SOME EXACT RESULTS IN EQUILIBRIUM AND
NON-EQUILIBRIUM STATISTICAL MECHANICS*†

by
J.L. Lebowitz
Belfer Graduate School of Science
Yeshiva University
New York, New York 10033

I. INTRODUCTION

One of the developments in statistical mechanics in the last few years has been the study of rigorous results. The study of intensive properties of very large systems has been at the focal point of this subject because of the realization that many of the interesting phenomena peculiar to macroscopic systems, such as phase transitions and irreversibility, are intimately connected with and can be treated precisely only in the limit when the size of the system becomes infinitely large; called the bulk or the thermodynamic limit. Hence, (in studying these important phenomena), it is essential to discover whether the thermodynamic limit 'exists'. This question we shall discuss in lectures I and II. In the following lectures we shall discuss the problem of analyticity of the thermodynamic functions, and in the fourth lecture outline some results for non-equilibrium statistical mechanics.

I will only attempt here to sketch some of the problems, ideas and results in this area and refer you to "The Book" by Ruelle (1969) and also to the review article by Lebowitz (1968), for details and references. All parts of these lectures which parallel closely the discussion in my review article, as well as all references contained there, will be omitted from these notes.

II. EXISTENCE OF THE THERMODYNAMIC LIMIT

We start with a physical system and assume that its structure and properties can be described by a Hamiltonian. We will also assume that we can neglect nuclear forces and gravitational forces and still obtain a realistic picture of macroscopic matter under normal conditions. Nuclear forces are so strong and short range and hold the nuclei so tightly together that we do not expect ordinary matter to look any different if the nuclei were charged mass points.

The gravitational forces on the other hand are so weak that the mutual gravitational interaction between particles in an ordinary sized object is negligible. As stated by Onsager (1967): thermodynamics is concerned with objects which are large compared to the size of a molecule, but small compared to the moon. The 'thermodynamic limit' should also be understood in this spirit. Ignoring also relativistic effects, which we do not know how to take into account in any consistent way, we can write the Hamiltonian of a system of N particles of mass m as

$$H_N = \sum_{i=1}^{N} p_i^2 / 2m + V_N (\underline{r}_1, \ldots, \underline{r}_N)$$

(This generalizes in an obvious way to a system of s species, of $N^{(j)}$ particles each, with masses m_j, $j=1, \ldots, s$.)

Using the statistical mechanics of Gibbs, we define the canonical partition function of a system of N particles in a container Ω, of volume $|\Omega|$, as

$$Z(\beta, N, \Omega) = \exp \left[-\beta A (\beta, N, \Omega) \right] = \exp \left[-\beta |\Omega| a (\beta, N/|\Omega|; \Omega) \right]$$

$$= \begin{cases} (N!)^{-1} (m/\beta h)^{3N} \int_\Omega \cdots \int d\underline{r}_1 \ldots d\underline{r}_N \exp(-\beta V_N) \text{; classical system} \\ = \text{trace} \exp \left[-\beta H_N \right] = \sum_\ell \exp \left[-\beta \Sigma E_\ell (N, \Omega) \right] \text{; quantum system} \end{cases} \quad (2)$$

where $\beta = 1/kT$ temperature and $a(\beta, N/ |\Omega|; \Omega) = |\Omega|^{-1} A(\beta, N, \Omega)$ is the Helmholtz free energy per unit volume. We now want to determine whether this prescription for finding the thermodynamic free energy of a system from its microscopic Hamiltonian really leads to a proper thermodynamics for macroscopic systems. Thus, we ask the following questions.

1. Does the free energy density $a(\beta, N/|\Omega|; \Omega)$ as defined by eq. (2) have the property of not depending on the shape of the system in the "thermodynamic limit", that is when N and $|\Omega|$ tend to infinity and $N/|\Omega|$ tends to a definite density ρ?: i.e. given a sequence of containers Ω_j and particle numbers N_j, $|\Omega_j| \to \infty$, $N_j/|\Omega_j| \to \rho$ does $\lim_{|\Omega| \to \infty} a(\beta, N/|\Omega|; \Omega) = a(\beta, \rho)$ exist independent of the shape of the container Ω (as long as it is a 'reasonable shape'). 2. Assuming that a (β, ρ) exists is $\beta a(\beta, \rho)$ a convex function of the density ρ and a concave function of the reciprocal temperature β? These two conditions will ensure the thermodynamic stability of our system. The answer to both these questions is yes.

