. \tag{30}$$

It is obvious that condition (29) implies that the events which take place beyond the correlation sphere do not correlate (independent events). Now, multiplying the normalisation condition by N, we can bring it into the form of the law of conservation of the number of particles:

$$\int_V n(\mathbf{r},\,t)\,\mathrm{d}\mathbf{r} = N\,, \tag{31}$$

where the density of particles is

$$n(\mathbf{r},\,t) = n_0\int_{-\infty}^{\infty} \mathscr{G}_{(1)}(\mathbf{r},\,\mathbf{p},\,t)\,\frac{\mathrm{d}\mathbf{p}}{\mathcal{P}^3}\,. \tag{32}$$

In addition, we define the mean velocity of particles $\mathbf{c}(\mathbf{r},\,t)$ by an obvious relation

$$mn(\mathbf{r},\,t)\,\mathbf{c}(\mathbf{r},\,t) = n_0\int_{-\infty}^{\infty} \mathbf{p}\,\mathscr{G}_{(1)}(\mathbf{r},\,\mathbf{p},\,t)\,\frac{\mathrm{d}\mathbf{p}}{\mathcal{P}^3}\,, \tag{33}$$

and the temperature $\Theta(\mathbf{r},\,t)$, which has the meaning of the kinetic energy of thermal chaotic motion, is given by a similarly straightforward formula

$$\frac{3}{2}\,n(\mathbf{r},\,t)\,\Theta(\mathbf{r},\,t) = n_0\int_{-\infty}^{\infty} \frac{(\mathbf{p}-m\mathbf{c})^2}{2m}\,\mathscr{G}_{(1)}(\mathbf{r},\,\mathbf{p},\,t)\,\frac{\mathrm{d}\mathbf{p}}{\mathcal{P}^3}\,. \tag{34}$$

Some other physical parameters of the system (for example, the density of potential energy) can be defined in a similar fashion.

4.4 Local conservation laws

Upon transition to the thermodynamic limit, the global conservation laws lose sense because the values of N, $E_{(N)}$ and $S_{(N)}$ go to infinity†. They must therefore be replaced with local laws. The latter can be obtained in the standard way with the aid of the BBGKY hierarchy.

Integrating the first equation in the hierarchy, which defines $\mathscr{G}_{(1)}$, and taking due account of Eqns (32) and (33), we get the continuity equation

$$\frac{\partial n}{\partial t} - \frac{\partial (nc_\alpha)}{\partial r_\alpha} = 0\,, \tag{35}$$

which has the meaning of the law of conservation of the number of particles. Multiplying the equation for $\mathscr{G}_{(1)}$ by $\mathbf{p}_1$

†Of course, the ratios $E_{(N)}/N$ and $S_{(N)}/N$ remain finite. The meaning of these ratios in the case of nonequilibrium systems, however, is not clear.

and integrating with respect to $\mathbf{p}_1$, we get the local law of conservation of momentum

$$mn\,\frac{\mathrm{d}c_\alpha}{\mathrm{d}t} = -\frac{\partial P_{\alpha\beta}}{\partial r_\beta} \tag{36}$$

where $P_{\alpha\beta}$ is the stress tensor whose particular form we do not specify here). Similarly, multiplying the first equation in the hierarchy by $(\mathbf{p} - m\mathbf{c})^2$ and integrating with respect to $\mathbf{p}$, we get the local law of conservation of temperature (that is, the kinetic energy of thermal chaotic motion):

$$n\,\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{3}{2}\,\Theta\right) = -\frac{\partial J_\alpha^{(\Theta)}}{\partial r_\alpha} + q^{(\Theta\Phi)}\,,$$

where $\mathbf{J}^{(\Theta)}$ is the thermal flux vector, and $q^{(\Theta\Phi)}$ is the strength of source responsible for the conversion of kinetic energy into the potential energy. Since $q^{(\Theta\Phi)}$ can be represented as

$$q^{(\Theta\Phi)} = -\frac{\partial J_\alpha^{(\Theta\Phi)}}{\partial r_\alpha}\,,$$

we finally get

$$n\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{3}{2}\,\Theta\right) = -\frac{\partial J_\alpha}{\partial r_\alpha}\,, \quad \mathbf{J} = \mathbf{J}^{(\Theta)} + \mathbf{J}^{(\Theta\Phi)}\,. \tag{37}$$

Finally, the local law of conservation of entropy can be derived from the global law (20) using all equations in the BBGKY hierarchy:

$$n\,\frac{\mathrm{d}s}{\mathrm{d}t} = -\frac{\partial I_\alpha^{(s)}}{\partial r_\alpha} + q^{(s)}\,, \tag{38}$$

where $\mathbf{I}^{(s)}$ is the entropy flux vector, and $q^{(s)}$ is the source of entropy (detailed derivation can be found in Refs [2, 3]). The source in Eqn (38) does not contradict in any way the Liouville theorem, since the latter only holds for closed isolated systems, whereas Eqn (38) describes processes within the correlation sphere which is an open system.

4.5 Comments

The material presented in this section can be found in any textbook on statistical mechanics (with the exception of Eqn (38)). At the same time, the conclusions that can be based on the above formulas, are much less known.

Firstly, if we carefully examine the train of thought which has brought us to the BBGKY hierarchy, we note that each consecutive step is forced, and, which is most important, predetermined by the results obtained at the previous step. As soon as we found that the paths of particles cannot be calculated in principle, the only remaining possibility was to describe the state of the system with the methods of the theory of probability. As soon as we introduced the global probability $\mathscr{G}_{(N)}$ into classical mechanics using the concept of the Gibbs ensemble, we needed the Liouville equation to define $\mathscr{G}_{(N)}$. Comparison of $\mathscr{G}_{(N)}$ with those assumptions which are incorporated into the definition of the Gibbs ensemble, however, shows that the Liouville equation defines not the probability we need. This called for transition to the local description in terms of the l-particle distribution functions. These functions in turn can only be defined with the aid of equations of the BBGKY hierarchy.

Secondly, I would like to emphasise that we can only go over to the BBGKY hierarchy after transition to the thermodynamic limit, which makes the global description in terms of the N-particle distribution function totally impossible: it is as though the transition to the thermodynamic limit breaks the linkage of the equations of the BBGKY hierarchy and the local conservation laws with those global relations which gave rise to them in the first place. Among other things, this transition simplifies the task considerably: while with the global approach we had to define the distribution function $\mathscr{G}_{(N)}$ which depends on an infinite number of coordinates, the local approach requires defining the correlation in the behaviour of a few tens or hundreds of particles which fall within the correlation sphere; all other particles have no effect on the state of matter at the given point $\mathbf{r}$.

The BBGKY hierarchy is by no means the final step in the modification of the initial Newtonian equations. Of course, we may use Eqns (32) – (34) to impose additional restrictions on the distribution functions whose introduction is required by the initial concept of the Gibbs ensemble. The BBGKY equations still involve time derivatives, which means that their solution requires imposing initial conditions. This, however, would imply uniqueness of the solution, which does not agree with the notion of chaos which reigns in molecular systems (see Section 3.4).

No less important is the following. The BBGKY hierarchy involves the only symbolic parameter $n_0 = N/V$ which has the meaning of the density established in the system when it finally arrives at the thermodynamic equilibrium at $t = \infty$. Accordingly, the solution of the hierarchy must also be a function of n_0. This, however, contradicts the causality principle which states that physically meaningful solutions can only depend on those parameters that are defined at the time $t' \leqslant t$; they cannot depend on the density $n(\mathbf{r}, t = \infty) = n_0$. Therefore, the work on the BBGKY hierarchy must be continued.

5. Expansion in ε

Starting with the Newtonian equations and moving along the only avenue available, we arrived at the BBGKY hierarchy. The latter, however, features a number of properties which seem to make it not suitable for solving the problems faced by the theory. We can only hope that there are physically meaningful equations hidden inside the hierarchy itself. Our task consists in finding them. As we shall see, this task is accomplished by expanding the equations of the hierarchy in a small parameter ε.

5.1 Characteristic parameters of the system

Any macroscopic system has at least two characteristic microscopic parameters: the radius of the correlation sphere R_c, and the characteristic time of evolution towards equilibrium within the correlation sphere τ. In addition, any closed isolated system has two characteristic parameters: the system size L, and the characteristic time of relaxation of the entire system towards equilibrium T. This allows introducing two dimensionless parameters

$$\varepsilon = \frac{R_c}{L}\,, \qquad \chi = \frac{\tau}{T}\,, \tag{39}$$

whose numerical values may, of course, vary considerably depending on the particular properties of the system in question. The simplest estimates indicate, however, that for the majority of macroscopic systems (although by no means for all) they are not just small, but infinitesimal — of the order

of 10^{-8} or less. In the end, this is a consequence of the fact that inequalities

$$R_c \ll L\,, \qquad \tau \ll T\,. \tag{40}$$

are almost always satisfied.

The discussion to follow will only be concerned with such systems and such processes that comply with the above inequalities; systems and processes for which at least one of these inequalities does not hold call for special treatment.

5.2 'Fast' and 'slow' distribution functions

Having such small parameters at hand, it would be natural to try using them for solving the BBGKY hierarchy. This task, however, is not that simple, since neither ε nor χ enter explicitly the equations of the hierarchy. Accordingly, the first thing to be done is to introduce these parameters into the equations.

Obviously, both macroscopic and microscopic processes take place in any nonequilibrium macroscopic system. Since the BBGKY hierarchy gives a complete description of the system, it must involve the distribution functions for the processes of both kinds. Observe that, on the one hand, all hydrodynamic variables (that is, functions $n(\mathbf{r},\,t)$, $\mathbf{c}(\mathbf{r},\,t)$ and $\Theta(\mathbf{r},\,t)$) exhibit substantial variations only over distances of the order of L and time of the order of T. Therefore, they depend on the dimensionless distance $\mathbf{r}/L$ and dimensionless time t/T:

$$n = n\left(\frac{\mathbf{r}}{L},\,\frac{t}{T}\right), \quad \mathbf{c} = \mathbf{c}\left(\frac{\mathbf{r}}{L},\,\frac{t}{T}\right), \quad \Theta = \Theta\left(\frac{\mathbf{r}}{L},\,\frac{t}{T}\right). \tag{41}$$

Now, since the hydrodynamic variables are linked with the one-particle distribution function $\mathscr{G}_{(1)}$ via relations (32)–(34), the function $\mathscr{G}_{(1)}$ must depend on the same dimensionless variables (and the dimensionless momentum $\mathbf{p}/\mathcal{P}$):

$$\mathscr{G}_{(1)}\left(\frac{\mathbf{r}}{L}\,,\,\frac{\mathbf{p}}{\mathcal{P}}\,,\,\frac{t}{T}\right) = \exp\left\{\omega_{(1)}\left(\frac{\mathbf{r}}{L}\,,\,\frac{\mathbf{p}}{\mathcal{P}}\,,\,\frac{t}{T}\right)\right\}. \tag{42}$$

Therefore $\mathscr{G}_{(1)}$ and hydrodynamic variables n, $\mathbf{c}$, and Θ form the group of slow functions.

On the other hand, making use of the condition of attenuation of correlations (29), we can represent the multi-particle distribution functions $\mathscr{G}_{(l)}$, $l \geqslant 2$ in the form

$$\mathscr{G}_{1,\ldots,l} = \exp(\Omega_{1,\ldots,l}) \prod_{i=1}^{l} \mathscr{G}_i\,, \quad \Omega_1 \equiv 0\,, \tag{43}$$

where

$$\Omega_{1,\ldots,l} = \Omega_{(l)}\left(\frac{\mathbf{r}_1}{R_c}\,,\ldots,\frac{\mathbf{r}_l}{R_c};\,\frac{\mathbf{p}_1}{\mathcal{P}}\,,\ldots,\,\frac{\mathbf{p}_l}{\mathcal{P}};\,\frac{t}{\tau}\right) \to 0 \quad \text{at} \quad r_{ij} \to \infty\,. \tag{44}$$

The functions $\Omega_{(l)}$, defined in this way, describe mutual correlation of particles within the correlation sphere. They form the group of 'fast' functions, which vary considerably over the time $t \simeq \tau$ and the distance of the order of R_c (and vanish outside the correlation sphere).

By virtue of inequalities (40), all 'slow' functions remain constant over distances of the order of R_c, or, to be more precise, their variations by the order of magnitude do not exceed ε. For example, the variation of density over $\delta r \lesssim R_c$ is

$$\delta n = \frac{\partial n(\mathbf{r}/L,\,t/T)}{\partial \mathbf{r}} \cdot \delta\mathbf{r} \lesssim \frac{\partial n}{L\partial(r/L)}\;R_c = \varepsilon\,\frac{\partial n}{\partial(r/L)} \simeq \varepsilon n\,. \tag{45}$$

At the same time, similar changes for the 'fast' functions are

$$\delta\Omega_{(l)} = \frac{\partial\Omega_{(l)}}{\partial\mathbf{r}} \cdot \delta\mathbf{r} \lesssim \frac{\partial\Omega_{(l)}}{R_c\partial(r/R_c)}\;R_c = \frac{\partial\Omega_{(l)}}{\partial(\mathbf{r}/R_c)} \simeq \Omega_{(l)}\,. \tag{46}$$

Therefore, when solving equations for $\Omega_{(l)}$, one may assume that the functions $\mathscr{G}_{(1)}$ and n, $\mathbf{c}$ and Θ are constant and independent of $\mathbf{r}$.

