

## STRUCTURE OF SIMPLE FLUIDS

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One of the most important of the many achievements of Willard Gibbs was the derivation of a single equation of universal validity, by which the properties of a macroscopic system in equilibrium could be expressed in terms of the submicroscopic mechanical properties of the molecules composing it. I wish to discuss the present status of the methods of numerical evaluation of one problem using this equation.

It is known experimentally, with a simple extrapolation from thermodynamic theory, that any system composed of real molecules at any finite nonzero temperature,  $T$ , and at infinite dilution, for which the number density,  $\rho = N/V$ , of molecules approaches zero, exists as a perfect gas. For the perfect gas the pressure,  $P$ , is given by the equation,  $P = \rho kT$ , with  $k$  equal to Boltzmann's constant,  $k = 1.38 \times 10^{-16}$  ergs/deg °K. The energy of the perfect gas depends only on  $T$ , and not on the density,  $\rho$ . At sufficiently high temperature, and what is high or low depends on the type of molecule, the material remains gaseous even if the pressure is increased to any experimentally attainable value. The perfect gas equation is no longer obeyed exactly at high densities, but  $P$  remains a smooth, and presumably analytic, monotonic function of  $\rho$ . At low temperatures, below the critical temperature, condensation occurs as the density is increased. If only one species of molecule is present the condensation is abrupt on the pressure plot, that is the density increases discontinuously from that of the gas to that of the condensed phase. Below the triple point temperature the condensed phase is crystalline. (The one exception is helium for which the triple point does not exist above zero.) Above the triple point the condensed phase is a liquid.

The thermodynamic properties of a system are completely determined if one knows the equation for the energy,  $E_0$ , as a function of  $T$  in the perfect gas state,  $E_0(T)$ , and the equation of state, that is the equation for the pressure as a function of density and temperature,  $P = P(\rho, T)$ . The energy,  $E_0(T)$ , of the perfect gas, can be readily expressed from the Gibbs formulation as  $3NkT/2$  plus a sum over the internal quantum states of the molecules, and even for relatively

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complicated molecules the equations can be evaluated numerically, often even with greater precision than calorimetric measurements achieve. For the gas, the pressure, at a given temperature, may be expressed as a power series in the density,  $\rho$ . The temperature dependent coefficient of  $\rho^\nu$ , known as the  $\nu$ 'th virial coefficient, can be expressed as an integral of a function of their mutual potential over the relative position coordinates of  $\nu$  molecules. Although numerical evaluation for coefficients higher than the second is relatively difficult, no fundamental problem seems to be involved.

For the condensed phase the situation is less satisfactory. At low temperatures, for which the material condenses to a crystal, one proceeds by making use of this empirically known fact, and the known crystal structure. The integrand, which occurs in the Gibbs formulation, is then assumed to have a (computable) maximum when the atoms are all situated on the lattice sites of the known experimental lattice. The energy is then assumed to be quadratic in the small displacements from these equilibrium positions, and by the method of normal coordinates reasonably satisfactory computations are possible.

For the intermediate temperature range between the triple point and the critical point, and for which the condensed phase is a liquid, the situation is in still poorer shape. In the liquid (as also in the very high density gas), each molecule is simultaneously in interaction with a large number of neighbors. The development of the virial expansion, in which one considers first pair interactions, then triples, etc., no longer converges. On the other hand there is no single, regular, periodic configuration of dominant probability, which can be used as a starting point of a development for small displacements, as in the crystal. One is forced to a general consideration of the fundamental equations.

The computation of the thermodynamic properties does not answer all possible questions about a liquid. Among others one would certainly wish to know what may be vaguely called its structure. For some time even a precise question had not been formulated, the answer to which would describe the structure of a liquid unambiguously. At the present time, possibly unwisely, one assumes the description to be answered best in terms of the probability densities,  $\rho_n$ , for  $n = 1, 2, 3, \dots$  molecules. The function,  $\rho_1(\mathbf{r})$ , is defined conceptually by the statement that  $\rho_1(\mathbf{r})d\mathbf{r}$  is the probability that a molecule will be found at the position  $\mathbf{r}$  in the volume element  $d\mathbf{r}$ . For a fluid  $\rho_1(\mathbf{r})$  is a trivial constant equal to the average number density  $\rho$ . The quantity  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2$  is defined as the probability of finding

simultaneously a molecule at  $\mathbf{r}_1$  in  $d\mathbf{r}_1$  and one at  $\mathbf{r}_2$  in  $d\mathbf{r}_2$ . This pair density,  $\rho_2$ , is a function only of the distance,  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ , in a fluid, and can be found experimentally as the Fourier transform of the X-ray scattering intensity. The higher probability densities, such as  $\rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ , proportional to the probability of simultaneously finding molecules at  $\mathbf{r}_1$ ,  $\mathbf{r}_2$ , and  $\mathbf{r}_3$ , are experimentally unobservable, at least at present, but are essential concepts in almost any attempt to treat the transport properties of fluids such as viscosity or conductivity. These probability densities for the equilibrium system are also formally derivable from the general Gibbs equation.

