Statistical Mechanics: A Survey of Recent Lines of Investigation

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IN this survey I shall try to describe what are, in my view, some of the main lines along which the work in statistical mechanics has developed in recent years, and what are the difficulties encountered. In doing so I shall leave out of consideration more specialized fields of application of statistical mechanics, like solid state, ferromagnetism, superconductivity, and superfluidity. I shall also concentrate on general problems and broad lines of development rather than on any attempt at surveying the recent literature systematically.

As is well known statistical mechanics aims at establishing relations between the observed properties of large systems composed of many identical particles (gases, liquids, solids) and the mechanical properties of these particles and their interaction. The subject naturally subdivides into two parts, one dealing with the properties of many-particle systems which are in equilibrium in the thermodynamical sense, the second treating systems in nonequilibrium situations and dealing with irreversible processes.

I. STATISTICAL MECHANICS OF SYSTEMS IN EQUILIBRIUM

This is perhaps the best instance of a subject where at first sight everything seems to be known, since the basic equations are formally very simple and are familiar to every student of physics. The free energy F of a system in thermal equilibrium at temperature T (canonical ensemble theory) is, classically first and then quantum-mechanically,

$$\exp(-F/kT)=(\hbar^{3N}N!)^{-1}\int \exp(-H/kT)d\mathbf{r}_1\cdots d\mathbf{r}_N \times d\mathbf{p}_1\cdots d\mathbf{p}_N=\sum_\alpha \exp(-E_\alpha/kT) \quad (1)$$

(N number of particles, H Hamiltonian, E_α eigenvalues of the energy). The value at equilibrium of a quantity A is given by

$$\langle A\rangle=(\hbar^{3N}N!)^{-1}\int A\exp[(F-H)/kT]d\mathbf{r}_1\cdots d\mathbf{p}_N =\sum_\alpha\langle A\rangle_\alpha\exp[(F-E_\alpha)/kT]. \quad (2)$$

($\langle A\rangle_\alpha$ expectation value of A in the quantum state α).

The simplicity of these equations is only apparent, as is well known. The difficulties find their origin in the fact that the relevant properties of the systems studied manifest themselves only when these sytsems are sufficiently large, so the above equations have to be used in the case of large N (asymptotic limit $N\to\infty$) where their formal compactness is completely misleading. This explains why a fully satisfactory derivation of physical predictions on the basis of (1) and (2) could, until now, only be achieved in very few cases. The problems met with in this connection can roughly be classified in three groups of increasing difficulty, to be described in succession hereafter.

Imperfect Systems

We shall understand under imperfect systems the many-particle systems with a Hamiltonian $H=H_0+V$ split into a main term H_0 giving rise through separation of variables to a simple evaluation of (1) or (2) and a small perturbation term V mixing the modes of motion which are independent under H_0 alone. This is the simplest type of situation, since all complications connected with the large value of N enter only through the small perturbation term V. As examples we quote imperfect but still very dilute gases (V is here the intermolecular interaction), crystal lattices (the anharmonic forces play the role of perturbation), the Bloch theory of metals (V is the interaction between conduction electrons and lattice vibrations), impurity problems in solid state. Although such problems seem to reduce at first sight to simple applications of perturbation calculus, they actually may present non-negligible difficulties due to the fact that the perturbation, even when small per particle, is in total made large by the presence of many particles. Perturbation theory must, to be adapted to this circumstance, undergo considerable modifications which until now have been carried out in full detail only for classical dilute gases.[1]

How difficult such perturbation problems may be is illustrated by the example of the imperfect Bose-Einstein gas, where the effect of the intermolecular interaction on the Bose-Einstein condensation phenomenon is still unknown, even for the simplest case where the range of the forces is very small compared with the mean de Broglie wavelength. The solution of this problem, in addition to its intrinsic interest, would probably be quite instructive for our understanding of the superfluidity of liquid helium at low temperature. Similarly, a complete understanding of the physical effects resulting from the interaction between Bloch electrons and lattice vibrations in a metal should be very helpful for the eventual explanation of the mecha-

[1] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), Chap. 13.

nism of superconductivity. Needless to say, the existing treatments of these problems are still very incomplete.