5.3 Expansion in ε

Substituting Eqn (42) and Eqn (44) into the BBGKY hierarchy (28) and going over to dimensionless variables, we get

$$\chi\,\frac{\partial\omega_1}{\partial t} + \varepsilon\,\frac{\mathbf{p}_1}{m}\cdot\frac{\partial\omega_1}{\partial\mathbf{r}_1} = -\mathbf{F}_{(1)}\cdot\frac{\partial\omega_1}{\partial\mathbf{p}_1} + \eta_{(1)}\,, \tag{47}$$

$$\chi\,\frac{\partial\Omega_{1,\ldots,l}}{\partial t} = \sum_{i=1}^{l}\left\{-\frac{\mathbf{p}_i}{m}\cdot\frac{\partial\Omega_{1,\ldots,l}}{\partial\mathbf{r}_i} - \left[-\frac{\mathrm{d}U_{1,\ldots,l}}{\mathrm{d}\mathbf{r}_i} + \left(\mathbf{F}_{1,\ldots,(i),\ldots,l} - \mathbf{F}_{(i)}\right)\right]\cdot\frac{\partial\omega_i}{\partial\mathbf{p}_i} + \frac{\mathrm{d}U_{1,\ldots,l}}{\mathrm{d}\mathbf{r}_i}\cdot\frac{\partial\Omega_{1,\ldots,l}}{\partial\mathbf{p}_i} + \left(\eta_{1,\ldots,(i),\ldots,l} - \eta_{(i)}\right)\right\}. \tag{48}$$

In these equations the collective force $\mathbf{F}_{1,\ldots,(i),\ldots,l}$ which acts upon particle i from the side of the rest $N-l$ particles in the system where the coordinates of particles $11,\ldots,i,\ldots,l$ are fixed is

$$\mathbf{F}_{1,\ldots,(i),\ldots,l} = -\frac{n_0}{\mathcal{P}^3}\int_{\Gamma_{(N)}} \frac{\mathrm{d}\Phi_{i,l+1}}{\mathrm{d}\mathbf{r}_i}\;\mathscr{G}_{l+1} \times \exp\left[\Omega_{1,\ldots,l+1} - \Omega_{1,\ldots,l}\right]\,\mathrm{d}(l+1)\,. \tag{49}$$

The functions

$$\eta_{1,\ldots,(i),\ldots,l} = \frac{n_0}{\mathcal{P}^3}\int_{\Gamma_{(N)}} \frac{\mathrm{d}\Phi_{i,l+1}}{\mathrm{d}\mathbf{r}_i}\;\mathscr{G}_{l+1} \times \exp\left[\Omega_{1,\ldots,l+1} - \Omega_{1,\ldots,l}\right]\,\frac{\partial\Omega_{1,\ldots,l+1}}{\partial\mathbf{p}_i}\,\mathrm{d}(l+1)\,, \tag{50}$$

which also appear in Eqns (47) and (48), have the meaning of sources of correlation entropy (I am not going to dwell upon this matter, referring the reader to Ref. [2]).

Since the BBGKY hierarchy now involves the parameters ε and χ, it can be solved by means of expansion in these parameters. Before doing this, it is expedient to set $\varepsilon = \chi$, since these parameters are of the same order of magnitude:

$$\varepsilon \simeq 10^{-7} - 10^{-10}\,, \qquad \chi \simeq 10^{-8} - 10^{-12}\,. \tag{51}$$

This done, we set

$$\begin{aligned} \omega_1 &= \omega_1^{(0)} + \varepsilon\omega_1^{(1)} + \ldots\,, \\ \mathscr{G}_1 &= \mathscr{G}_1^{(0)} + \varepsilon\,\mathscr{G}_1^{(1)} + \ldots = \mathscr{G}_1^{(0)}(1 + \varepsilon\omega_1^{(1)} + \ldots)\,, \\ \Omega_{1,\ldots,l} &= \Omega_{1,\ldots,l}^{(0)} + \varepsilon\Omega_{1,\ldots,l}^{(1)} + \ldots \end{aligned} \tag{52}$$

and proceed in the standard manner: substitute these expansions into Eqns (47) and (48) and collect similar terms — that is, follow the regular prescriptions of the perturbation theory.

5.4 Comments

To end this section, I would like to emphasise once again that the purpose of expansion consists not only (and not so much) in simplifying the BBGKY hierarchy. Rather, it serves to select the groups of those equations which really describe physical processes. In this respect, on the way towards constructing the theory the expansion is a step as fundamental as is, for example, the transition from the Liouville equation to the BBGKY hierarchy.

6. Thermodynamic equilibrium

We start our study of the expansion in ε by analyzing the terms of the zero order, which, as we shall demonstrate, describe the state of local thermodynamic equilibrium.

6.1 BBGKY hierarchy in the zero order in ε

In the zero order in ε we simply drop in Eqns (47) and (48) all terms containing ε and χ. Taking into account the symmetry of all functions with respect to subscript inversion, which follows from the symmetry of the initial Hamiltonian of the system (17), we may drop the summation sign in Eqn (48). Then we get

$$-\mathbf{F}^{(0)}_{(1)}\cdot\frac{\partial\omega^{(0)}_1}{\partial\mathbf{p}_1}+\eta^{(0)}_{(1)}=0\,, \tag{53}$$

$$-\frac{\mathbf{p}_1}{m}\cdot\frac{\partial\Omega^{(0)}_{1,\ldots,l}}{\partial\mathbf{r}_1}-\left[-\frac{\mathrm{d}U_{1,\ldots,l}}{\mathrm{d}\mathbf{r}_1}+\mathbf{F}^{(0)}_{(1),\ldots,l}\right]\cdot\frac{\partial\omega^{(0)}_1}{\partial\mathbf{p}_1}+\frac{\mathrm{d}U_{1,\ldots,l}}{\mathrm{d}\mathbf{r}_1}\cdot\frac{\partial\Omega^{(0)}_{1,\ldots,l}}{\partial\mathbf{p}_1}+\eta^{(0)}_{(1),\ldots,l}=0\,. \tag{54}$$

Our manipulations, however, do not end at this point. Observe first that the collective force $\mathbf{F}^{(0)}_{(1)}$ which acts upon particle 1 from the side of all the other $N-1$ particles of the system, is the total force acting on this particle, since there are no other forces in the equation of the zero approximation (53). This force must be equal to zero, because otherwise particle 1 would have started moving under the action of this force. This would eventually change the density of matter, which is forbidden since equations (53), (54) do not depend on the time. Accordingly, we must set $\mathbf{F}^{(0)}_{(1)}=0$, whence

$$\mathscr{G}^{(0)}_{(1)}=\exp\{\omega^{(0)}\}=\exp\left\{-\frac{(\mathbf{p}-m\,\boldsymbol{\pi})^2}{2m\tilde{\Theta}}+\tilde{\omega}\right\}, \tag{55}$$

where $\tilde{\omega}$, $\tilde{\Theta}$, $\boldsymbol{\pi}$ are the arbitrary integration constants which can be found from Eqn (32)–(34):

$$\tilde{\omega}=\ln\frac{n(\mathbf{r},t)}{n_0}\,,\qquad \boldsymbol{\pi}=\mathbf{c}(\mathbf{r},t)\,,\qquad \tilde{\Theta}=\Theta(\mathbf{r},t)\,, \tag{56}$$

where n, $\mathbf{c}$ and Θ are the exact values of the hydrodynamic variables†.

The slow dependence of n, $\mathbf{c}$ and Θ on r/L and t/T, defined by these formulas, does not contradict the assumption that they remain constant with respect to the fast variations of r/R_{c} and t/τ as used in solving the equation $\mathbf{F}^{(0)}_{(1)}=0$ (recall that n, $\mathbf{c}$ and Θ are constant to within the terms of the order of ε, which in the zero approximation are dropped).

A second simplifying assumption is that not only the force $\mathbf{F}^{(0)}_{(1)}$, but also all sources of local entropy must be equal to zero, because otherwise the local entropy would have been time-dependent, contrary to the zero-approximation equations. From condition $\eta_{(1),\ldots,l}=0$ it follows that

$$\frac{\partial\Omega^{(0)}_{1,\ldots,l}}{\partial\mathbf{p}_1}=0\,,\qquad l\geqslant 2\,. \tag{57}$$

As a result of these simplifications, the equation for the one-particle distribution function becomes an identity $0=0$, and the equations for the higher functions take the form of equations of balance of forces acing upon particle 1 in the system where the coordinates of particles $1,\ldots,l$ are fixed:

$$\Theta\,\frac{\partial\Omega^{(0)}_{1,\ldots,l}}{\partial\mathbf{r}_1}=-\frac{\mathrm{d}U_{1,\ldots,l}}{\mathrm{d}\mathbf{r}_1}+\mathbf{F}^{(0)}_{(1),\ldots,l}\,,\quad l=2,\,3,\,\ldots,\,\infty\,. \tag{58}$$

Indeed, on the right-hand side of Eqn (58) we have the 'individual' force $-\mathrm{d}U_{1,\ldots,l}/\mathrm{d}\mathbf{r}_1$, which acts on particle 1 from the side of all fixed particles, and the 'collective' force

$$\mathbf{F}^{(0)}_{(1),\ldots,l}=-n\int_V\frac{\mathrm{d}\Phi_{1,l+1}}{\mathrm{d}\mathbf{r}_1}\exp\bigl(\Omega^{(0)}_{1,\ldots,l+1}-\Omega^{(0)}_{1,\ldots,l}\bigr)\,\mathrm{d}^3r_{l+1}\,, \tag{59}$$

which acts upon particle 1 from the side of those $N-l$ particles of the system whose coordinates are involved in the averaging. These forces are counterbalanced by the force of thermal motion of the particles $-\Theta\,\mathrm{d}\Omega_{(l)}/\mathrm{d}\mathbf{r}_1$ on the left-hand side of Eqn (58).

6.2 Gibbs distribution, theory of fluids and the first law of thermodynamics

The potential of pairwise interaction $\Phi(r)$ under the integral in Eqn (59) is usually modelled by the Lenard-Jones potential

$$\Phi(r)=4\lambda\left\{\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right\}, \tag{60}$$

where λ is the energy constant, and σ is the effective diameter of particles. Hence it follows that with $r\geqslant R_\Phi\simeq(5-10)\,\sigma$ the integral becomes practically equal to zero. Because of this, the integral in Eqn (59) is usually taken not over the entire volume V, but rather over the sphere of radius R_Φ. Assume that this sphere contains M_Φ densely packed particles. Then the particle whose number is $l=M_\Phi+1$ falls outside of the sphere of radius R_Φ, and will therefore not contribute to the collective force. Because of this, the difference $\Omega_{1,\ldots,l+1}-\Omega_{1,\ldots,l}$ will cease to depend on l when $l>M_\Phi$, and the collective force $\mathbf{F}^{(0)}_{(1),\ldots,l}$ will vanish because the integrand in Eqn (58) contains an odd function of $\mathbf{r}$. Then the BBGKY hierarchy becomes

$$\frac{\mathrm{d}\Omega^{(0)}_{1,\ldots,l}}{\mathrm{d}\mathbf{r}_1}=-\frac{1}{\Theta}\,\frac{\mathrm{d}U_{1,\ldots,l}}{\mathrm{d}r_1}\,,$$

whence

$$\Omega^{(0)}_{(l)}=-\frac{U_{1,\ldots,l}}{\Theta}\,,\qquad l>M_\Phi\,. \tag{61}$$

†Recall that averaging in the Gibbs ensemble must always be carried out with strictly fixed values of these variables.

Monte-Carlo numerical calculations confirm the conclusion that at

$$l > M_\Phi \simeq \left(\frac{R_\Phi}{\sigma}\right)^3 \simeq 1000$$

the BBGKY hierarchy takes the form of Eqn (61): they indicate that in this case the result ceases to depend on the number of particles l in the cell.

Now let us consider a physically infinitesimal volume $\delta V \simeq (\delta R)^3$. We assume that its diameter is $\delta R \gg R_\Phi$, and at the same time $\delta R \ll L$ (the latter ensures that the values of the hydrodynamic variables within δV can be assumed to be constant). The matter outside of the volume δV will be referred to as thermostat, whereas inside is the system of M particles under investigation. As follows from Eqn (61) and Eqns (55) and (56), the M-particle distribution function of the system is

$$\mathscr{G}_{(M)} = \exp\left\{-\frac{H_{1,\ldots,M}}{\Theta} + \tilde{\Omega}\right\}, \tag{62}$$

and is thus the local Gibbs distribution ($\tilde{\Omega}$ in Eqn (62) is the normalisation constant). A standard procedure, proposed by Gibbs himself, can be used for deriving the fundamental thermodynamic equation $\Theta S_{(M)} = E_{(M)} - \mathcal{F}_{(M)}$ (where $S_{(M)}$, $E_{(M)}$ and $\mathcal{F}_{(M)}$ are, respectively, the entropy, the internal energy, and the free energy of the volume δV), whence follow all the identities of thermodynamics which are implications of its first law. Generally speaking, if $\mathscr{G}_{(M)}$ is known, it is possible not only to derive all the identities, but also to calculate all the relevant variables (which is done, for instance, using the Monte-Carlo method). Along with this, it is possible to transform the equilibrium BBGKY hierarchy (58) into the Ornstein–Zernike equation for the two-particle distribution function $\mathscr{G}_{(2)}$ and seek solution of this equation. This approach leads to the so-called statistical theory of fluids, which has a number of definite advantages over the methods of numerical experiment.

6.3 Comments

Even the analysis of the zero approximation in ε indicates that we are on the right track. Indeed, equation (56) has enabled us to eliminate the nonphysical constant n_0 from the equilibrium hierarchy (53) and (54), replacing it with the local density $n(\mathbf{r}, t)$. As will be shown below, the same applies to all higher approximations in ε. More than that, we have used the local Maxwell distribution (55) to introduce into the hierarchy the local temperature $\Theta(\mathbf{r}, t)$ which has the meaning of the kinetic energy of thermal chaotic motion of particles. Finally, in the zero approximation in ε the time derivatives have disappeared from equations of the hierarchy — hence, it is no longer necessary to solve the Cauchy problem and to formulate the initial conditions for the distribution functions. Rather than that, we describe the system with the aid of the local Gibbs distribution, which is known to occupy the maximum possible volume in the phase space and thus to perform automatically averaging of the parameters of the matter over the largest possible number of microscopic states of the system, compatible with the given values of hydrodynamic variables. To conclude, from arguments developed above it follows that equilibrium described by the BBGKY hierarchy in the zero order is, generally speaking, local rather than global thermodynamic equilibrium.

7. BBGKY hierarchy in the first order in ε

7.1 System of Eulerian transport equations

In the preceding section we made a tacit assumption that the values of hydrodynamic variables are known — otherwise the solution of the zero-approximation equations would have been not possible because the BBGKY hierarchy in the zero order in ε involves the density $n(\mathbf{r}, t)$ and the temperature† $\Theta(\mathbf{r}, t)$ as independent parameters. Obviously, before solving the equations of the hierarchy, one has to define the local values of these parameters in some way or other. They can only be found from equations of balance (35), (36), and (37) which describe processes on the scale of the entire macroscopic system.

The solution of equations of balance must start with the expansion of the latter in ε. Since in the zero approximation in ε we assumed that the exact values of n, $\mathbf{c}$ and Θ are known (see Eqn (56)), the left-hand sides of equations of balance need not be expanded‡; it is only the right-hand sides that are to be expanded in ε. It is easy to prove that in the zero approximation in ε the stress tensor $P_{\alpha\beta} = \delta_{\alpha\beta} P^{(0)}$, where $P^{(0)}(n, \Theta)$ is the equilibrium pressure whose value can be calculated, for example, with the methods of the statistical theory of fluids. In the same zero approximation, the heat flux $\mathbf{J}$ in Eqn (37) is found to be equal to zero. As a result, the equations of balance (35)–(37) reduce to the set of five Euler equations in five unknown hydrodynamic variables:

$$\frac{\partial n}{\partial t} + \frac{\partial (n c_\alpha)}{\partial r_\alpha} = 0, \tag{63}$$

$$n\,\frac{\mathrm{d}(m c_\alpha)}{\mathrm{d}t} = -\frac{\partial P^{(0)}}{\partial r_\alpha}, \qquad \alpha = x, y, z, \tag{64}$$

$$n\,\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{3}{2}\,\Theta\right) = 0 \tag{65}$$

(in hydrodynamics it is usually assumed that $P^{(0)} = P^{(0)}(n, \Theta)$ rather than $n = n(P^{(0)}, \Theta)$, but currently this does not concern us).