The existence of the thermodynamic limit was proven some time ago for a large class of systems whose Hamiltonian satisfies two conditions. These two conditions are chosen so as to prevent the possibility of the system collapsing, as would happen in a gravitational system, or exploding like a system of positively charged particles would. The first condition is the 'H-stability' condition which requires that there be a lower bound on the energy per particle, i.e.

$$V_N (\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) \geq - NB; \quad B < \infty,$$ independent of N and $\underline{r}_i$: \hfill (3a)

when treating this system quantum mechanically, we would replace this condition by

$$E_o(N) \geq - NB \hfill (3b)$$

where $E_o(N)$ is the ground state energy: (3a) implies (3b) but not conversely.

The second condition on the interaction potential is the tempering condition, and prevents the potential from being too positive at large separations and ensures against explosion. If we have two regions of

space separated by a distance r, containing N_1 and N_2 particles respectively then the tempering condition requires that the interaction between the two groups have an upper bound of the form

$$V(N_1 \oplus N_2) - V(N_1) - V(N_2) \leq C \, N_1 N_2 \, r^{-d-\epsilon}, \text{ for } r > r_o \tag{4}$$

where C and r_o are constants, d is the dimensionality of the system and ϵ is a positive constant. When V_N is a sum of pair potentials, $V_N(\underline{r}_1 \cdots \underline{r}_N) = \sum v(\underline{r}_i - \underline{r}_j)$ and $v(r)$ is a Lennard-Jones type potential then both of these conditions are satisfied. We are thus all right for systems whose basic units are taken to be neutral 'spherical' atoms or molecules. This is not entirely satisfactory, however, in that we believe, as mentioned earlier, that the true interaction potential relevant for macroscopic matter is the Coulomb potential and we should be able to prove the existence of the thermodynamic limit directly for a system of Coulomb charges if the system is overall neutral (or 'approximately' neutral).

Now it is clear that a system of point charges whose pair interaction is $e_i e_j / |\underline{r}_i - \underline{r}_j|$ does not have a lower bound on its potential energy and hence does not satisfy (3a), (unless of course all the charges e_i are of the same sign which is not interesting since such a system clearly does not have any thermodynamics). When the particles have hard cores, however, i.e. there is a minimum distance of approach, R, between the particles, then Onsager showed the existence of a lower bound of this type. (The following form of Onsager's proof was suggested to me by O. Penrose.) The Coulomb interaction energy between different particles can be written in the form

$$V_N = \frac{1}{2} \int \underline{E}^2 \, d\underline{r} - \sum_{i=1}^{N} U_i \geq -N \, \underset{i}{\text{Max}} \, U_i = -NB \qquad (5)$$

where $\underline{E}$ is the electric field and U_i is the self-energy of the i $\underline{th}$

particle which is finite if the charges are assumed to be distributed

over a sphere of radius R. For real (point) charge particles however

only the quantum version of H-stability, (3b) is possible and was re-

cently proven by Dyson and Lenard. They show that (3b) will hold for

any set of charges and masses provided that the negative particles and/or

the positive ones are fermions. (It is curious that although stability

of a small number of charged particles, say an atom, comes about mainly

through the uncertainty principle, which keeps the oppositely charged

particles apart, to obtain (3b) it is also necessary to keep the negative

(or positive) particles apart from each other through the Pauli principle.)

The second requirement; that the potentials be 'tempered', is also ob-

viously not satisfied by the Coulomb potential, which is a long-range

potential. Thus, the proofs which make use of tempering do not apply

However, Lebowitz and Lieb (1969) have been able to overcome these diffi-

culties and prove the existence of the thermodynamic limit also for

Coulomb systems which are overall neutral.