The discussion of the status of the attempt to obtain a general treatment by which the formal Gibbs equations can be evaluated numerically is my subject. Any such general treatment would apply equally to crystal, or to dilute gases, although in these cases more special methods lead to simpler solutions.

The mathematical problem may be stated to be the evaluation for small values of  $n$ ,  $n=0, 1, 2$ , etc., of a set of functions,  $G_n\{n\}$ , given by the equation,

$$(1) \quad G_n\{n\} = \sum_{N \geq 0} \frac{z^N}{N!} \int \int_V \cdots \int G_{n+N}^{(0)}\{\{n\} + \{N\}\} d\{N\},$$

where the symbol  $\{n\}$  is used for the  $3n$  cartesian coordinates of  $n$  molecules in 3-dimensional space,

$$(2) \quad \mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_n,$$

and  $d\{n\}$  for the  $3n$ -dimensional volume element,

$$(3) \quad d\{n\} = d\mathbf{r}_1 \cdots d\mathbf{r}_n.$$

The parameter  $z$  is real positive, and we are interested in values up to those for which  $zV$  may be very large,  $zV \cong 10^{28}$ . The functions,  $G_N^{(0)}$ , are real positive symmetric functions of the coordinates of  $N$  molecules, such that the function  $G_{N+M}^{(0)}$  approaches in value the product of functions  $G_N^{(0)}G_M^{(0)}$  when the coordinates,  $\{N\}$ , of  $N$  of the molecules are all very far distant from all the coordinates,  $\{M\}$ , of  $M$  of them,

$$(4) \quad G_{N+M}^{(0)}\{\{N\} + \{M\}\} \rightarrow G_N^{(0)}\{N\}G_M^{(0)}\{M\},$$

if  $r_{nm} \rightarrow \infty$ ,  $1 \leq n \leq N$ ,  $N+1 \leq m \leq N+M$ .

The function  $G_1^{(0)}(r_i)$  is unity, so that,

$$(5) \quad G_N^{(0)}\{N\} \rightarrow \prod_{i=1}^{i=N} G_1^{(0)}(r_i) = 1, \quad r_{ij} \rightarrow \infty, N \geq i > j \geq 1.$$

Furthermore the functions  $G_N^{(0)}$  approach zero in value if any of the distances,  $r_{ij}$ , approach zero,

$$(6) \quad G_N^{(0)} \{N\} \rightarrow 0, \quad \text{any } r_{ij} \rightarrow 0.$$

The volume,  $V$ , over which the integration is to be extended, is to be taken as very large compared to  $r_0^3$  if  $r_0$  is the significant distance compared to which the relations (4), (5), and (6) become valid.

The physical interpretation of the problem is that of the computation of the equation of state, with the Grand Canonical Partition Function of Gibbs, after summation over the internal molecular quantum states, and integration over the momenta. A macroscopic system of one kind of molecule, in equilibrium, has its thermodynamic state specified by three variables, one of which must determine the over-all size of the system, and may be chosen as the volume,  $V$ . The other two may be chosen as intensive variables, one of which determines the concentration of energy in the system, and the other the concentration of molecules. Of these, the first is usually chosen as the absolute temperature,  $T$ . The other, that which determines the concentration of molecules or density, we choose as the activity,  $z$ . This is related to the chemical potential,  $\mu$ , of Gibbs, by the equation,

$$(7) \quad z = \exp [(\mu - \mu_0)/kT],$$

where  $\mu_0$  is so chosen that  $z$  becomes equal to the number density,

$$(8) \quad \rho = N/V,$$

at the limit that both become zero,

$$(9) \quad \lim_{z \rightarrow 0} \left[ \frac{z}{\rho} \right] = 1, \quad (\text{determines } \mu_0),$$

for which density the system always approaches a perfect gas in properties.