The BBGKY hierarchy can also be used for deriving, apart from the equations of balance in n, $\mathbf{c}$ and Θ, the equation of balance for the local entropy (38), as well as a number of other relations, like the equation of balance of potential energy $e^{(\Phi)}$:

$$n\,\frac{\mathrm{d}e^{(\Phi)}}{\mathrm{d}t} = -\frac{\partial I_\alpha^{(\Phi)}}{\partial r_\alpha}. \tag{66}$$

Now what information do they carry? Using equation (56), which defines $\mathscr{G}_{(1)}$ in the zero approximation, and the expressions which link $\mathbf{I}^{(s)}$, $\mathbf{I}^{(\Phi)}$ and q to the distribution functions, it is easy to show that in the zero approximation these equations assume the form

†Generally speaking, the equations in the BBGKY hierarchy ought to involve also the mass velocity $\mathbf{c}(\mathbf{r}, t)$. In the zero approximation in ε, however, this velocity is assumed to be constant, and, according to Galileo's relativity principle, the physical properties of a system do not depend on the constant velocity at which this system is moving.

‡I would like to remind once more that n, $\mathbf{c}$ and Θ are precisely those parameters which are assumed to be fixed when one formulates the notion of 'the ensemble of Gibbs copies'.

$$n\,\frac{\mathrm{d}e^{(\Phi)}}{\mathrm{d}t}=0\,,\qquad n\,\frac{\mathrm{d}s}{\mathrm{d}t}=0\,,\tag{67}$$

where

$$n\,\frac{\mathrm{d}A}{\mathrm{d}t}=\frac{\partial(nA)}{\partial t}+\frac{\partial(c_\alpha nA)}{\partial r_\alpha}$$

and A may denote both $e^{(\Phi)}$ and s. So it turns out that in the zero approximation in ε the isolines of Θ, $e^{(\Phi)}$ and s are kind of frozen into the corresponding elements of the volume of the fluid δV, and drift in the space together with these elements. This implies that the moving isolines of the internal energy

$$e=\frac{3}{2}\,\Theta+e^{(\Phi)}$$

and the entropy s *do not obey* the laws of thermodynamics derived in Section 6. Indeed, assume that at the time $t=0$ the functions $\Theta(\mathbf{r},0)$, $e^{(\Phi)}(\mathbf{r},0)$ and $s(\mathbf{r},0)$ were constant over the volume of the system. From Eqn (67) it follows that they will remain constant at any other time $t>0$. On the other hand, from thermodynamics it follows that

$$\mathrm{d}e=\frac{\Theta}{k_\mathrm{B}}\,\mathrm{d}s+P^{(0)}\,\frac{\mathrm{d}n}{n^2}\,,$$

which complies with the condition $\mathrm{d}e=\mathrm{d}s=0$ only if $\mathrm{d}n=0$. The condition $\mathrm{d}n=0$, however, can only be satisfied in the approximation of incompressible fluid; in the more realistic models of matter we have $n(\mathbf{r},t)=\mathrm{var}$, and the thermodynamic relations are incompatible with the transport equations. This incompatibility is not accidental.

The cause of incompatibility is that the processes described by the transport equations and the evolution of thermodynamic parameters develop on different time scales. We shall consider this in greater detail in Section 9; currently we just note that, by definition, all the processes in the closed isolated systems (which are the only object of our interest) end by the time $t=T$, where T is the time of relaxation of the system towards equilibrium. At the same time, the changes in the thermodynamic parameters, which are dealt with in thermodynamics, take place without violating the thermodynamic equilibrium. This is only possible as long as they occur over the time $\delta t\gg T$. This is the reason why the thermodynamic phenomena just do not have enough time to manifest themselves before the transport processes are through. In other words, we must forget about thermodynamics when studying the transport processes. At first this statement may seem too radical. Recall, however, that all macroscopic parameters in thermodynamics are functions of n and Θ, and that thermodynamics establishes certain linkage between the increments of these parameters. If we had taken this linkage into account, the system of transport equations would have been overdetermined, and would therefore have no solution. Thus, in the zero approximation in ε (that is, in the Eulerian approximation) we must forget about equations of balance (67).

And one final remark is as follows. We saw that the one-particle distribution function must satisfy the normalisation condition

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

(see Eqn (31)). In the thermodynamic limit $N=\infty$, and the normalisation condition becomes meaningless. Its place is taken over by the system of transport equations which defines the values of density n at any point $\mathbf{r}$ and at any time t. The structure of transport equations is such that their solutions automatically satisfy all global conservation laws, including the law of conservation of particles (which implies satisfying the same normalisation condition).

7.2 BBGKY hierarchy in the first order in ε

In this approximation, equation (47) for $\omega^{(1)}$ takes on the form

$$\frac{\partial\omega_1^{(0)}}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial\omega_1^{(0)}}{\partial\mathbf{r}_1}=-\mathbf{F}_{(1)}^{(1)}\cdot\frac{\partial\omega_1^{(0)}}{\partial\mathbf{p}_1}+\eta_{(1)}^{(1)}\,.\tag{68}$$

We are going to solve this equation by the method used by Chapman and Enskog for solving the Boltzmann equation. Since, according to Eqn (55),

$$\omega^{(0)}=\ln\frac{n(\mathbf{r},t)}{n_0}-\frac{\left[\mathbf{p}-m\mathbf{c}(\mathbf{r},t)\right]^2}{2m\Theta(\mathbf{r},t)}\,,\tag{69}$$

we may differentiate this expression with respect to t to eliminate the time derivative $\partial\omega^{(0)}/\partial t$ from Eqn (68). With this purpose, we differentiate Eqn (69) with respect to t, and use the earlier obtained Euler equations to replace the derivatives $\partial n/\partial t$, $\partial\mathbf{c}/\partial t$ and $\partial\Theta/\partial t$ with the derivatives with respect to $\mathbf{r}$. As a result, after some cumbersome calculations we arrive at the following expression:

$$\begin{aligned}\frac{\partial\omega_1^{(0)}}{\partial t}+\frac{\mathbf{p}_1}{m}\cdot\frac{\partial\omega_1^{(0)}}{\partial\mathbf{r}_1}&=\left\{1-\frac{1}{\Theta}\left(\frac{\partial P^{(0)}}{\partial n}\right)_\Theta\right\}\frac{\hat{p}_\alpha}{m}\,\frac{1}{n}\,\frac{\partial n}{\partial r_\alpha}\\&+\left\{\frac{\hat{p}^2}{2m\Theta}-\frac{1}{n}\left(\frac{\partial P^{(0)}}{\partial\Theta}\right)_n\right\}\frac{\hat{p}_\alpha}{m}\,\frac{1}{\Theta}\,\frac{\partial\Theta}{\partial r_\alpha}\\&+\frac{\hat{p}_\alpha\hat{p}_\beta}{m\Theta}\,D_{\alpha\beta}+\left(\frac{\hat{p}^2}{m\Theta}-1\right)\frac{1}{3}\,\frac{\partial c_\alpha}{\partial r_\alpha}\\&=\sum_{k=1}^{4}X^{(k)}x^{(k)}\,,\end{aligned}\tag{70}$$

where $\hat{\mathbf{p}}=\mathbf{p}-m\,\mathbf{c}$, $x^{(k)}$ are the gradients of hydrodynamic variables,

$$x^{(1)}=\frac{\partial n}{\partial\mathbf{r}}\,,\quad x^{(2)}=\frac{\partial\Theta}{\partial\mathbf{r}}\,,\quad x_{\alpha\beta}^{(3)}=D_{\alpha\beta}\,,\quad x^{(4)}=\frac{\partial c_\alpha}{\partial\mathbf{r}_\alpha}\,,$$

$X^{(k)}$ are the corresponding coefficients from Eqn (70), and

$$D_{\alpha\beta}=\frac{1}{2}\left(\frac{\partial c_\alpha}{\partial r_\beta}+\frac{\partial c_\beta}{\partial r_\alpha}\right)$$

is the velocity deformation tensor.

Observe now that the equations of the first order in ε are linear with respect to the unknown variables $\omega^{(1)}$ and $\Omega_{(l)}^{(1)}$. Accordingly, their solution may be sought as a sum of the four solutions,

$$\omega^{(1)}=\sum_{k=1}^{4}\psi_1^{(k)}\,x^{(k)}\,,\qquad\Omega_{1,\ldots,l}^{(1)}=\sum_{k=1}^{4}\Psi_{1,\ldots,l}^{(k)}\,x^{(k)}\,,\tag{71}$$

where $\psi^{(k)}$ and $\Psi_{(l)}^{(k)}$ are new unknown functions. Substituting these expressions into Eqn (68), we come to the set of four equations for $\psi_1^{(k)}$:

$$X^{(k)}=-\mathbf{F}_{(1)}^{(k)}\cdot\frac{\hat{\mathbf{p}}_1}{m}+\eta_{(1)}^{(k)}\,,\tag{72}$$

which, of course, must be supplemented by the relevant equations for $\Psi^{(k)}_{(l)}$, $l = 2, 3, \ldots, \infty$.

7.3 Comments

This section contains two nontrivial results: the first is that the transport equations are incompatible with the relations of thermodynamics, and the second is Eqn (71) which tells us that the general solution of the BBGKY hierarchy in the first order in ε is a sum of four particular solutions, each of which is proportional to its own gradient. This is a consequence of the fact that the equations of the first order in ε are linear with respect to the unknown functions $\omega^{(1)}$ and $\Omega^{(1)}_{(l)}$. Since this linearity with respect to $\omega^{(k)}$ and $\Omega^{(k)}_{(l)}$ remains in the k approximation in ε, this additivity is the universal property of the sought-for solution.

8. Transport equations

8.1 Navier–Stokes–Fourier transport equations

In order to obtain the transport equations in the first order in ε, we must go back to the exact equations of balance of number of particles (35), momentum (36), and temperature (37). Like in the case of the Euler equations, the derivatives of hydrodynamic variables on the left-hand side of these equations need not be expanded because they are equal to their exact values; we only expand the right-hand sides of the equations of balance which involve the stress tensor $P_{\alpha\beta}$ and the heat flux $\mathbf{J} = \mathbf{J}^{(\Theta)} + \mathbf{J}^{(\Theta\Phi)}$. For example, let us consider the kinetic component of the heat flux $\mathbf{J}^{(\Theta)}$, which, as we readily surmise, has the form

$$\mathbf{J}^{(\Theta)} = n_0 \int_{-\infty}^{\infty} \frac{\hat{\mathbf{p}}}{m} \frac{\hat{p}^2}{2m} \mathscr{G}_{(1)}(\mathbf{r}, \mathbf{p}, t) \frac{\mathrm{d}^3 p}{\mathcal{P}^3}, \quad \hat{\mathbf{p}} = \mathbf{p} - m\mathbf{c}. \tag{73}$$

Substituting here $\mathscr{G}_{(1)} = \mathscr{G}^{(0)}_{(1)}(1 + \varepsilon\omega^{(1)})$ and using $\mathscr{G}^{(0)}_{(1)}$ as defined by Eqn (55), we get

$$\mathbf{J}^{(\Theta)} = n \int_{-\infty}^{\infty} \frac{\hat{\mathbf{p}}}{m} \frac{\hat{p}^2}{2m} \exp\left(-\frac{\hat{p}^2}{2m\Theta}\right) \frac{\mathrm{d}^3 p}{\mathcal{P}^3} + n \int_{-\infty}^{\infty} \frac{\hat{\mathbf{p}}}{m} \frac{\hat{p}^2}{2m} \exp\left(-\frac{\hat{p}^2}{2m\Theta}\right) \omega^{(1)} \frac{\mathrm{d}^3 p}{\mathcal{P}^3}. \tag{74}$$

The first integral on the right-hand side is zero because of the odd function $\mathbf{p}$ in the integrand; with the aid of Eqn (71) the second integral can be represented as a sum of four integrals:

$$J^{(\Theta)}_{\alpha} = -\tilde{\mu}^{(n)} \frac{\partial n}{\partial r_\alpha} - \tilde{\mu}^{(\Theta)} \frac{\partial \Theta}{\partial r_\alpha} - \tilde{\mu}^{(D)}_{\beta} D_{\alpha\beta} - \tilde{\mu}^{(c)}_{\alpha} \frac{\partial c_\gamma}{\partial r_\gamma}, \tag{75}$$

where, for example,

$$\tilde{\mu}^{(n)} = -n \int_{-\infty}^{\infty} \frac{\hat{\mathbf{p}}}{m} \frac{\hat{p}^2}{2m} \exp\left(-\frac{\hat{p}^2}{2m\Theta}\right) \boldsymbol{\psi}^{(1)}(\hat{\mathbf{p}}) \frac{\mathrm{d}^3 p}{\mathcal{P}^3} \tag{76}$$

(the remaining coefficients are obtained from Eqn (76) by replacing $\boldsymbol{\psi}^{(1)}_1$ with $k = 2, 3, 4$).

It is easy to demonstrate that the gradients in the expansions of $P_{\alpha\beta}$ and $\mathbf{J}^{(\Theta\Phi)}$ can be factored out of the integrals. As a result, we get

$$P_{\alpha\beta} = \delta_{\alpha\beta} P^{(0)} - \lambda^{(n)}_{\alpha} \frac{\partial n}{\partial r_\beta} - \lambda^{(\Theta)}_{\alpha} \frac{\partial \Theta}{\partial r_\beta} - \lambda^{(D)} D_{\alpha\beta} - \lambda^{(c)}_{\alpha\beta} \frac{\partial c_\gamma}{\partial r_\gamma},$$

$$J_\alpha = -\mu^{(n)} \frac{\partial n}{\partial r_\alpha} - \mu^{(\Theta)} \frac{\partial \Theta}{\partial r_\alpha} - \mu^{(D)}_{\beta} D_{\alpha\beta} - \mu^{(c)}_{\alpha} \frac{\partial c_\gamma}{\partial r_\gamma}, \tag{77}$$

where $\mu^{(n)} = \tilde{\mu}^{(n)} + \tilde{\tilde{\mu}}^{(n)}$, etc.

In the case of multicomponent systems these relations must be supplemented by similar formulas for the mass flow of each component.