Liquids and Dense Gases

The problems connected with the liquid state and with the gaseous state at high densities are much more difficult than those related to imperfect systems because the complexities resulting from the large number of degrees of freedom, instead of appearing through a small correction term in the Hamiltonian, now play a dominant role. Neither for the calculation of thermodynamic properties, nor for the prediction of the observable local structure properties (e.g., the pair distribution function) does one have theoretical methods deriving the main part of the results from basically simple calculations and providing an approximation scheme of reasonably fast convergence to deal with the remaining corrections.

The most natural approximation method, initiated by Lennard-Jones and Devonshire,[2] pictures each particle of the fluid as moving in the average field of force of the neighboring particles, thus neglecting all correlation effects. Much work has been devoted to the improvement of this so-called cell theory of liquids by including interparticle correlations in various ways. Although, as shown by de Boer,[3] the introduction of correlations involving more and more particles can be constructed as a systematic scheme of successive approximations, the convergence is too poor to make this approach really successful. Another approach, first proposed by Kirkwood and taken over with minor modifications by Born and Green,[4] postulates a simple expression of the three-particle correlation in terms of two-body correlations. Beyond lacking any basic justification for the densities of interest, this approximation turns out to be quantitatively rather poor and it does not seem to lend itself to convenient inclusion of further corrections.[5]

It seems fair to say that no truly satisfactory theory of liquids has been found so far. The reason for this failure can be formulated by saying that liquid structure has not revealed any clear-cut element of simplicity similar to the scarcity of intermolecular collisions in dilute gases, or to the smallness of anharmonic forces in the crystalline state. Still it is not obvious that such elements of simplicity are altogether absent. Thus, despite the complicated n-body correlations present in liquids (with n going perhaps up to $n \gtrsim 10$), there is the striking fact that all correlation effects are of short range (except in the immediate neighborhood of the critical point), a simplifying feature which one might expect to be quite significant. Whether it can form the basis of a more fruitful theoretical approach is not known.

Phase Transitions

While the structure of liquids and dense gases confronts us with the problems just discussed, the occurrence of a discontinuous phase transition between these two states of matter for all temperatures below a certain critical temperature is an even more striking phenomenon to be accounted for. In view of its great generality, this condensation phenomenon must be explainable in terms of the qualitative properties of the intermolecular force (strongly repulsive at short distance, attractive at larger separations beyond which it rapidly converges to zero). Considerable work has been devoted in the last twenty years to the statistical mechanics of the gas-liquid transition and of similar transition phenomena (order-disorder transition in binary alloys, ferromagnetism, etc.), in an attempt to derive the existence and exact nature of the transition from first principles without recourse to *ad hoc* thermodynamical arguments.

Indeed, if arguments of the latter sort are admitted, the theoretical prediction of phase transitions is nowadays a simple matter, and such a half-phenomenological approach has met with repeated success for various kinds of systems, starting with the pioneer work of van der Waals who derived the liquid-gas transition and the existence of a critical point from the simplified equation of state bearing his name. This equation of state gives below the critical temperature an analytical $p-v$ curve (p pressure, v volume per particle) with $\partial p/\partial v > 0$ over an interval of v values, from which one then obtains by application of the Maxwell rule the observed non-analytical $p-v$ curve with a horizontal part ($p=$ constant) outside of which the inequality $\partial p/\partial v < 0$ holds. The Maxwell rule is in this case the *ad hoc* thermodynamical argument. The condensation problem to be discussed here consists in establishing without any such argument the occurrence of the observed phase transition. Relevant to its understanding is the fact that, from the principles of canonical ensemble theory, the inequality $\partial p/\partial v \leqslant 0$ is bound to hold (implying the equivalence of the canonical and grand canonical ensemble theories) as a consequence of the general shape of the intermolecular potential.[6] From a calculation of the sum of states (1) condensation must be found as a $p=$ constant part in the $p-v$ curve, i.e., as analytical singularities in the thermodynamical functions. Since for finite number N of particles the expression (1) is a perfectly regular function of the total volume Nv, we must conclude that the abovementioned singularities can only appear when the limiting process $N \to \infty$ is carried out. It will have to be found from a proper treatment of this difficult limiting case.

Despite many attempts nobody has however suc-

[2] J. E. Lennard-Jones and A. F. Devonshire, Proc. Roy. Soc. (London) **A163**, 63 (1937); *ibid.*, **A164**, 1 (1938).

[3] J. de Boer, Physica **20**, 655 (1954).