We have also shown, when the system is not strictly neutral that as long

as the excess charge per unit surface area tends to zero as $|\Omega| \to \infty$,

one always obtains the same canonical free energy as for the neutral system.

If the excess charge per unit surface area tends to infinity, however, the

free energy does not exist in the thermodynamic limit. And finally, if

the excess charge per unit surface area tends to a constant then the free

energy approaches a limit equal to the free energy of the neutral system

plus the energy of a surface layer of the excess charge as given by

elementary electrostatics.

6

The same methods which are used in the proof of the existence of the free energy density in the thermodynamic limit also show that this free energy density is thermodynamically stable. It is furthermore possible to show that the microcanonical and grand canonical ensembles yield thermodynamic potentials equivalent to those obtained from the canonical ensemble in the thermodynamic limit. Thus, it has been shown for a large class of systems, that the thermodynamic quantities as calculated from statistical mechanics are well defined in the bulk limit and have the required stability properties.

II. PHASE TRANSITIONS

While the existence of the thermodynamic limit was initially proven for 'rigid wall' boundary conditions at the surface of Ω the results have recently been extended, for some systems, also to different boundary conditions; e.g. systems on a torus (periodic boundary conditions), and systems for which the normal derivative of the wave function vanishes on the surface of Ω, (Fisher and Lebowitz, 1970; Robinson, 1970). There is little doubt that all free energy densities, (in the bulk limit), are independent of the boundary conditions. What is perhaps more interesting is that quantities like the magnetization per unit volume $m(\beta, \mathcal{H}; \Omega)$, which is the <u>derivative</u> of the free energy density $\varphi(\beta, \mathcal{H}; \Omega)$ of a lattice spin system of volume $|\Omega|$ in the presence of an external magnetic field $\mathcal{H}$, <u>do</u> depend sometimes on the boundary conditions even in the limit $|\Omega| \to \infty$. This was proven first by Peierls for a two dimensional Ising spin system with nearest neighbor ferromagnetic interactions at $\mathcal{H} = 0$ and β large (low temperatures). The two different boundary conditions considered were (1) the spins at the surface all point up and (2) they all point down. Peierls' result implies the non-interchangeability

of the order of taking the limit $|\Omega| \to \infty$ of $\varphi(\beta,\mathcal{N};\Omega) \to \varphi(\beta,\mathcal{N})$ and taking

the derivative of $\varphi(\beta,\mathcal{N};\Omega)$ with respect to $\mathcal{N}$. It follows from this

that the thermodynamic free energy density $\varphi(\beta,\mathcal{N})$ will have, at low temper-

atures, a discontinuity in its first derivative, (the magnetization

$m(\beta,\mathcal{N}) = \partial\varphi(\beta,\mathcal{N})/\partial\mathcal{N})$, at H = 0, i.e. the system will have a phase trans-

ition. This can be seen simply (as pointed out to me by E. Lieb) from

the fact that $\varphi(\beta,\mathcal{N};\Omega)$ is, for different Ω, a sequence of convex functions

of $\mathcal{N}$ which approach a limit $\varphi(\beta,\mathcal{N})$. The limit function must therefore

also be convex and $\partial\varphi(\beta,\mathcal{N}:\Omega)/\partial\mathcal{N} \to \partial\varphi(\beta,\mathcal{N})/\partial\mathcal{N}$ for all values of $\mathcal{N}$ at

which the latter is continuous.

The Peierls argument and results have been extended to higher dimensions
and more general kinds of spin and lattice gas systems (c. f. Ginibre 1970).
this way the existence of 'phase transitions' in a variety of lattice
systems has been proven. In addition, as is well know, the exact solution
of some two dimensional lattice models by Onsager and Lieb have explicitly
shown the existence of phase transitions in these systems.

This is very satisfactory as far as it goes as it agrees with our
experience of the ubiquity of phase transitions in macroscopic systems.
What is less satisfactory, however, is the lack of proof, so far, of the
existence of any phase transitions, such as the vapor-liquid transition,
in continuum systems with reasonable pair potentials between the particles.
It is only for the limiting case of an infinitely long range potential that
the existence of a phase transition has been established rigorously in
continuum systems.