It is obvious that the above transport coefficients λ and μ are functions of n and Θ. At the same time, they exhibit no explicit dependence on $\mathbf{r}$ and t; the dependence on the latter is parametrical, since $n = n(\mathbf{r}, t)$ and $\Theta = \Theta(\mathbf{r}, \mathbf{t})$.

Substituting Eqn (77) into the initial equation of balance, we get the generalised system of Navier–Stokes–Fourier (NSF) transport equations, which holds up to the terms of the order of ε^2:

$$\frac{\partial n}{\partial t} - \frac{\partial (c_\alpha n)}{\partial r_\alpha} = 0, \tag{78}$$

$$n \frac{\mathrm{d}(mc_\alpha)}{\mathrm{d}t} = -\frac{\partial P^{(0)}}{\partial r_\alpha} + \frac{\partial}{\partial r_\beta}\left(\lambda^{(n)}_{\alpha} \frac{\partial n}{\partial r_\beta}\right) + \frac{\partial}{\partial r_\beta}\left(\lambda^{(\Theta)}_{\alpha} \frac{\partial \Theta}{\partial r_\beta}\right) + \frac{\partial}{\partial r_\beta}\left(\lambda^{(D)} D_{\alpha\beta}\right) + \frac{\partial}{\partial r_\beta}\left(\lambda^{(c)}_{\alpha\beta} \frac{\partial c_\gamma}{\partial r_\gamma}\right), \tag{79}$$

$$n \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{3}{2}\Theta\right) = \frac{\partial}{\partial r_\alpha}\left(\mu^{(n)} \frac{\partial n}{\partial r_\alpha}\right) + \frac{\partial}{\partial r_\alpha}\left(\mu^{(\Theta)} \frac{\partial \Theta}{\partial r_\alpha}\right) + \frac{\partial}{\partial r_\alpha}\left(\mu^{(D)}_{\beta} D_{\alpha\beta}\right) + \frac{\partial}{\partial r_\alpha}\left(\mu^{(c)}_{\alpha} \frac{\partial c_\gamma}{\partial r_\gamma}\right). \tag{80}$$

In the case of multicomponent systems, these equations must be supplemented by equations of conservation of mass of the i component, which are similar in structure to Eqn (80).

8.2 Comments

In a sense, the NSF equations are the culmination of the theory. Accordingly, they deserve a lengthier comment.

The first thing that draws our attention is that the transport equations constitute a unified closed set of five equations in five unknown hydrodynamic variables n, c_α and Θ. This is only natural, since each of these has the meaning of a conservation law: Eqn (78) is the conservation of mass (number of particles), Eqn (79) is the conservation of momentum and Eqn (80) expresses the conservation of kinetic energy of thermal chaotic motion of particles (temperature). Obviously, these three laws must hold simultaneously for any macroscopic process, which is ensured by the system of transport equations. It is interesting that the entropy does not figure among the 'fundamental' hydrodynamic variables, since, unlike the mass, the momentum and the temperature, it is not conserved (see the equation of entropy balance (38) which includes the entropy source q). In other words, the local entropy is no longer an integral of motion. As noted above, the reason is that the correlation sphere, which determines all the local parameters of matter, is an open system which continuously exchanges particles, momentum and energy with the environment. The principle of conservation of entropy only holds for closed (completely isolated) systems.

No less important is the fact that the system of transport equations, together with equations of the BBGKY hierarchy, gives a complete description of the system. Indeed, having

solved the transport equations and found n and Θ, one can use the equations of the equilibrium theory to find the distribution functions in the zero order in ε which allow calculating all thermodynamic parameters of the system. Then, having solved the first-order equations with the known n and Θ, one can calculate all coefficients of transfer with the aid of formulas of the type of Eqn (76).

From practical point of view, however, more important is the fact that our system of transport equations is somewhat different from the commonly used equations, since each of the equations of our system involves terms containing the gradients of *all* hydrodynamic variables (recall that the conventional Navier–Stokes equation contains terms proportional only to $D_{\alpha\beta}$ and $\partial c_\gamma/\partial r_\gamma$, and the conventional Fourier heat transfer equations involves only the term with $\partial\Theta/\partial\mathbf{r}$). This implies that our equations describe cross effects, neglected by the conventional transport equations.

The above derivation of transport equations also clarifies their physical meaning. For example, the heat transfer equation (80) is usually treated as the equation of balance of heat, whose increment is given by

$$\delta Q = \int_{\Theta_0}^{\Theta} C_V(n, \Theta)\, \mathrm{d}\Theta\,, \tag{81}$$

where

$$C_V = \frac{\Theta}{k_\mathrm{B}} \left(\frac{\partial s}{\partial \Theta}\right)_n$$

is the heat capacity at constant volume. Actually, Eqn (80) has the meaning of the equation of balance of temperature — that is, of the kinetic energy of thermal chaotic motion of particles — and does not involve C_V.

Observe finally that all the results obtained above are based on the expansion in $\varepsilon = R_\mathrm{c}/L$. Alternatively, this expansion may be regarded as expansion in the gradients of hydrodynamic variables, because the zero approximation in ε corresponds to n, $\mathbf{c}$ and $\Theta = \mathrm{const}$, the first approximation in ε corresponds to the linear values of these gradients, and so on.

9. The second law of thermodynamics

Our discussion of the theory of nonequilibrium processes would have been incomplete if we had not touched upon the problem of entropy increase. Early in this century this problem attracted keen attention; these days the interest has subsided considerably, not because the problem had been solved, but rather because everyone got used to the thought that this problem has no solution†. I believe, however, that such pessimism is hardly justified. In order to explain, however, how one can marry up the two seemingly incompatible statements — the conservation of entropy which follows from the laws of mechanics, and the entropy increase according to the second law of thermodynamics — it is necessary to perform a comprehensive analysis of foundations of the latter. This is what we are going to do.

9.1 Static and dynamic processes

The first and the second laws of thermodynamics are sometimes supplemented by the so-called 'zero law', which states that *any closed isolated system gradually evolves to the state of thermodynamic equilibrium, and in no circumstances will spontaneously* (*that is, without external aid*) *leave it*.

As a matter of fact, this law is equivalent to the second law, because it establishes the direction of evolution of the system. We shall see that it is this formulation of the second law that is better suited for the purposes of statistical mechanics.

Assume that the equilibrium mentioned in the zero law is established over the time T (time of relaxation of the system towards equilibrium). This time marks a natural watershed between two types of processes, the static processes and the dynamic ones. Obviously, if at $t = t_0$ we start to change the external parameters of the system (volume V, surface temperature Θ^s, etc.), this will eventually result in the exchange of energy between the system and the environment. This exchange may proceed either very slowly — over the time

$$\delta t = t - t_0 \gg T \tag{82}$$

(quasistatic, or, for short, static processes), or quickly — over the time

$$\delta t = t - t_0 \lesssim T \tag{83}$$

(dynamic processes). In the first case the system, having received a dose of external energy $\mathrm{d}E^\mathrm{ext}$, has enough time to come back to the state of thermodynamic equilibrium, which implies that constant pressure n and constant temperature Θ are established throughout the entire volume of the system. Since all thermodynamic parameters of the system at equilibrium are functions of n and Θ, we can make a more general statement: in the course of static processes, the values of all thermodynamic parameters of the system are always constant throughout its volume and therefore do not depend on the spatial coordinate $\mathbf{r}$. Of course, the parameters still depend on the time t, because otherwise nothing would have changed in the system, and the system would have been at absolute rest. In static processes the functions

$$n = n(t), \qquad \Theta = \Theta(t) \tag{84}$$

may be arbitrary, since they are governed by the external parameters of the system. It is only important that they change slowly:

$$\frac{1}{n}\,\frac{\mathrm{d}n}{\mathrm{d}t} \ll \frac{1}{T}\,, \qquad \frac{1}{\Theta}\,\frac{\mathrm{d}\Theta}{\mathrm{d}t} \ll \frac{1}{T}\,. \tag{85}$$

If all thermodynamic parameters are constant throughout the volume of the system V, then the gradients of all thermodynamic parameters in the course of static processes are always equal to zero,

$$\frac{\partial n}{\partial \mathbf{r}} = \frac{\partial \Theta}{\partial \mathbf{r}} = \frac{\partial P^{(0)}}{\partial \mathbf{r}} = \ldots = 0\,, \tag{86}$$

which in turn implies that static processes do not give rise to any transport processes (recall that the flows of mass, momentum and energy are always proportional to the gradients of hydrodynamic variables; if the gradients are zero, the flows are zero as well). Thus, in the course of static processes the energy is only exchanged with the environment, which is the agency that gives rise to all processes that take place in the system. There is no exchange of energy between different parts of the system itself. Because of this, each elementary volume of the system δV is practically isolated

†To quote from Landau and Lifshits, "It is unlikely ... that the law of entropy increase could ever be derived on the basis of classical mechanics" [4].

from the rest, and the system seems to consist of separate 'bricks' which do not interact with one another.

Of course, gradients exist in the system no matter how slow the action is, because otherwise the disturbance would not be able to propagate across the volume of the system, and so our neglect of the gradients is an idealisation. However, as implied by the transport equations and convincingly confirmed by experiments, this idealisation is the closer to reality, the slower the exchange of energy with the environment is; it becomes perfectly true in the limit of infinitely slow processes.

If the processes of exchange with the environment are fast enough (that is, if conditions (85) do not hold), then the gradients can no longer be neglected. The nature of all effects is changed dramatically, since the existence of gradients gives rise to the flows of mass, momentum and energy — that is, the exchange processes between adjacent elements of the volume of the system δV. As a result, the additivity, which is characteristic of the static processes, is violated, the system ceases to be a collection of noninteracting 'bricks' and becomes a whole. Each of the 'bricks' δV contributes to the evolution of the other 'bricks' $\delta V'$. It is important that this contribution depends not only on the state of $\delta V'$ at the given time t, but also on its state at the earlier times $t' < t$, because the signal from $\delta V'$ reaches δV with a certain lag. Because of this, the system becomes sluggish, the external perturbation propagates at a finite speed — in other words, we observe effects which were not present in case of static processes. In essence, this is explained by the fact that the response of the system to fast dynamic action is determined by those degrees of freedom of the system which had been blocked in case of slow static processes. This is the reason why, for example, the concept of transfer coefficients is not used in the theory of equilibrium processes: they have no effect on the properties of equilibrium systems. We start our analysis of dynamic and static processes with the latter.

9.2 Global static entropy

In thermodynamics, the system under investigation is regarded as a kind of 'black box' capable of exchanging energy with the environment. Only a small number of the external parameters of the system is assumed to be known: the volume V, the surface temperature Θ^{s}, the amount of energy supplied to the system $\mathrm{d}E^{\mathrm{ext}}$, etc. The task of thermodynamics is to gain as much information about the 'black box' as possible with the minimum number of assumptions on the properties of matter inside the box. In case of static processes this is done with the aid of the energy conservation law (the first law of thermodynamics).

The energy conservation law states that the external energy $\mathrm{d}E^{\mathrm{ext}}$ supplied to the body is always equal to the increment of the internal energy $\mathrm{d}E^{\mathrm{int}}$. Assuming that $\mathrm{d}E^{\mathrm{ext}} = \mathrm{d}W + \mathrm{d}Q$, where $\mathrm{d}W$ is the mechanical work, and $\mathrm{d}Q$ is the heat, we get

$$\mathrm{d}E^{\mathrm{ext}} = \mathrm{d}W + \mathrm{d}Q = \mathrm{d}E^{\mathrm{int}}_{(N)} \,. \tag{87}$$

It is proved in thermodynamics and confirmed by statistical mechanics that

$$\Theta\, \mathrm{d}S_{(N)}\big|_V = k_{\mathrm{B}}\, \mathrm{d}E^{\mathrm{int}}_{(N)} \,. \tag{88}$$

Since $\mathrm{d}W = 0$ when $\mathrm{d}V = 0$, we combine Eqn (87) and (88) to get

$$\mathrm{d}S_{(N)}\big|_V = k_{\mathrm{B}}\, \frac{\mathrm{d}Q}{\Theta} \,. \tag{89}$$

Now we use Eqn (89) to eliminate $\mathrm{d}Q$ from Eqn (88) and obtain the final formulation of the first law of thermodynamics:

$$\Theta\, \mathrm{d}S = k_{\mathrm{B}}\big(\mathrm{d}E^{\mathrm{int}}_{(N)} + \mathrm{d}W\big) \,. \tag{90}$$

If we now compare the resulting expression for the increment of entropy with the second law of thermodynamics, we immediately see that it is the 'wrong' entropy. Indeed, by the second law of thermodynamics the entropy can only increase, whereas the static entropy $S_{(N)}$ as defined by Eqn (90) may either increase or decrease depending on whether we supply heat to the body ($\mathrm{d}Q > 0$) or take it away ($\mathrm{d}Q < 0$). Therefore, let us continue our analysis.

9.3 Global dynamic entropy

So far we have been considering open systems capable of exchanging energy with the environment throughout the entire time taken by a given process. Let us now turn to closed isolated systems which can only host spontaneous processes leading to thermodynamic equilibrium (the zero law of thermodynamics). By definition, that latter are always dynamic processes since they come to an end by the time $t = T$, where T is the relaxation time. Because of this, the analysis of closed isolated systems is equivalent to the analysis of dynamic processes.

We start with a more precise definition of the concept of a 'closed system'. Systems which are once and for all isolated from the outside world are of no interest to us because they always are in the state of thermodynamic equilibrium (any deviations would have long relaxed to equilibrium). Therefore, the term 'closed isolated systems' will refer to such systems which are 'closed' for external action only for the duration of the dynamic processes — that is, at $0 \leqslant t \leqslant T$. At $t < 0$ the system is assumed to be open, which allows us to use external forces for 'preparing' the desired initial distribution (generally speaking, nonequilibrium). We also assume that the system is open after the process is through (at $t > T$), which will permit us to study the outcome of the process. In this way, our system is a 'black box' only at $0 \leqslant t \leqslant T$, at all other times it is open. This definition of the 'black box' obviously differs from the one we used in Section 8. Such systems, however, are of special interest to us, because it is only such systems that are considered by nonequilibrium statistical mechanics (see Section 3).

So, let us consider a closed system, in which by the time $t = 0$ we have 'prepared' a nonequilibrium initial state. When we 'close' the system, it begins to evolve spontaneously from the initial (nonequilibrium) state to the final equilibrium state. Its total energy E remains constant in the course of this evolution, and the work W done by the system on the external bodies is zero. According to (90), the increment of global entropy $\mathrm{d}S_{(N)}$ in such process must also be equal to zero. Thermodynamics, however, argues (and this is confirmed experimentally) that by the time $t = T$ the entropy of the system always increases. This statement can be easily proved: when the system comes to equilibrium and is 'opened' again, we can bring it back to the initial state using quasistatic (that is, infinitely slow) action and compare its initial entropy $S^{(0)}_{(N)}$ with the final entropy $S_{(N)}$. The result will always be the same:

$$\delta S_{(N)} = S_{(N)} - S_{(N)}^{(0)} > 0\,. \tag{91}$$

How can we explain this? I believe that there is only one answer: the energy conservation law in the form of Eqn (90) only holds for infinitely slow static processes, whereas a closed system, by definition, can only host fast dynamic processes. The arising contradiction can only be explained by the different rates of static and dynamic processes.