If  $G_N^{(0)}$  is defined to be

$$(10) \quad G_N^{(0)} = \exp (-U_N \{N\}/kT),$$

with  $U_N \{N\}$  the mutual potential energy of the molecules,

$$(11) \quad U_N \{N\} \rightarrow 0 \quad \text{all } r_{ij} \rightarrow \infty, \quad N \geq i > j \geq 1,$$

$$(12) \quad U_N \{N\} \rightarrow \infty \quad \text{any } r_{ij} \rightarrow 0,$$

then the function  $G_0$  has the physical significance that

$$(13) \quad G_0 = e^{PV/kT}.$$

with  $P$  the pressure of the system. One might point out here that  $PV/kT$  is of the order of the number,  $\bar{N}$ , of molecules in the volume,  $V$ , and we wish to choose  $V$  large enough that this is something like  $10^{23}$ .

Since  $P$  is expressed by the equation (1) for  $n=0$  as a function of  $z$  and  $T$ , the thermodynamic relations,

$$(14) \quad z [\partial(P/kT)/\partial z]_T = \rho,$$

$$(15) \quad [\partial(P/kT)/\partial T]_z = H - H_0,$$

with  $H$  the Enthalpie and  $H_0$  the Enthalpie of the perfect gas state, serve to give the difference of all thermodynamic properties of the system from those of the perfect gas.

The computation of the thermodynamic properties of the perfect gas is not only formally given by the equations of Gibbs, but is numerically evaluated with high precision for many even relatively complicated molecules, using spectroscopic data. Given  $U_N$ , which is an appropriately averaged mutual potential over the internal molecular states, the evaluation of equation (1) for  $n=0$  would complete the computation of all of the thermodynamic properties at all temperatures and densities. Even for systems which are essentially quantum mechanical a modification of the meaning of  $G_N^{(0)}$ , leads to the correct equations. We might also mention that the extension to systems composed of several kinds of molecules does not introduce essentially new complications.

The functions  $G_n$  of Equation (1) for  $n=1, 2$ , etc., go beyond the thermodynamic specification of the system. In general the physical meaning is that

$$(16) \quad G_n \{n\} = e^{PV/kT} z^{-n} \rho_n \{n\},$$

where  $\rho_n \{n\}$  is the probability density that molecules will be found simultaneously at all of the positions  $\{n\}$ . Since for a fluid  $\rho_1(\mathbf{r}_i)$  is a constant,

$$(17) \quad \rho_1(\mathbf{r}) = \rho,$$

the equation for  $n=1$  gives no essentially new information, but  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$  for a fluid, which is a function of the distance,

$$(18) \quad r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|,$$

$$(19) \quad \rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho_2(r_{12}), \quad (\text{fluid})$$

is the Fourier transform of the X-ray scattering intensity, and hence is known experimentally, (Fig. 1).

For a fluid  $\rho_2(r_1, r_2) = \rho_2(|r_1 - r_2|)$

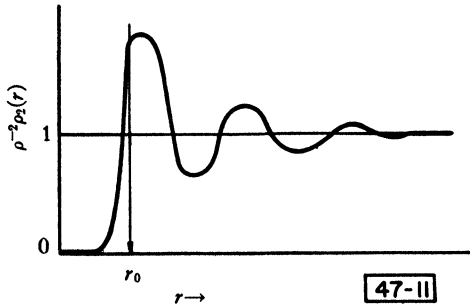


FIG. 1

The theoretical physicist has one great advantage over the pure mathematician as recompense for the difficulty of the problems which he is forced to undertake: he usually knows the correct answers to his problems, answers supplied by the experimentalists. The solutions of Equation (1) for  $n=0$  lead to curves of  $P$  versus  $z$  that look qualitatively like those of Fig. 2. Starting at the origin,  $P$  increases linearly with  $z$  with a slope  $kT$ . The curves then tend to bend upwards at all low temperatures, and at sufficiently low  $T$  values there is a singularity followed by an enormous increase in slope corresponding to the discontinuous density increase at the activity of condensation. For increasing  $T$  values the singularity moves toward

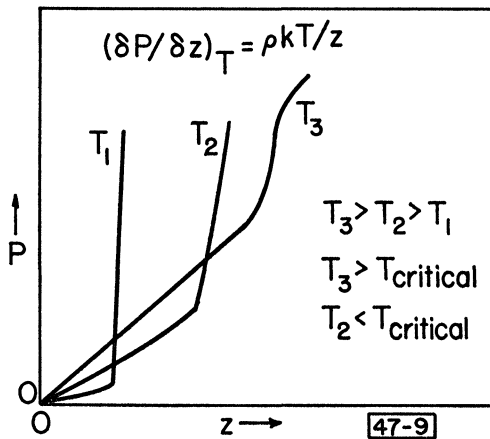


FIG. 2

increasing  $z$ -values, becomes less marked, and finally seems to disappear at the critical temperature,  $T_c$ . Above  $T_c$  the curves look smooth. Translated to plots of  $P$  versus  $\rho^{-1}$  these are the familiar  $P$  versus  $V$  plots of Fig. 3 with the shaded two-phase region for all temperatures below  $T_c$ , for which both gas and the condensed phase of liquid or crystal are coexistent.