[4] J. G. Kirkwood, J. Chem. Phys. **3**, 300 (1935); M. Born and H. S. Green, Proc. Roy. Soc. (London) **A188**, 10 (1946).

[5] For further details on the theories of the liquid state, see J. de Boer, Proc. Roy. Soc. (London) **A215**, 4 (1952).

[6] L. Van Hove, Physica **15**, 951 (1949).

ceeded in giving a mathematical treatment of the problem powerful enough to decide whether the canonical theory is able to account for the condensation phenomenon of gases. Still, very strong evidence that the question has to be answered in the affirmative was obtained from an exact study of a simplified two-dimensional model by Onsager.[7] This study, developed by Onsager for a model of ferromagnetism (the Ising model), has been extended by Yang and Lee[8] to a related model for a gas (the lattice gas). The result is that below a finite critical temperature condensation occurs with a $p=$ constant part in the $p-v$ curve. In the absence of any conclusive treatment of realistic cases, this result is of the utmost importance because none of the over-simplified features of the model seems likely to affect the significance of the conclusion.

Onsager's contribution stands alone, with its well-established positive result, in contrast to a variety of essentially unsuccessful attempts at settling the condensation problem for realistic systems. We shall mention one of these attempts here because much more work has been devoted to it in the last twenty years than to any other. It is the approach initiated by Mayer[9] and designed to derive the condensation point of a gas from the existence of analytic singularities in the functions expressing p and v^{-1} in terms of the activity z. For a dilute gas these functions are obtainable as power expansions in z, with coefficients readily expressed in terms of the intermolecular potential. The hope was that the analytic functions defined by these series, while representing correctly pressure and density for the whole region of existence of the gas, would exhibit a singularity at the condensation point (low density end of the $p=$ constant interval in the $p-v$ curve). Up to now all attempts at establishing these conjectures have however failed: neither could the occurrence of such a singularity be established, nor could one show that such a singularity, if found, would correspond to the condensation point. As to the latter question, a recent result concerning Bose-Einstein condensation shows that a negative answer is perhaps not so completely unlikely as was originally thought. For the ideal Bose gas, while the series expansions of p and v^{-1} in powers of z have long been known to exhibit a singularity at the condensation point, one now knows that the expansion of p in powers of the density v^{-1} (virial expansion) has a radius of convergence that, although finite, is much larger than the value of v^{-1} at condensation.[10] It is of course not excluded that for a classical imperfect gas a similar situation might hold not only for the virial expansion but also for the expansion in z.

In conclusion, despite extensive investigations by many authors, there is very little progress to report on the statistical mechanics of transition phenomena. This clearly shows how difficult the problem is and underlines the practical importance of the less ambitious half-phenomenological approaches (as the van der Waals theory of condensation and the quasi-chemical approximation for order-disorder phenomena) relying on a thermodynamical argument of the type of Maxwell's rule. It is therefore good to clarify a little more the position of such approaches with respect to the rigorous canonical ensemble theory. They all have in common one aspect which accounts very simply for the partial significance of their results. The approximations which they introduce are always based on the assumption that the system is homogeneous in space; in other words, only homogeneous configurations (i.e., configurations of constant density for the condensation problem, configurations of constant concentration for the order-disorder problem) are taken into account in the evaluation of the sum of states. This approximation, while reasonable outside the transition region, restricts in this region the choice of configurations to unstable ones (possibly metastable near both ends of the transition region) and excludes the infinitely more probable two phase configurations. This explains why under such an approximation the calculated thermodynamic quantities exhibit no singularity and why the observed quantities can be obtained from the calculated ones by thermodynamical criteria of stability. This may however also suggest the possibility of improved approximate discussions of the canonical sum of states which, although less ambitious than the direct attacks on the condensation problem attempted until now, would lead naturally to the observed singularities in the thermodynamic functions and would be such as to insure that the nature of these singularities would not be affected by the inclusion of further corrections.