To formalise this statement, we introduce the concept of a certain infinitely large time $T_\infty = \infty$ which can be identified with the time of completion of the static process. It is obvious that

$$\tau \ll T \ll T_\infty\,, \tag{92}$$

where τ is the characteristic microscopic time, and T is the macroscopic time of relaxation of the system towards equilibrium. The superfast microscopic evolution towards equilibrium within the correlation sphere occurs at $t \lesssim \tau$, the dynamic processes in the macroscopic system take place on the scale of

$$\tau \lesssim t \lesssim T \tag{93}$$

and superslow static processes correspond to

$$T \ll t \ll T_\infty \tag{94}$$

Accordingly the global entropy can be split into two parts:

$$S_{(N)}(t) = S_{(N)}^{\mathrm{st}}\left(\frac{t}{T_\infty}\right) + S_{(N)}^{\mathrm{din}}\left(\frac{t}{T}\right). \tag{95}$$

If t satisfies inequality (93), then $t/T_\infty \simeq 0$, $S_{(N)}^{\mathrm{st}}(t/T_\infty) \simeq S_{(N)}^{\mathrm{st}}(0) \simeq \mathrm{const}$, whereas $S_{(N)}^{\mathrm{din}}(t/T) = \mathrm{var}$. In this case

$$\mathrm{d}S_{(N)}(t) = \mathrm{d}S_{(N)}^{\mathrm{din}}\left(\frac{t}{T}\right) > 0\,, \qquad \mathrm{d}S_{(N)}^{\mathrm{st}}\left(\frac{t}{T_\infty}\right) = 0\,. \tag{96}$$

If t satisfies inequality (94), then, conversely, $S_{(N)}^{\mathrm{din}}(t/T) \simeq S_{(N)}^{\mathrm{din}}(\infty) = \mathrm{const}$, and

$$\mathrm{d}S_{(N)}(t) = \mathrm{d}S_{(N)}^{\mathrm{st}}\left(\frac{t}{T_\infty}\right) = \frac{k_{\mathrm{B}}}{\Theta}\left\{\mathrm{d}E_{(N)}^{\mathrm{int}}\left(\frac{t}{T_\infty}\right) + \mathrm{d}W\left(\frac{t}{T_\infty}\right)\right\}, \qquad \mathrm{d}S_{(N)}^{\mathrm{din}} = 0\,. \tag{97}$$

We see that Eqn (95) unites both laws of thermodynamics. The assumed additivity of static and dynamic entropies is the consequence of the fact that different degrees of freedom of the system are responsible for static and dynamic processes (see Section 11).

9.4 Local dynamic entropy

Let us define the local dynamic entropy by an obvious relation

$$S_{(N)}^{\mathrm{din}}\left(\frac{t}{T}\right) = \int_V n\left(\frac{\mathbf{r}}{L}\,,\,\frac{t}{T}\right) s^{\mathrm{din}}\left(\frac{\mathbf{r}}{L}\,,\,\frac{t}{T}\right) \mathrm{d}^3 r\,. \tag{98}$$

In the course of dynamic processes the local entropy can not only move from one location to another, it can also be generated, since otherwise it would be impossible to satisfy the inequality $\mathrm{d}S_{(N)}^{\mathrm{din}} > 0$. Therefore, the equation of balance of local dynamic entropy (cf. Eqn (38)) *is postulated* in thermodynamics of irreversible processes:

$$n\,\frac{\mathrm{d}s^{\mathrm{din}}}{\mathrm{d}t} = -\frac{\partial I_\alpha^{\mathrm{din}}}{\partial r_\alpha} + q^{\mathrm{din}}\,. \tag{99}$$

Integrating the latter over the volume of the system V, we get

$$\frac{\partial S_{(N)}^{\mathrm{din}}}{\partial t} = \int_V q^{\mathrm{din}}\left(\frac{\mathbf{r}}{L}\,,\,\frac{t}{T}\right) \mathrm{d}^3 r > 0\,. \tag{100}$$

This inequality holds either when for any $\mathbf{r}$ and t we have

$$q^{\mathrm{din}}\left(\frac{\mathbf{r}}{L}\,,\,\frac{t}{T}\right) \geqslant 0\,, \tag{101}$$

or when

$$\int_{V_+} q_+\left(\frac{\mathbf{r}}{L}\,;\,\frac{t}{T}\right) \mathrm{d}^3 r > -\int_{-V} q_-\left(\frac{\mathbf{r}}{L}\,;\,\frac{t}{T}\right) \mathrm{d}^3 r\,, \tag{102}$$

where $q_+ \geqslant 0$, $q_- \leqslant 0$.

In the first case the chaos is assumed to grow at every point of the system; in the second case the global growth of chaos, as indicated by the general increase in the entropy, may be accompanied by a local advance of order (like the emergence of crystallisation nuclei in supercooled liquid, or creation of biological structures in solutions).

Inequality (101) is postulated in thermodynamics of nonequilibrium processes and held as something like a universal truth: since all the processes in Nature are accompanied by the increase in entropy, inequality $q > 0$ indicates the direction of their development (or, metaphorically, 'defines the arrow of time'). Undoubtedly, the global entropy of a closed isolated system will always increase. This does not mean, however, that the same applies to the local entropy. Moreover, this last statement cannot be proved within the framework of thermodynamics. Indeed, during the entire dynamic process, which is only when the entropy can be generated, the system remains closed for external action. At the same time, the values of global entropy measured *before* commencement and *after* completion of the dynamic process (that is, at $t < 0$ and $t > T$) tell us nothing about the changes of local entropy *in the course* of the process. Even if we 'opened' the system at $0 \leqslant t \leqslant T$, we could still say nothing about the behaviour of the local entropy, because the equilibrium thermodynamics does not supply us with the tools for measuring the entropy of nonequilibrium systems.

Statistical mechanics seems to favour the second (less trivial) assumption, because it states that the value of q is proportional to the first power of gradients of hydrodynamic variables (see Eqn (107)). So the sign of q may change when a gradient changes its sign (this matter, however, call for further investigation).

9.5 Entropy in statistical mechanics

Let us now try to compare thermodynamic and statistical entropies. The difficulty become obvious at once: it is only the global entropy that is clearly defined in thermodynamics; we know little about the local entropy. Conversely, in statistical mechanics the global entropy $S_{(N)}$ does not seem to exist: in the thermodynamic limit it goes to infinity, and the only entropy-like quantity is the local entropy $s(\mathbf{r}, t)$. Nevertheless, this juxtaposition is useful because it will help to clarify the physical meaning of the concept of entropy.

We shall start our discussion of entropy with the analysis of another integral of motion, the global internal energy $E_{(N)}$.

From the fact that this energy is always constant in closed isolated system it does not yet follow that the structure of this parameter remains unchanged in the course of dynamic processes. Indeed, substituting the definition of Hamiltonian (17) into Eqn (19) for $E_{(N)}$, we find that $E_{(N)}$ is the sum of the mean values of kinetic and potential energy. It is obvious that one kind of energy in nonequilibrium systems may transform into the other. Since, by definition, the kinetic energy is

$$E_{(N)}^{\text{kin}} \propto \int \frac{p^2}{2m}\, \mathscr{G}_{(1)}\, \mathrm{d}(1)\,,$$

and the potential energy is

$$E_{(N)}^{(\Phi)} \propto \int \Phi \mathscr{G}_{(2)}\, \mathrm{d}(1)\, \mathrm{d}(2)\,,$$

the conversion of one type of energy into the other must be accompanied by the redistribution of energy with respect to correlations. If we had defined the potential energy of the system $U_{(N)}$ not as a sum of the two-particle potentials, $U_{(N)} = \sum \Phi_{ij}$, but had included also the three-particle potentials Φ_{ijk}, four-particle Φ_{ijkl}, etc, setting

$$U_{(N)} = \sum_{ij} \Phi_{ij} + \sum_{ijk} \Phi_{ijk} + \ldots + \Phi_{1,\ldots,N}\,,$$

then the flow of energy would not have been cut short at the second correlation (that is, at $\mathscr{G}_{(2)}$), but rather would continue further up to $\mathscr{G}_{(N)}$.

So we see that a flow of energy with respect to correlations is possible in nonequilibrium closed systems. A similar flow arises in the case of entropy. To find it, we set

$$\Omega_{(N)} = \sum_{ij} \omega_{ij} + \sum_{ijk} \omega_{ijk} + \ldots + \omega_{1,\ldots,N}\,.$$

Substituting this expression into the definition of global entropy (21), we get

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

where

$$S^{(l)}(t) \propto \int \omega_{1,\ldots,l}\, \mathscr{G}_{1,\ldots,l}\, \mathrm{d}(1) \ldots \mathrm{d}(l)\,.$$

Differentiating $S^{(l)}$ with respect to t, and defining the derivatives $\partial \mathscr{G}_{(l)}/\partial t$ with the aid of the BBGKY hierarchy, we write the increment of the l-particle global entropy $S^{(l)}$ in the form

$$\frac{\mathrm{d}S^{(l)}}{\mathrm{d}t} = J^{(l-1)} - J^{(l)}\,,$$

where

$$J^{(l)} \propto \int \frac{\partial \Phi_{1,l+1}}{\partial \mathbf{r}_1} \cdot \frac{\partial \omega_{1,\ldots,l+1}}{\partial \mathbf{p}_1}\, \mathscr{G}_{1,\ldots,l+1}\, \mathrm{d}(1) \ldots \mathrm{d}(l+1)$$

and $J^{(0)} = J^{(N)} = 0$. Hence directly follows the law of conservation of global entropy (20), since

$$\frac{\mathrm{d}S_{(N)}}{\mathrm{d}t} = \sum_{l=1}^{N} \frac{\mathrm{d}S^{(l)}}{\mathrm{d}t} = \left(J^{(0)} - J^{(1)}\right) + \left(J^{(1)} - J^{(2)}\right) + \ldots + \left(J^{(N-1)} - J^{(N)}\right) = J^{(0)} - J^{(N)} = 0\,.$$

This is only natural, because the BBGKY hierarchy had been obtained from the Liouville equation.

Let us now introduce the concept of the local correlation entropy, which will be defined as

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

Differentiating $s^{(l)}$ with respect to t, and replacing the derivatives $\partial \mathscr{G}_{(l)}/\partial t$ with the aid of the appropriate equations of the BBGKY hierarchy, we get the local law of conservation of correlation entropy:

$$n\, \frac{\mathrm{d}s^{(l)}}{\mathrm{d}t} = -\frac{\partial I_\alpha^{(l)}}{\partial r_\alpha} + q^{(l)}\,.$$

Since the total local entropy is

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

and

$$\mathbf{I}^{(s)} = \sum_{l=1}^{N} \mathbf{I}^{(l)}\,, \qquad q^{(s)} = \sum_{l=1}^{N} q^{(l)}\,,$$

by adding together the equations in $\mathrm{d}s^{(l)}/\mathrm{d}t$ we get equation of balance (38) for the total local entropy (cf. also Eqn (99)).

We saw that all the processes are determined by what happens within the correlation sphere. This completely applies to the local entropy. Since the entropy $S^{(l)}$ is proportional to the integral of $\omega_{(l)}$, $S^{(l)}$ goes to zero at $l \geqslant M$, where M is the maximum number of particles within the correlation sphere, because $\omega_{(l)} = 0$. Therefore,

$$\frac{\mathrm{d}S^{(l)}}{\mathrm{d}t} = J^{(l-1)} - J^{(l)} = \int_V q^{(l)}(\mathbf{r}, t)\, \mathrm{d}^3 r = 0 \quad \text{at} \quad l \geqslant M\,.$$

Hence it follows that

$$\tilde{J} = J^{(l-1)} = J^{(l)} = \text{const} \qquad \text{at} \quad l \geqslant M\,.$$

The condition $J^{(l)} = \tilde{J}$, however, cannot be satisfied at $l = N$, because, by definition, $J^{(N)} = 0$. Therefore,

$$\frac{\mathrm{d}S^{(N)}}{\mathrm{d}t} = J^{(N-1)} = \tilde{J} \neq 0\,.$$

To better understand the physical meaning of this equation, we note that

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

and hence

$$\frac{\mathrm{d}S^{(N)}}{\mathrm{d}t} = -\sum_{l=1}^{N-1} \frac{\mathrm{d}S^{(l)}}{\mathrm{d}t} \simeq -\sum_{l=1}^{M} \frac{\mathrm{d}S^{(l)}}{\mathrm{d}t} = -\frac{\mathrm{d}S^{(M)}}{\mathrm{d}t}\,, \qquad (103)$$

where

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

We see that the N-particle correlation entropy consumes all the surplus entropy generated inside the correlation sphere — that is, at $l \leqslant M$. The source of entropy (the correlation sphere) turns out to be extremely far removed from the sink (the N-particle correlation), because $M \lesssim 10^3$, and $N \simeq 10^{23}$.

All intermediate correlations with the numbers $M < l < N - 1$ act as conduits of the entropy, which transmit the latter without loss from the source to the sink. It is important that the nature of the source and the sink is different: the capacity of the source depends on what is going on inside the correlation sphere, and the capacity of the sink is governed by the response of the entire system. Upon transition to the thermodynamic limit, the 'sink' goes to infinity and disappears. The remaining global entropy related to one particle needs no longer to be constant:

$$\bar{s}(t) = \lim_{N\to\infty} \sum_{l=1}^{M} \frac{S^{(l)}(t)}{N} = \mathrm{var}\,.$$

This removes the main obstacle in the way of the mechanistic foundation of the laws of thermodynamics: the mechanical entropy ceases to be a constant quantity.