I am referring here to the so-called van der Waals limit of a system whose pair potential has the form

$$v(r) = q(r) + \gamma^d \, \varphi(\gamma r) \tag{6}$$

Here $q(r)$ is a potential containing a hard core and satisfying the tempering condition and $\gamma^d \varphi(\gamma r)$ is a Kac potential with range γ^{-1} such that

$$\int \gamma^d \, \varphi(\gamma r) \, d\underline{r} = \alpha \,, \tag{7}$$

independent of γ. It was shown by Kac, Uhlenbeck and Hemmer in one dimension, $d=1$, and later by Lebowitz and Penrose for any dimension that in the van der Waals limit $\gamma \to 0$, taken _after_ the thermodynamic limit $|\Omega| \to \infty$ such a system will exhibit, for a large class of Kac potentials, a first order gas-liquid phase transition of the classical van der Waals type. The treatment of Lebowitz and Penrose has been extended recently to more general Kac potentials by Gates and Penrose (1969).

IV NON-EQUILIBRIUM SYSTEMS

As can be seen from the earlier lectures, the rigorous study of equilibrium statistical mechanics has achieved notable results already. The comparable investigation of the infinite volume limit of non-equilibrium systems is much more difficult and has begun only recently. Results have been obtained by Lanford (1968 a,b), but are restricted to one-dimensional systems of classical point particles interacting by smooth, finite range pair forces F.

Let (q_i,p_i) represent the positions and velocities of a set of particles of unit mass each. Then Newton's equations of motion have the form

$$\frac{d\,q_i(t)}{dt} = p_i(t) \quad , \quad \frac{d\,p_i(t)}{dt} = \sum_{j\neq i} F\,(q_i(t) - q_j(t)) \qquad (8\ a,b)$$

where F is the interparticle force. If we have a finite number of particles then there is clearly a unique solution to this set of differential equations for all sets of initial conditions $\left\{q_i(0)\ ,\ p_i(0)\right\}$. The existence of a meaningful solution to Newton's equations, i.e. the existence of a time evolution of the system, becomes however far from trivial when we consider a system consisting (in some limit) of an infinite number of particles. In such a system it is quite possible to begin with a perfectly reasonable set of initial values $\left\{q_i(0)\ ,\ p_i(0)\right\}$ and find after some finite time t that there are an infinite number of particles in a finite region of space and that the right side of (8b) is infinite. We illustrate this with a simple example given by Lanford (1968 a). If there are no interparticle forces and if at time zero, $p_i = -q_i$ for each i, then all

the particles will be situated at the origin at time t = 1. Thus, we need to find a class of initial conditions for which such catastrophies do not happen. In fact, as we are interested in equilibrium statistical mechanics, we would like to show that those classes of initial conditions which have non-zero probability of occurring in equilibrium, do not give rise to such catastrophies. An even stronger desired result is to show that the time evolution of a part of the system contained in a fixed region of space D will, at any time t, be determined entirely by the state of the system at time t=0 in the neighborhood of D (how large this neighborhood is will of course depend on t). This was indeed proven by Lanford for one dimensional systems. He proves the existence for all times of a "regular" solution of Newton's equations of motion for a "regular" initial configuration. A regular configuration is, roughly speaking, one in which the number of particles in a unit interval and the magnitude of the momentum of any particle in that interval have a bound of the form $\delta \log R$ where R denotes the distance of the interval from the origin. It is further shown that, at equilibrium, if either the activity is small or the interparticle potential is positive, the set of non-regular configuration has probability zero.

A question left open by these results is whether a state which at time t=0 is described by a set of correlation functions can still be described by a set of correlation functions when t≠0. This was investigated by Gallavotti, Lanford and Lebowitz (1970) who proved that, for certain classes of initial states, the time-evolving state is described by correlation functions and that these correlation functions satisfy the BBGKY hierarchy in the sense of distributions.