II. STATISTICAL MECHANICS OF NON-EQUILIBRIUM PROCESSES

In contrast to the case of thermodynamical equilibrium, no general set of equations is known to describe the behavior of many-particle systems whenever their state is different from the equilibrium state and, in view of the unlimited diversity of possible nonequilibrium situations, the existence of such a set of equations seems rather doubtful. Still there are at least two broad questions concerning nonequilibrium states which seem precise enough to be answerable: (i) under which conditions does a many-particle system move toward thermodynamical equilibrium from what may reasonably be called almost every nonequilibrium state, and (ii) by which equations can one describe this tendency toward equilibrium under properly specialized assumptions on the initial state (taking possibly into account the presence of external constraints preventing the system from attaining equilibrium). These are the questions dealt with in the theory of nonequilibrium (or irreversible) processes. Although complete answers

[7] L. Onsager, Phys. Rev. **65**, 117 (1944).
[8] C. N. Yang and T. D. Lee, Phys. Rev. **87**, 404 and 410 (1952).
[9] J. E. Mayer, J. Chem. Phys. **5**, 67 (1937). See also B. Kahn, "On the theory of the equation of state," thesis, Utrecht (1938).
[10] W. H. J. Fuchs, J. Rational Mech. Anal. **4**, 647 (1955).

still seem very far out of sight, considerable progress has been booked in recent years and the prospect for further development is hopeful.

The recent contributions deal mainly with the second question, but they provide at the same time special answers to problem (i). As is well known, from the desire to solve the latter problem in entirely general terms has grown the whole body of ergodic theory, resulting some twenty-five years ago in the establishment of ergodic theorems (von Neumann, Birkhoff, E. Hopf) of great mathematical scope.[11] Such theorems however suffer from the very generality of the conditions they state for ergodicity, inasmuch as the validity of these conditions for actual physical systems is overwhelmingly difficult to establish and is still undecided. This line of work has therefore advanced little in recent years.[12]

Turning now to less general investigations, we have to mention first the development by Onsager[13] of a phenomenological theory describing in macroscopic terms the irreversible behavior of systems for not too large deviations from equilibrium. This theory plays for irreversible processes a role analogous to that played by ordinary thermodynamics for equilibrium systems and it is ordinarily referred to as the thermodynamics of irreversible processes. Lately it has given rise to a large number of applications and to a critical review of the statistical foundations.[14]

In the last ten years a strong revival of interest is to be noted for the investigation of statistical transport equations, i.e., equations describing the time evolution of some statistical property of the system studied as it moves toward equilibrium. The oldest and best known of these equations is the Boltzmann equation describing how the one-particle distribution function f of a dilute gas varies as a result of interparticle collisions. In familiar notation[15] and for the case of a system homogeneous in space, without external forces, this equation reads

$$\frac{\partial f}{\partial t}+\int (ff_1-f'f_1')ad\mathbf{c}_1d\omega=0, \qquad (3)$$

where the last term is the so-called collision term. Equation (3) is valid to lowest order in the density $\rho=v^{-1}$ (v volume per particle) and is accordingly restricted to the effect of binary collisions. Both the derivation of this equation and its extension to higher orders in the density have been the object of various investigations. Much clarification has been achieved on the main difficulty involved in deriving (3) from the reversible Newtonian equations of motion (or from the Liouville equation describing the reversible time evolution of a probability distribution for the total system in its $6N$-dimensional phase space), namely, the need for an exact formulation and proper justification of the assumption being made on the states of the system and accounting for the irreversible nature of the equation to be established (for Boltzmann this assumption was the Stosszahlansatz).[16]

On the other hand a unique procedure has been proposed by Bogoliubov to extend Eq. (3) to general order in the density.[17] It is based on a far-reaching assumption concerning the interparticle correlations in the gas, namely, that they are time-independent functionals of the one-particle distribution function, so that their time variation results entirely from the time variation of the latter. This assumption is supposed to hold after some initial time interval short compared to the time needed to reach equilibrium. With its help and with an additional assumption on the vanishing of correlations in the remote past Bogoliubov obtains a unique prescription to calculate the time evolution of the one-particle distribution function f to all orders in the density. The result is of the form

$$\frac{\partial f(t)}{\partial t}+A[f(t)]=0,$$

where the time-independent functional A is found as a power series in the density. In lowest order Eq. (3) is obtained.

Another approach to the same problem has been adopted by M. S. Green.[18] It is based on a very elegant formal solution (in powers of the density) of the infinite set of equations following from the Liouville equation for the one-particle, two-particle, etc., distribution functions (the so-called hierarchy). An analysis of this formal solution enables Green to investigate in detail the significance and validity of Bogoliubov's assumptions.