Let us now return to the equation of balance of local entropy (38). Expanding this equation in ε, we found that $s^{(0)} = \mathrm{const}$ in the zero approximation. Since, however, the zero-approximation equation itself only holds when $t \lesssim T$ (this follows from the fact that equilibrium is established is a closed isolated system at $t \gtrsim T$, and Eqn (38) degenerates into an identity $0 = 0$), the condition $s^{(0)} = \mathrm{const}$ also holds only for $t \lesssim T$. When $t \gg T$ (that is, in the course of static processes), the local entropy may change. All this prompts us to identify the latter with the static entropy:

$$s^{(0)}(t) = s^{\mathrm{st}}\left(\frac{t}{T_\infty}\right). \tag{104}$$

At the same time, from Eqn (38) in the first order in ε it follows that

$$n\,\frac{\mathrm{d}s^{(1)}}{\mathrm{d}t} = -\frac{\partial I_\alpha^{(1)}}{\partial r_\alpha} + q^{(1)}\,.$$

Since this equation describes variations of the local entropy over distances of the order of L and time of the order of T, the function $s^{(1)}$ as defined by this equation must be identified with the dynamic entropy:

$$s^{(1)}(\mathbf{r},\,t) = s^{\mathrm{din}}\left(\frac{\mathbf{r}}{L}\,;\,\frac{t}{T}\right). \tag{105}$$

Thus, from the expansion in ε it follows that

$$s\,(\mathbf{r},\,t) = s^{\mathrm{st}}\left(\frac{t}{T_\infty}\right) + s^{\mathrm{din}}\left(\frac{\mathbf{r}}{L}\,;\,\frac{t}{T}\right), \tag{106}$$

which obviously coincides with the purely thermodynamic formula (95).

The above-defined global dynamic entropy $S_{(N)}^{\mathrm{din}} = N\bar{s}^{\,\mathrm{din}}$ may, of course, vary with the time. So far, however, we have no evidence that it always increases in accordance with the second law of thermodynamics. It does not seem likely, however, that any controversy could arise on this matter. Moreover, I believe that the proof of increasing entropy is not too important for the construction of self-consistent statistical theory.

As a matter of fact, in the first order in ε (as well as in all higher orders) the substitution of solution (71) of the BBGKY hierarchy into the right-hand side of Eqn (38) results in the expression

$$n\,\frac{\mathrm{d}s^{\mathrm{din}}}{\mathrm{d}t} = \sum_{k=1}^{4}\left\{-\frac{\partial}{\partial r_\alpha}\left(\gamma_{(k)}\,x^{(k)}\right) + q_{(k)}\,x^{(k)}\right\}, \tag{107}$$

in which $\gamma_{(k)}$ and $q_{(k)}$ are found by solving the BBGKY hierarchy in the first order in ε, and the gradients $x^{(k)}$ can be found from the transport equations. This implies that the right-hand side of Eqn (107) is a known function of $\mathbf{r}$ and t, and so the calculation of $s^{\mathrm{din}}(\mathbf{r},\,t)$ reduces to simply taking the integral with respect to t. The latter implies that the leading role in the tandem 'transport equations – entropy' belongs to the transport equations which define the right-hand side of Eqn (107) and thus the local entropy. If it can be proved that the transport equations admit solutions which comply with the zero law of thermodynamics, then we need not care about the entropy: it will always behave properly. In particular, from Eqn (107) it follows that when the system arrives at thermodynamic equilibrium and all the gradients vanish, the dynamic entropy also ceases to grow.

9.6 Comments

In equilibrium thermodynamics, the entropy $S_{(N)}$ and the internal energy $N_{(N)}$ are the two fundamental quantities, while in the theory of nonequilibrium phenomena the entropy occupies a secondary place. Why?

In mechanics there are just three quantities — the mass (the number of particles), the momentum and the energy — whose values must always be conserved. In addition, there is the entropy (the logarithm of the phase volume of the system) whose value must remain constant, but only in case of closed isolated systems. In open systems the entropy is not conserved. As a matter of fact, this gives the answer to our question.

At equilibrium, from transport equations, which have the meaning of conservation laws for mass, momentum and energy, it follows that the values of all five hydrodynamic variables (that is, n, c_α, and Θ) must be constant throughout the entire volume of the system. According to Galileo's relativity principle, however, the physical parameters of matter which is at rest in an inertial system of coordinates cannot depend on the velocity at which this system is moving. Therefore, the number of independent parameters which define the state of matter reduces from five to two, n and Θ. In particular, the local internal energy and the local entropy are also found to be functions of n and Θ: $e = e(n,\,\Theta)$, $s = s(n,\,\Theta)$. If n and Θ are constant, the global conservation laws for internal energy and entropy, which hold for any closed isolated system, are automatically satisfied.

Recall now that equilibrium thermodynamics is in fact always concerned with closed isolated systems, whose state is determined by three global parameters† N, $E_{(N)}$, and $S_{(N)}$. Since the local values of $e(n,\,\Theta)$ and $s(n,\,\Theta)$ are constant throughout the volume of the system, the equations $E_{(N)} = Ne$ and $S_{(N)} = Ns$ establish a one-to-one correspondence between global ($E_{(N)}$ and $S_{(N)}$) and local (e and s) parameters. Because of this, uniquely defined are also the derivatives of the global variables with respect to n and Θ, which are in fact the main subject of the science of thermodynamics. And since it is always possible to invert the equations $E_{(N)} = E_{(N)}(n,\,\Theta)$ and $S_{(N)} = S_{(N)}(n,\,\Theta)$, representing them as $n = n\,(E_{(N)},\,S_{(N)})$ and $\Theta = \Theta(E_{(N)}, S_{(N)})$, it is clear that the two global para-

†Of course, apart from $E_{(N)}$ and $S_{(N)}$, thermodynamics also deals with other characteristic functions. One must bear in mind, however, that they all are combinations of $E_{(N)}$ and $S_{(N)}$ (for example, the free energy is $\mathcal{F}_{(N)} = E_{(N)} - S_{(N)}(\Theta/k_{\mathrm{B}})$). Because of this, little is changed by switching to other characteristic functions.

meters $E_{(N)}$ and $S_{(N)}$ unambiguously define the state of the entire closed isolated system.

In nonequilibrium systems, the functions $n(\mathbf{r}, t)$ and $\Theta(\mathbf{r}, t)$ still define all parameters of matter at a given point $\mathbf{r}$. However, the linkage between these variables and e^{din} and s^{din} is not functional, as in the case of equilibrium, but integral:

$$\delta e^{\mathrm{din}} = \int_0^t \left\{ \mathbf{I}_{(l)}^{(1)} \cdot \frac{\partial n}{\partial \mathbf{r}} + \ldots \right\} \mathrm{d}t\,,$$

$$\delta s^{\mathrm{din}} = \int_0^t \left\{ \mathbf{I}^{(1)} \cdot \frac{\partial n}{\partial \mathbf{r}} + \ldots \right\} \mathrm{d}t$$

(see Eqn (107)). This dependence cannot be inverted, and we can no longer assume that, for example, $n = n(e^{\mathrm{din}}, s^{\mathrm{din}})$ — hence, there is no one-to-one correspondence between $e = e^{\mathrm{st}} + e^{\mathrm{din}}$, $s = s^{\mathrm{st}} + s^{\mathrm{din}}$ and the other parameters of the system. It follows that the fundamental (universal) dependence is the dependence of all parameters of matter on the density and the temperature, rather than on the internal energy and the entropy. As a result, the entropy loses its privileged position, and behind this downfall are the three conservation laws of classical mechanics (and Galileo's relativity principle).

10. Irreversibility of dynamic processes

There are at least two reasons why the problem of entropy increase attracts so much attention. First, it was not clear until now how to reconcile the increase in thermodynamic entropy, required by the second law of thermodynamics, with the constancy of mechanical entropy which follows from the Liouville theorem. Secondly, until now it was tacitly assumed that it is the increasing entropy that is the primary cause of irreversibility of dynamic processes.

The first issue was resolved when we demonstrated that the BBGKY hierarchy defines entropy in such a way that it must not necessarily remain constant (the term with source q in the equation of balance (38)). This does not conflict with the Liouville theorem, since the latter only holds for closed isolated systems, whereas the equation of balance (38) describes processes taking place within the correlation sphere which is an open system continuously exchanging particles, momentum and energy with the environment. Admittedly, there is no proof so far that the source of entropy q in the equation of balance (38) is always positive. It does not seem likely, however, that further studies are going to reveal any contradictions with thermodynamics.

The second issue is also settled, because, in accordance with Eqn (107), it is not the entropy that governs the transport processes, but the other way round. Hence it follows that the increase in entropy must only be regarded as a criterion of irreversibility of processes taking place in the system, and, as will be shown presently, not the only one. In essence, this criterion was promoted by thermodynamics to the rank of a law just because out of the three global parameters (N, $E_{(N)}$, and $S_{(N)}$) only the entropy is sensitive to the irreversibility.

10.1 Cause of irreversibility

So, the increasing entropy is not the cause of irreversibility. Then who is the culprit? Irreversibility is due to the properties of Newtonian equations which create chaos in unstable dynamic systems. In greater detail this issue was discussed in Section 2; here I will just briefly summarise our arguments.

Classical mechanics is based on two postulates: the Newtonian equations of motion and the assumption of the absolute accuracy of measurements (the latter is overlooked in all textbooks). If the second postulate is true (that is, the system is stable), then the evolution of the system is deterministic; otherwise the evolution is random, chaotic, and the entire picture is changed dramatically. The motion of particles in deterministic systems is described by their paths whose shape can be calculated in advance by solving the Cauchy problem for Newtonian equations. In case of nondeterministic systems we can only speak of the probability of a particle to occur at one part of space or another. This probability can be calculated only using the concept of ensemble of Gibbs copies.

The motion of particle along a path is reversible: if we revert its momentum at $t = t'$ (see Eqn 6)), it will retrace the same path back to the starting point. In chaotic systems, however, as demonstrated in Section 2, the particles after the turning point may go anywhere else but not to where they had started. Moreover, in the case of nondeterministic systems this reversal will have little effect in general on the evolution of the system, since the system on the average will always move from the less probable state to the more probable, regardless of the direction of motion of individual particles. In fact, this follows immediately from the Boltzmann formula $\mathcal{P}_{(N)} \sim \exp(N\bar{s}/k_{\mathrm{B}})$, since $\bar{s}(t)$ can only increase in closed isolated systems (here $S_{(N)} = N\bar{s}$)). Having attained the most probable value $\mathcal{P}_{\max}$, corresponding to $\bar{s} = \bar{s}_{\max}$, the system will remain in this state forever.

10.2 Irreversibility and expansion in ε

We see that the primary cause of irreversibility of macroscopic processes is chaos arising in dynamic systems. As I said before, however, both the Newtonian equations and the BBGKY hierarchy, which is a direct implication of the former, may describe both deterministic and chaotic systems. At the same time, the transport equations which follow from the BBGKY hierarchy only describe the chaotic systems, because they are time-irreversible. Indeed, from Eqn (32)–(34) it follows that if we replace t with $-t'$, and $\mathbf{p}$ with $\mathbf{p}'$, (see Eqn (6)), the hydrodynamic variables will be transformed according to

$$n(\mathbf{r}, t) \to n'(\mathbf{r}, -t')\,, \quad \mathbf{c}(\mathbf{r}, t) \to -\mathbf{c}'(\mathbf{r}, -t')\,,$$
$$\Theta(\mathbf{r}, t) \to \Theta'(\mathbf{r}, -t')\,. \tag{108}$$

If we now apply transformation (6) to the Euler equations, and take due account of Eqn (108), we find that the Euler equations remain the same. This means that they are time-reversible. If, however, the same transformation is applied to the generalised Navier–Stokes–Fourier equations, some of the terms will change sign, and some will not. As a result, the 'reverted' equation will differ from the initial one, and after the 'turnpoint' the system will never come back home — is has become irreversible. Obviously, this irreversibility has nothing to do with the entropy: it is a consequence of the expansion in ε, which has allows us to select the class of irreversible solutions out of all solutions of the BBGKY hierarchy.

10.3 Local criteria of irreversibility

If we may say so, the overall increase in the entropy of the system is a global criterion of irreversibility. In addition, it is possible to formulate local criteria of irreversibility on the basis of the zero law of thermodynamics.

Figure 4 shows a certain nonequilibrium distribution of density $n^{(\gamma)}(\mathbf{r}, t)$ of particles of kind γ in a multicomponent system. Since the total number of particles $N^{(\gamma)}$ remains unchanged in the course of diffusion, the equilibrium distribution established in the system at $t \to \infty$ must appear in the diagram as a horizontal straight line bisecting the curve $n^{(\gamma)}(\mathbf{r}, t)$ in such a way that the hatched areas above and below $n_0^{(\gamma)}$ are equal to each other (otherwise the particles in the area of excess would be not sufficient to make up for the deficit of particles in the depleted area). In order that the process should be directed towards equilibrium, the particles must drift from the area of excess to the depleted area. In the case of the state shown in Fig. 4, this is only possible if the diffusion flux

$$\mathbf{I}^{(\gamma)} = -D^{(\gamma)} \frac{\partial n^{(\gamma)}}{\partial \mathbf{r}}$$

is directed counter to the density gradient. It is easy to see that $\mathbf{I}^{(\gamma)} < 0$ only when the coefficient of diffusion $D^{(\gamma)}$ is positive. Similarly, one can show that the coefficients of heat conduction $\mu^{(\Theta)}$ and viscosity $\lambda^{(D)}$ in the expressions for the flux of temperature and the flux of momentum are also positive. As a result, we come to inequalities

$$D > 0, \qquad \mu^{(\Theta)} > 0\,, \qquad \lambda^{(D)} > 0\,, \tag{109}$$

which ensure compliance with the zero law of thermodynamics, which can be aptly called 'the law of irreversibility'.

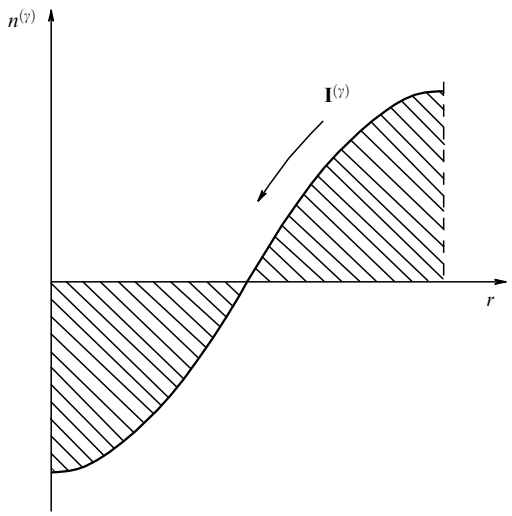

Figure 4. Direction of the diffusion flux $\mathbf{I}^{(\gamma)}$ in a closed isolated system.

10.4 Comments

So, what is the cause of irreversibility of all macroscopic processes? To put it in a nutshell, one can say that the irreversibility is due to a trivial cause — to the fact that all macroscopic parameters of matter are functions of the density and the temperature. Since the density and the temperature do not change their values when the time is reversed (see Eqn (108)), all the other parameters of matter remain indifferent to time reversal. In other words, the macroscopic state of matter does not depend on the direction of motion of individual particles; it only responds to the values of n and Θ, which have the meaning of values averaged over coordinates and momenta of individual particles. The reversible Newtonian equations transform into the irreversible transport equations at the stage when the BBGKY hierarchy is expanded in ε, since it is then that the initial conditions are eliminated from the equations, and the explicit time-dependence of the distribution function is replaced with the parametrical dependence on t via the functions $n(\mathbf{r}, t)$ and $\Theta(\mathbf{r}, t)$.