The initial states we consider can be described as follows: Suppose that the system is in equilibrium at temperature β^{-1} and activity z under the influence of a pair potential and an external potential h which is localized in a finite region I_h. At time t=0 we switch off the external field and the system begins to evolve. We prove that if the activity is sufficiently small (i.e. if we are deep inside the gaseous phase) the system can always be described by a set of correlation functions which vary in time according to the BBGKY hierarchy. We are, however, unable to prove even that the time averaged correlation functions evolve toward the correlation functions which correspond to the equilibrium state at temperature β^{-1} and activity z (in absence of external field) as would be expected. We are, however, able to prove that the time averaged correlation functions coverage to a limit satisfying the stationary BBGKY hierarchy.

While initial states of the kind just described suffice, in principle, for the study of transport properties such as diffusion at low activity an alternative, sometimes more direct way to study transport processes is through the van Hove time displaced distribution functions (t.d.f.) These are time dependent correlation functions which correspond to different types of initial conditions from those just considered. Instead of considering the time evolution of an initial ensemble density having the form, (for a fixed number of particles),

$$\mu (x_i, \ldots, x_N; t = 0) = \mu_{eq} (x_1, \ldots, x_N) \, \Psi (x_1, \ldots, x_N)$$

where $x_i = (q_i, p_i)$, μ_{eq} is the equilibrium Gibbs canonical ensemble density corresponding to the correct Hamiltonian for $t > 0$ and Ψ

is a symmetric function of the x_i the t.d.f. are correlation functions
obtained from an initial ensemble which is in equilibrium with one or
more _particles_ having specified positions and momenta. A typical en-
semble density of this kind is

$$\mu (x_1,\ldots, x_N; t = 0 = [\mu_{eq} (x_1,\ldots, x_N)/f_{eq}(x_1)]\delta(x_1 - x_1^0)$$

where $f_{eq} (x_1)$ is the equilibrium distribution function of particle one.
The distribution function of this particle at time $t, f(x_1, t)$, is the
time displaced one particle self distribution function. (If we integrate
this function over velocities we obtain the van Hove self function which
is important in neutron scattering experiments.) The self-diffusion con-
stant can be obtained directly from $f(x,t)$ and other transport coefficents
can be obtained from similarly defined t.d.f.

We (Lebowitz and Percus, 1967: Lebowitz, Percus and Sykes, 1968,1969)
have made an extensive study of these t.d.f. for a one dimensional system
of hard rods of diameter R obtaining many of them in explicit form. The
self-diffusion constant for example, (defined, of course, in the thermo-
dynamic limit), is given by $D = (2 \pi \beta m)^{-\frac{1}{2}} (1-\rho R) / \rho$

Much remains to be done in this field.

REFERENCES

Fisher, M.E. and Lebowitz, J.L., "Asymptotic Free Energy of a System With Periodic Boundary Conditions", to appear in Communications in Mathematical Physics, 1970.

Gallavotti, G., Lanford, III, O.E. and Lebowitz, J.L., "Thermodynamic Limit of Time Dependent Correlation Functions for One Dimensional Systems", to appear in Journal of Mathematical Physics, 1970.

Gates, D.J. and Penrose, O., Communications in Mathematical Physics, 15, 255 (1969): 16, 231 (1970).

Ginibre, J., Colloques Internationaux Du Centre National De La Recherche Scientifique, 181, 163 (1970).

Lanford, O. E. (1968) Communications in Mathematical Physics, 9, 176, (1968): 11, 257, (1969)

Lebowitz, J. L., Annual Review of Physical Chemistry, 19, 389, (1968).

Lebowitz, J.L. and Lieb, E.H., Physical Review Letters, 22, 631, (1969).

Lebowitz, J.L. and Percus, J.K., Physical Review, 155, 122 (1967).

Lebowitz, J.L., Percus, J.K. and Sykes, J., Physical Review, 171, 224, (1968): 188, 487 (1969).

Onsager, L., The Neurosciences, Rockefeller - University Press, 1967.

Robinson, D., Communications in Mathematical Physics, 16, 290 (1970).

Ruelle, D., "Statistical Mechanics" (Benjamin, New York, 1968)