Another type of statistical transport equation, also frequently used and especially well adapted to quantum theory, is the equation describing the irreversible time evolution of the probability distribution of the whole system over a complete set of states. Let us consider (compare with the imperfect systems of part I) a quantum system with a Hamiltonian $H=H_0+V$ containing a perturbation term V to be held responsible for the irreversible behavior. The equation in question, now

[11] For a discussion of these theorems and their significance for statistical mechanics, see L. Rosenfeld, Acta Phys. Polon. **14**, 3 (1955).

[12] For a critical study of the quantum-mechanical ergodic theorem see the recent paper of M. Fierz, Helv. Phys. Acta **28**, 705 (1955).

[13] L. Onsager, Phys. Rev. **37**, 405 (1931) and **38**, 2265 (1931).

[14] Two monographs on the subject are I. Prigogine, *Etude Thermodynamique des Processes Irréversibles* (Dunod, Paris, and Desoer, Liège, 1947), and S. R. de Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951).

[15] See, for example, D. ter Haar, *Elements of Statistical Mechanics* (Rinehart Publishing Corporation, New York, 1954), p. 38, Eq. (2.507).

[16] See on this subject the Proceedings of the "Colloque International sur les Phénomènes de Transport en Mécanique Statistique" (Bruxelles, September, 1956).

[17] N. N. Bogoliubov, *Dynamical Problems in Statistical Physics* (in Russian), (Moscow, 1946).

[18] M. S. Green, J. Chem. Phys. **25**, 836 (1956).

often called the master equation, involves the probabilities P_α that the system be in the various stationary states α of the unperturbed part H_0 of the Hamiltonian. It is only valid in lowest order in V and reads

$$\frac{dP_\alpha}{dt}=\sum_\beta(W_{\alpha\beta}P_\beta-W_{\beta\alpha}P_\alpha). \tag{4}$$

$W_{\alpha\beta}$ is a transition probability of second order in V. Equation (4) was first derived by Pauli[19] on the assumption that the phases of the wave function in the unperturbed representation α are randomly distributed at all times. It was recently realized that the perturbations occurring in the many-particle systems of quantum statistics (as examples see the imperfect systems mentioned in part I) possess remarkable analytical properties which essentially result from the systems being very large and the perturbations coupling together their many degrees of freedom. On the basis of this recognition it was possible to give a new derivation of Eq. (4), requiring randomness of phases at the initial time only, and to generalize (4) to arbitrary order in the perturbation. The extended master equation thus obtained is integrodifferential in the time and corresponds to a non-Markoffian stochastic process.[20]

The classical analog of the quantum-mechanical master equation (4) has also been considered. Prigogine and Brout, using action and angle variables, have expressed classically the special properties of the perturbation which had been recognized in the quantum case as being responsible for the irreversible motion. They have thereby achieved in lowest order of the perturbation a satisfactory derivation of a classical master equation.[21] Brout has derived in lowest order in the density a master equation for the irreversible motion of a dilute gas.[22] The relation of such an equation to the Boltzmann equation (3) had been previously clarified by an investigation of Kac using a simplified model.[23]

It is clear from this review of recent work that the statistical theory of irreversible processes is in a period of rapid development. The results attained are undoubtedly fragmentary, but the techniques used to derive them are far from being fully exploited and further progress is to be expected. As a problem which still presents considerable difficulty we might mention the treatment of situations where external constraints (like temperature gradients, concentration gradients, etc.) prevent the system under study from reaching equilibrium. For instance the statistical foundation of the phenomenological equations known to describe nonequilibrium steady state processes has not been sufficiently clarified. Another much more ambitious question is the statistical mechanics of nonequilibrium processes in liquids and dense gases. On this last subject we are greatly hampered by the absence of formal techniques properly adapted to the liquid state (see part I), although there are indications that at least for slow irreversible changes this difficulty might not be so essential.[24]

[19] W. Pauli, *Festschrift zum 60 Geburtstage A. Sommerfelds*, (Hirzel, Leipzig, 1928), p. 30.

[20] L. Van Hove, Physica **21**, 517 (1955) reference 16 and Physica (to be published).

[21] R. Brout and I. Prigogine, Physica **22**, 621 (1956).

[22] R. Brout, Physica **22**, 509 (1956).

[23] M. Kac, "Foundations of kinetic theory," Proceedings Berkeley Symposium on Mathematical Statistics (1954).

[24] M. S. Green, J. Chem. Phys. **20**, 1281 (1952) and **22**, 398 (1954); N. G. van Kampen, Physica **20**, 603 (1954).