11. Equilibrium and nonequilibrium systems

Now we ask ourselves, what is the difference between equilibrium and nonequilibrium systems? If we are only interested in what happens on the macroscopic level, the answer is very simple: the gradients of hydrodynamic variables and the resulting flows are zero in equilibrium systems, and nonzero in nonequilibrium ones. But what happens on the microscopic level?

Let us turn to Eqn (43), according to which the l-particle distribution function $\mathscr{G}_{(l)}$ has the form

$$\mathscr{G}_{1,\ldots,l} = \exp(\Omega_{1,\ldots,l}) \prod_{i=1}^{l} \mathscr{G}_i\,.$$

In equilibrium systems we have

$$\mathscr{G}_i = \mathscr{G}_i^{(0)} = \exp\left(-\frac{p_i^2}{2m\Theta}\right)$$

(see Eqn (55)), and $\Omega_{1,\ldots,l} = \Omega_{(l)}(\mathbf{r}_1, \ldots, \mathbf{r}_l)$ is a function of only $\mathbf{r}_i$ (see Eqn (57)). This means that here the subspace of momenta is entirely separate from the subspace of coordinates, and in the subspace of momenta the probability of the event 'the momentum of ith particle is $\mathbf{p}_i$' does not depend on the momenta $\mathbf{p}_j$, $j \neq i$ of other particles of the same group. These events are independent because the probability $\mathscr{G}_{1,\ldots,l}^{(0)}$ in Eqn (43) is proportional to the product of probabilities $\mathscr{G}_{(1)}^{(0)}(\mathbf{p}_i)$. Now, if all particles of the system move independently of one another, then this system is in the state of utmost chaos. This chaos, however, reigns only in the subspace of momenta. The subspace of coordinates is to some extent ordered, because certain correlation exists between the molecules within the correlation sphere, described by the correlation functions $\Omega_{(l)}^{(0)}$. Since at $r_{ij} > R_c$ the functions $\Omega_{(l)}^{(0)}$ turn to zero, all correlations vanish in the subspace of coordinates outside of the correlations sphere, and complete chaos reigns here too (this applies not only to gases and liquids, but also to crystals).

In nonequilibrium systems, for which $\Omega_{(l)} = \Omega_{(l)}^{(0)} + \varepsilon\,\Omega_{(l)}^{(1)}$, the situation is different, because $\Omega_{(l)}^{(1)}$ are now functions not only of the coordinates, but also of the momenta. As a result, certain correlations between particles arise also in the subspace of momenta, which makes the chaos, so to say, more ordered. As the system comes closer to thermodynamic equilibrium, these correlations subside gradually, and the degree of chaos in the subspace of momenta increases. Since the measure of chaos is the dynamic entropy, the latter increases as the system approaches the state of equilibrium, and reaches its maximum when equilibrium is attained. At the same time, no correlations arise in the subspace of momenta in the course of infinitely slow static processes, because in this case the system permanently occurs at the state of thermodynamic equilibrium. Accordingly, the variations of static entropy have nothing to do with the second law of thermodynamics. We see that it is different degrees of freedom of the system that are responsible for static and dynamic processes (see Section 9.1).

In the case of equilibrium systems all correlations between the particles of a given group disappear when at least one of the particles escapes from the correlation sphere. The same happens in nonequilibrium systems. The only exception is the highest N-particle correlation between all N particles of the system. Indeed, from Eqn (103) it follows that

$$dS^{(M)}(t) = -\,\mathrm{d}S^{(N)}(t)\,,$$

where

$$S^{(N)}(t) \propto \int \omega_{1,\ldots,N}\,\mathscr{G}_{1,\ldots,N}\,\mathrm{d}(1)\ldots\mathrm{d}(N)$$

is the N-particle correlation entropy. And since we have $\mathrm{d}S^{(M)} \neq 0$ in nonequilibrium systems, $\mathrm{d}S^{(N)}$ must also be nonzero. It follows that, apart from the short-range correlations, which vanish outside the correlation sphere, there must also be a global correlation embracing the entire system†. This correlation is established by transport equations whose solutions describe regularity in the motion of particles no matter how far they are from one another. As a result, the equation $\mathrm{d}S^{(N)} = -\,\mathrm{d}S^{(M)}$ may be interpreted as one describing the conversion of the entropy of macroscopic ordered motion $S^{(N)}$ into the entropy of chaotic motion of particles $S^{(M)}$. At equilibrium we have $S^{(M)} = 0$, since there are no macroscopic correlations in equilibrium systems. Therefore, $S^{(N)}$ can only decrease on the way towards equilibrium, and this means that the increment of the macroscopic entropy can be only negative, $\mathrm{d}S^{(N)} \leqslant 0$. Accordingly, the increment of the dynamic entropy can be only positive, $\mathrm{d}S^{(M)} \geqslant 0$, in full agreement with the second law of thermodynamics.

12. Alternative theories

In the construction of the theory of nonequilibrium phenomena we moved step by step from one box of the diagram in Fig. 1 to another, and I repeated again and again that this is the only way possible. Now I will briefly recapitulate the logic behind this scheme, to make it clear why the alternative theories, which digress from this scheme, cannot claim to be consistent.

12.1 Scheme of construction of theory

As noted above, the postulates of the theory actually lay down the guidelines for construction of the theory. Indeed, as soon as we found that the Newtonian equations give rise to chaos, it became clear that the evolution of such systems can only be described by the methods of probability theory. The probability theory, however, always deals with mass experiments, whose outcome is averaged to define the sought-for probability. In classical mechanics, 'repeatability' can only be implemented with the aid of Gibbs ensembles. As soon as we defined the N-particle distribution function $\mathscr{G}_{(N)}$ within the framework of Gibbs ensemble, we immediately faced the problem of equation which defines this function, etc., which brought us to the formulations of the BBGKY hierarchy. Admittedly, at this point we met with a certain ambiguity. We saw that the state of any macroscopic system is characterised by parameters ε and χ. Their values must be selected depending on the characteristics of the system in question, and especially on the properties we are concerned with. We have only investigated one possibility, $\varepsilon \simeq \chi \ll 1$. This choice immediately brought us to the equilibrium thermodynamics and the theory of transport processes; a different choice of ε and χ would have taken us elsewhere (for example, $\varepsilon \simeq \chi \simeq 1$ would have brought us to the theory of Brownian motion; see Section 12.3). A more detailed study of the available options is a task for the future. However, even what is already known may turn out to be useful in other respects.

If we try to sort out the various directions of development of the contemporary theory of nonequilibrium processes, we find that from almost any box of the diagram in Fig. 1 we can draw one or more additional links. How promising are they? Making such forecasts is a thankless task. If, however, in our construction of statistical mechanics we have really selected the right avenue, and, most importantly, if we know well why we are pursuing this direction, we must be able to state clearly the reasons why we did not go in other directions. This is what I will try to do now.

12.2 Theories based on Liouville equation

In the long run, the entire statistical mechanics is based on the Liouville equation. In this context, however, I am going to discuss only those theories which attempt to solve the Liouville equation without going over to the BBGKY hierarchy (for example, the method of projection operator). How promising are they? To answer this question, let us recall why we went from the Liouville equation to the BBGKY hierarchy.

The Liouville equation defines the N-particle distribution function $\mathscr{G}_{(N)}$, which characterises the state of all N particles of the system at the same time. Its value is determined by just three global parameters N, $E_{(N)}$, and $S_{(N)}$; the local state of the system remains undefined. At equilibrium this is of no importance, because the global and the local parameters are linked together by trivial relations $E_{(N)} = Ne$ and $S_{(N)} = Ns$. In nonequilibrium systems, however, the same values of N, $E_{(N)}$, and $S_{(N)}$ correspond to infinitely many local states. Since these states are not identified when we define $\mathscr{G}_{(N)}$, we must assume that $\mathscr{G}_{(N)}$ is defined as average over the ensemble which represents all possible macroscopic states of the system. The deficiency of this definition is obvious. To remove ambiguity, we introduced the concept of the one-particle distribution function $\mathscr{G}_{(1)}$, whose value is defined by five basic macroscopic parameters of the system, $n(\mathbf{r}, t)$, $c_\alpha(\mathbf{r}, t)$, and $\Theta(\mathbf{r}, t)$. This in turn called for introducing other l-particle distribution functions, and brought us eventually to the BBGKY hierarchy. Because of this, any attempt to bypass the BBGKY hierarchy seems futile to me. As far as I know, the history of the theory of nonequilibrium processes supports this conclusion, because so far no feat of this kind has been a success.

12.3 Theory of Brownian motion

So, if the way from equations of motion of classical mechanics to the BBGKY hierarchy is uniquely predetermined, then the BBGKY hierarchy (along with the Newtonian equations) may claim the role of fundamental equations of statistical mechanics. Statistical mechanics, however, is not only thermodynamics and transport equations — it also includes the theory of fluctuations. Is the BBGKY hierarchy suitable for describing the fluctuation processes? To answer this question, let us discuss the theory of Brownian motion.

With this purpose we consider a colloid solution consisting of large colloid particles of diameter a, suspended in a liquid whose molecules have the size $\sigma \ll a$. We assume that

†For example, in the flow of liquid inside an arbitrarily long pipe, all particles have a velocity component parallel to the walls of the pipe.

the system is at thermodynamic equilibrium, which serves as background for the fluctuations of solvent molecules, which eventually give rise to Brownian motion of the colloid particles. Since these fluctuations occur on the length scale of $L \simeq R_c$ and the time scale of $T \simeq \tau$, the parameters ε and χ are of the order of unity:

$$\varepsilon \simeq \chi \simeq 1\,, \tag{110}$$

this implies that we have to retain the time derivatives in equations of the BBGKY hierarchy. In this approximation, the first equation in the hierarchy becomes

$$\frac{\partial \mathscr{G}_1}{\partial t} = -\frac{\mathbf{p}}{M}\cdot\frac{\partial \mathscr{G}_1}{\partial \mathbf{r}} + n_0 \int \frac{\partial \Phi_{12}}{\partial \mathbf{r}_1}\cdot\frac{\partial \mathscr{G}_{12}}{\partial \mathbf{p}_1}\,\frac{\mathrm{d}^3\, r_2\, \mathrm{d}^3 p_2}{\mathcal{P}^3} + v_0 \int \frac{\partial \Psi_{12}}{\partial \mathbf{r}_1}\cdot\frac{\partial G_{12}}{\partial \mathbf{p}_1}\,\frac{\mathrm{d}^3 r_2\, \mathrm{d}^3 p_2}{\mathcal{P}^3}\,, \tag{111}$$

where $\mathscr{G}_{(1)}$ is the one-particle distribution function of the colloid component, M is the mass of colloid particle, Φ_{12} is the potential of interaction of colloid particle with solvent molecules, $\mathscr{G}_{12}$ is the two-particle distribution function which describes interaction of colloid particle with solvent molecules, Ψ_{12} is the potential of interaction between two colloid particles, and G_{12} is the corresponding distribution function. Since the concentration of colloid particles v is assumed to be small compared with the concentration of solvent molecules n,

$$v \ll n\,, \tag{112}$$

the second integral in (111) may be dropped.

Multiplying Eqn (111) by the equilibrium concentration of colloid particles v, and integrating with respect to momenta, we get (cf. Eqn (32), (33))

$$\frac{\partial v}{\partial t} = -\frac{\partial (v v_\alpha)}{\partial r_\alpha}\,, \tag{113}$$

where

$$v(\mathbf{r},\, t) = v_0 \int_{-\infty}^{\infty} \mathscr{G}_{(1)}(\mathbf{r},\, \mathbf{p},\, t)\,\frac{\mathrm{d}^3 p}{\mathcal{P}^3} \tag{114}$$

is the instantaneous density of colloid particles, and

$$v(\mathbf{r},\, t)\,\mathbf{v}(\mathbf{r},\, t) = v_0 \int_{-\infty}^{\infty} \frac{\mathbf{p}}{M}\,\mathscr{G}_{(1)}(\mathbf{r},\, \mathbf{p},\, t)\,\frac{\mathrm{d}^3 p}{\mathcal{P}^3} \tag{115}$$

is their instantaneous velocity. Assuming that deviations from equilibrium are small, we may write

$$v = v_0(1 + \delta v) \simeq v_0,$$

$$\mathscr{G}_{(1)} = \exp(\omega^{(0)} + \delta\omega) = \mathscr{G}_{(1)}^{(0)}(1 + \delta\omega)\,, \tag{116}$$

where the equilibrium distribution function is

$$\mathscr{G}_{(1)}^{(0)} = \exp\left(-\frac{p^2}{2M\Theta}\right).$$

Substituting Eqn (116) into Eqn (114), we get

$$v_0(1 + \delta v) = v_0 \int_{-\infty}^{\infty} \mathscr{G}_{(1)}^{(0)}\,\frac{\mathrm{d}^3 p}{\mathcal{P}^3} + v_0 \int_{-\infty}^{\infty} \mathscr{G}_{(1)}^{(0)}\delta\omega\,\frac{\mathrm{d}^3 p}{\mathcal{P}^3}\,. \tag{117}$$

Equating v_0 to the first integral, and δv to the second, we get the normalisation condition

$$1 = \frac{1}{\mathcal{P}^3}\int_{-\infty}^{\infty} \exp\left(-\frac{p^2}{2M\Theta}\right)\,\mathrm{d}^3 p \tag{118}$$

and the definition of probability

$$\delta v = \int_{-\infty}^{\infty} \mathscr{G}_{(1)}^{(0)}\,(p^2)\,\delta\omega\,\frac{\mathrm{d}^3 p}{\mathcal{P}^3}\,. \tag{119}$$

Accordingly, from Eqn (115) we get

$$\mathbf{v}(\mathbf{r},\, t) = \int_{-\infty}^{\infty} \frac{\mathbf{p}}{M}\,\mathscr{G}_{(1)}^{(0)}\,(p^2)\,\delta\omega(\mathbf{r},\, \mathbf{p},\, t)\,\frac{\mathrm{d}^3 p}{\mathcal{P}^3}\,, \tag{120}$$

since at equilibrium the velocity of particles is $\mathbf{v}_0 = 0$.

Observe now that, since the system at equilibrium is spatially homogeneous, the velocity $\mathbf{v}$ cannot depend explicitly on $\mathbf{r}$ and t; the dependence of $\mathbf{v}$ on $\mathbf{r}$ and t can only be parametrical, $\mathbf{v} = \mathbf{v}\big(\delta v\,(\mathbf{r},\, t)\big)$. Taking advantage of the smallness of δv, and expanding $\mathbf{v}$ into a series, we get

$$\mathbf{v}(\mathbf{r},\, t) = -D\,\frac{\partial \delta v}{\partial \mathbf{r}} + \ldots\,, \tag{121}$$

where D is a so far unknown constant. Substituting this into Eqn (113) and cancelling out v_0, we come to the diffusion equation

$$\frac{\partial \delta v}{\partial t} = D\,\boldsymbol{\Delta}\,\delta v\,, \tag{122}$$

which was used by Einstein as a basis for his theory of Brownian motion (in Eqn (122) $\boldsymbol{\Delta}$ is the Laplacian).

Now we multiply Eqn (111) by $\mathbf{p}/M$ and integrate with respect to $\mathbf{p}$, getting as a result the equation of balance of momentum

$$\frac{\partial v_\alpha}{\partial t} = -\frac{\partial P_{\alpha\beta}}{\partial r_\beta} + F_\alpha\,, \tag{123}$$

in which the stress tensor

$$P_{\alpha\beta} = \int_{-\infty}^{\infty} \frac{p_\alpha p_\beta}{M^2}\,\mathscr{G}_{(1)}^{(0)}\delta\omega\,\frac{\mathrm{d}^3 p}{\mathcal{P}^3} \tag{124}$$

has the meaning of the force acting from the side of colloid particle on solvent molecules, and the collective force

$$F_\alpha = -n_0 \int \frac{\partial \Phi_{12}}{\partial r_\alpha}\,\mathscr{G}_{12}^{(0)}\,\delta\Omega_{12}\,\frac{\mathrm{d}^3 p_1\, \mathrm{d}^3 p_2}{\mathcal{P}^6}\,\mathrm{d}^3 r_2 \tag{125}$$

has the meaning of the random force on colloid particle from the side of solvent molecules. Since the colloid particle is 'almost' a macroscopic body, the term $\partial P_{\alpha\beta}/\partial r_\beta$ must be balanced out by the force of friction from the side of solvent, which, according to Stokes' law, is

$$\frac{\partial P_{\alpha\beta}}{\partial r_\beta} = 6\pi\eta a v_\alpha\,,$$

where η is the viscosity. Substituting this expression into Eqn (123), we come to the Langevin equation

$$\frac{\partial \mathbf{v}}{\partial t} = -6\pi\eta a\mathbf{v} + \mathbf{F}\,, \tag{126}$$

which can also serve as basis for the theory of Brownian motion. To make the two approaches tally with each other, in the Einstein equation we must set

$$D = \frac{\Theta}{6\pi\eta a} \,. \tag{127}$$

We see that the theory of Brownian motion can be constructed on the basis of the BBGKY hierarchy, and thus the hierarchy may claim the role of fundamental equations of statistical mechanics.

12.4 Kinetic theory of gases

For a long time the statistical theory of nonequilibrium processes had been virtually identified with the kinetic theory of gases. As a matter of fact, the structure of the kinetic theory is very similar to the structure of statistical mechanics: first the Newtonian equations are used to derive the kinetic Boltzmann equation, then the latter is used for formulating the exact equations of balance for the mass, the momentum and the energy, and finally, these equations are transformed into the transport equations by solving the Boltzmann equation. If we replace the words 'Boltzmann equation for the one-particle distribution function' with 'equations of the BBGKY hierarchy for l-particle distribution functions', it will be just impossible to tell one theory from the other. Of course, there is one very important distinction: the Boltzmann equation is an approximate implication of the Newtonian equations, whereas the BBGKY hierarchy is the exact consequence of the latter. Given this, could it be possible to regard the kinetic theory as a particular case of the statistical theory in the limit of dilute gas? To answer this question, we must examine once again the physical assumptions of both theories.

The Boltzmann equation, like the first equation in the hierarchy, has the form

$$\frac{\partial \mathscr{G}_1}{\partial t} = -\frac{\mathbf{p}_1}{m} \cdot \frac{\partial \mathscr{G}_1}{\partial \mathbf{r}_1} + I_1 \,, \tag{128}$$

with the difference that the collision integral is

$$I_1 = I_{\mathrm{B}} = n_0 \int \frac{p_{12}}{m}\, \eta \left[\mathscr{G}_1' \mathscr{G}_2' - \mathscr{G}_1 \mathscr{G}_2\right] \mathrm{d}\Omega\, \frac{\mathrm{d}^3 p_2}{\mathcal{P}^3} \,, \tag{129}$$

in the Boltzmann equation, and

$$I_1 = I_{\mathrm{BBGKY}} = n_0 \int \frac{\partial \Phi_{12}}{\partial \mathbf{r}_1} \cdot \frac{\partial \mathscr{G}_{12}}{\partial \mathbf{p}_1}\, \mathrm{d}^3 r_2\, \frac{\mathrm{d}^3 p_2}{\mathcal{P}^3} \tag{130}$$

in the BBGKY hierarchy (here $p_{12} = |\mathbf{p}_1 - \mathbf{p}_2|$ and η is the scattering cross-section). In addition, in Eqn (129) the prime at functions $\mathscr{G}_1$ and $\mathscr{G}_2$ indicates that the momenta $\mathbf{p}_1$ and $\mathbf{p}_2$ of particles 1 and 2 are measured before collision, and the absence of prime at $\mathscr{G}_1$ and $\mathscr{G}_2$ indicates that $\mathbf{p}_1$ and $\mathbf{p}_2$ are measured after collision. Since it is assumed that the collision itself obeys the laws of classical mechanics, the conditions of conservation of momentum and energy are imposed on $\mathbf{p}_1$ and $\mathbf{p}_2$:

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}_1' + \mathbf{p}_2' \,, \qquad p_1^2 + p_2^2 = p_1'^2 + p_2'^2 \,. \tag{131}$$

Stricken with the amazing similarity of the two equations, Bogolyubov attempted to derive the Boltzmann equation from the BBGKY hierarchy. His approach was based on two ideas: to reduce the hierarchy to a sequence of kinetic equations with the aid of expansion in powers of n_0, and then to transform each equation in the sequence into a Boltzmann-type equation. Let us start with the first idea.

Since n_0 enters the equations of the BBGKY hierarchy only as a factor in front of the integral terms, in the zero order in n_0 all these integral terms vanish, and the BBGKY hierarchy reduces to a set of differential equations. In particular, as follows from Eqn (128), the first equation in the hierarchy takes on the form

$$\frac{\partial \mathscr{G}_1^{(0)}}{\partial t} = -\frac{\mathbf{p}_1}{m} \cdot \frac{\partial \mathscr{G}_1^{(0)}}{\partial \mathbf{r}_1} \,.$$

Its solution is

$$\mathscr{G}_1^{(0)} = \mathscr{G}_{(1)}^{(0)} \left(\mathbf{r}_1 - \frac{\mathbf{p}_1}{m}\, t\right) ,$$

whence it follows that particle 1 at $t \to \infty$ flies away to infinity. All the other equations in the zero approximation have similar solutions, which means that particles of an arbitrary set of l particles, $l = 1, 2, \ldots$, after collision always scatter to infinity. Bogolyubov invented a clever trick to avoid divergence at $t \to \infty$; further studies revealed, however, that the Bogolyubov method ensures convergence of only the first two terms in the expansion in n_0, whereas the remaining terms still diverge. Today, almost fifty years later, no-one has succeeded in reducing the BBGKY hierarchy to a sequence of kinetic equations. And I believe that no-one ever will. The fact is that, as we have seen, n_0 is a nonphysical parameter (see Section 4.5). It is not surprising then that the expansion in n_0 leads to nonphysical results. The structure of a correct expansion must always be such that the zero-order term should describe the state of thermodynamic equilibrium: otherwise it will be not possible to eliminate n_0 and replace it with n and Θ†. If this statement is correct — and I believe it is — then the BBGKY hierarchy is not reducible to a sequence of kinetic equations because, by definition, the kinetic equations must contain time derivatives, whereas at equilibrium we have $\partial \mathscr{G}_{(l)}/\partial t = 0$.

The second idea of Bogolyubov is also unlikely to be feasible, because the Boltzmann collision integral I_{B} involves one-particle distribution functions defined at $t - \tau$ and $t + \tau$ — that is, before and after collision. In this case the transition to $\tau \to 0$ is not possible, because the concept of 'collision' itself becomes meaningless. Apart from that, the Boltzmann theory assumes that in the interval between $t - \tau$ and $t + \tau$ the particles move along paths defined by the Newtonian equation. At the same time, in the BBGKY hierarchy the values of all distribution functions $\mathscr{G}_{(l)}$ are defined at one and the same time t, and the concept of 'path' is altogether expelled from the theory. It is obvious that the assumptions of the Boltzmann theory and the BBGKY hierarchy are incompatible. For the same reason, Bogolyubov's attempt to transform the first (converging) term if the expansion in n_0 with the aid of time-shift operator is unlawful, because this operator introduces new time $t - \tau$ into the hierarchy, and shifts back the particles along their paths, thus tacitly implanting the concept of path into the theory. If, however, we renounced the deterministic description of motion of particles along their paths at the early start (when we carried out averaging over the ensemble of Gibbs copies and in the derivation of the BBGKY hierarchy), we just cannot go back to the deterministic description of the system at the end of the day (when solving the equations of the hierarchy).

So we see that the kinetic Boltzmann theory cannot be regarded as a limiting case of the BBGKY hierarchy at $n \to 0$.

†Recall that $n(\mathbf{r}, t)$ and $\Theta(\mathbf{r}, t)$ are those local macroscopic parameters that must be fixed in order to define the concept of 'ensemble of Gibbs copies'.

This does not mean, however, that Boltzmann's theory is wrong: it can exist in its own right as an approximate theory of nonequilibrium ideal gas. I would like to recall here the Van der Waals equation. This equation also cannot be derived from the exact equations of statistical mechanics. This fact, however, does not prevent it from being one of the best, if not the very best equation of state.

12.5 Thermodynamics of irreversible processes

This theory is based on the attempt to use the equations of equilibrium thermodynamics for describing local dynamic processes. First it is assumed that each physically infinitesimal element of volume of matter δV is at the state of local equilibrium and hence obeys the equation

$$\frac{\Theta}{k_{\mathrm{B}}}\,\mathrm{d}(\delta S) = \mathrm{d}(\delta E) + P\,\mathrm{d}(\delta V)\,,$$

or, with due account for the time-dependence of processes,

$$\frac{\Theta}{k_{\mathrm{B}}}\,\frac{\mathrm{d}(\delta S)}{\mathrm{d}t} = \frac{\mathrm{d}(\delta E)}{\mathrm{d}t} + P\,\frac{\mathrm{d}(\delta V)}{\mathrm{d}t}\,. \tag{132}$$

Then, replacing the time derivatives in Eqn (132) by respective fluxes, after some straightforward manipulations we come to the equation of entropy balance (38), in which the entropy source $q^{(s)}$ is a positive quadratic form

$$q^{(s)} = \sum_k J_i\,x^{(i)} > 0\,, \tag{133}$$

where $J_i = \sum_k \mathcal{L}_{ik}\,x^{(k)}$ are the fluxes caused by the gradients $x^{(k)}$, and $\mathcal{L}_{ij}$ are the transport coefficients (cf. (77)).

This substantiation of formula (133) cannot be accepted. Of course, we can use Eqn (132), but one must bear in mind that functions δS, δE, and δV, which enter this equation, depend on the 'slow' time t/T_∞, that is, $\delta S = \delta S(t/T_\infty)$, etc. At the same time the flow used in transforming Eqn (132) are functions of the 'fast' time t/T. Since inequality (133) is assumed to describe the process of entropy production in the course of dynamic processes (that is, at $0 \leqslant t \leqslant T$), the use of Eqn (132) is not justified, because equation (132) on these time intervals degenerates into an identity $0 = 0$. Accordingly, there are no grounds for identifying q in Eqn (133) with the source of local entropy. This does not mean, however, that Eqn (133) itself is wrong. We saw that the zero law of thermodynamics imposes certain restrictions on the transport coefficients, which must always be positive (see Eqn (109)). Since, however, thermodynamics of nonequilibrium processes is based on inequality (133) rather than on equation (132), all results of the theory still hold — it is the proof that must be changed. Earlier it had been assumed that inequality (133) is a consequence of the second law of thermodynamics; now we must accept that it has nothing to do with the entropy, and follows from the zero law of thermodynamics.

13. Conclusions

In the Introduction to this paper I said that 'statistical mechanics belongs to fundamental sciences', and any 'fundamental theory must only derive from first principles — any simplifying assumption immediately makes the theory approximate rather than fundamental'. I hope that I have managed to implement this program statement. In any case, starting from the Newtonian equations, we have derived the macroscopic transport equations which describe processes in continuous media. And, which is important, we did not use any additional hypotheses.

The results are primarily of methodological value because we have succeeded in resolving most of the contradictions which made classical mechanics and thermodynamics seemingly irreconcilable, and in defining more clearly the scheme of construction of statistical mechanics and its tasks. I shall briefly recapitulate some of the results.

1. In Section 2 we showed that the transition from deterministic description of molecular systems in terms of paths to probabilistic description is absolutely necessary.

2. In Section 3 we showed that the description of molecular systems with the aid of Liouville equation is not sufficient, and it is necessary to go over to the BBGKY hierarchy and the concept of l-particle distribution functions.

3. In Sections 4 and 5 we showed that the BBGKY hierarchy involves nonphysical parameters which can only be eliminated by expanding the distribution functions in small parameter ε.

4. In Sections 6 – 8 we showed that Gibbs distribution and the entire equilibrium thermodynamics follow from the BBGKY hierarchy in the zero order in ε, and all transport equations in the first order in ε.

5. In Sections 9 and 11 we showed that entropy in nonequilibrium systems may increase in full agreement with the second law of thermodynamics, and without violating the laws of classical mechanics.

6. In Section 10 we showed that expansion in ε resolves the eternal paradox of irreversibility, which consists in that the initial Newtonian equations, which describe the system on the microscopic level, are time-reversible, whereas the transport equations, which follow from the Newtonian equations and describe the system on the macroscopic level, are irreversible.

Apart from their methodological value, however, our results may find practical application. I will only point to two possibilities.

Firstly, the first-principle system of transport equations somewhat differs from the equations used so far. This may affect the results of some particular calculations.

Secondly, we have obtained new expressions which permit calculating the transport coefficients from first principles.

The relative order that we have set among the multitude of theories of nonequilibrium phenomena may also be regarded as a practical result.

And one final remark. The theory presented here is purely classical: we have not made a single reference to quantum effects. The attentive reader will readily notice here many features typical of a quantum theory. These analogies call for special analysis.

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