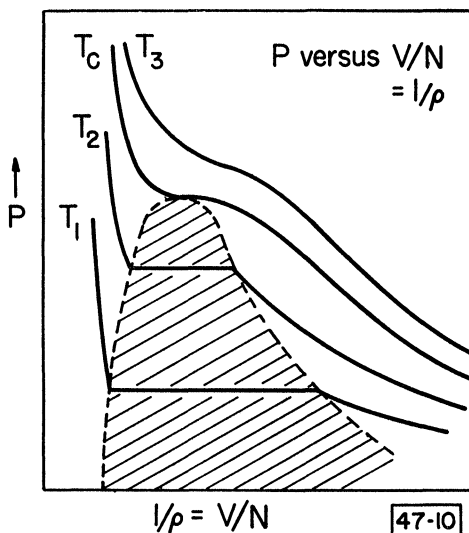


FIG. 3

Finally to make the characteristics of the functions  $G_N^{(0)}$  more explicit we may mention that for simple spherical, or nearly spherical, chemically saturated molecules, one generally assumes  $U_N$  to be a sum of mutual pair potentials,

$$(20) \quad U_N = \sum_{N \geq i > j \geq 1} u(r_{ij})$$

with the potential of a single pair given by the Lennard-Jones 6-12 potential,

$$(21) \quad u(r) = u_0 [(r_0/r)^{12} - 2(r_0/r)^6],$$

with a minimum value,  $u = -u_0$ , at  $r = r_0$ , (Fig. 4). For such molecules the pressure will be a universal function of  $kT/u_0$  and  $zr_0^3$ , a statement equivalent to the "Law of Corresponding States."

Returning now to the mathematical problem of evaluation of equation (1), we see that the assumption of a zero potential,

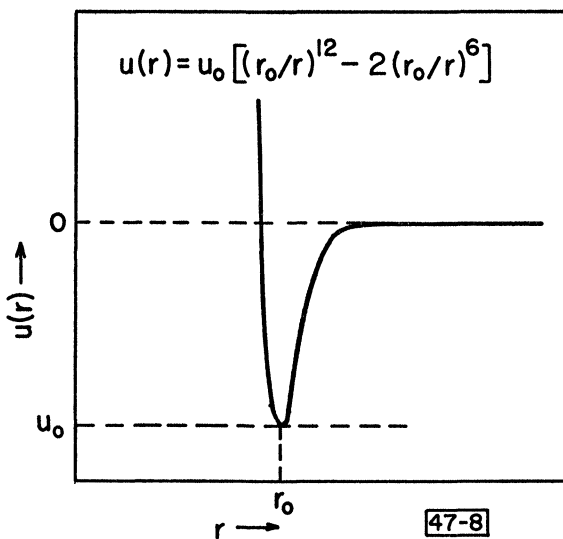


FIG. 4

$$(22) \quad U_N = 0, \quad G_N^{(0)} = 1,$$

leads to the trivially simple result,

$$(23) \quad G_0 = e^{PV/kT} = \sum_{N \geq 0} \frac{z^N}{N!} V^N = e^{Vz},$$

$$(24) \quad P/kT = z$$

which, with equation (14) gives  $z = \rho$ , or the perfect gas equation,  $\rho = N/V$ , that

$$(25) \quad PV/NkT = 1.$$

This is the starting point for the solution at low values of  $z$ . We write  $G_N^{(0)}$  as unity, the value which it has when all molecules are far apart, plus correction terms which are nonzero only when there are clusters of molecules close together. There will be  $N(N-1)/2$  terms which are nonzero when single pairs are close together. The correction terms for two pairs are the products of the terms for the two single pairs. Those for  $n_2$  pairs,  $n_3$  triples,  $\dots$ ,  $n_\nu$   $\nu$ -fold clusters, are the product of functions of  $n_2$  pair corrections,  $n_3$  triple corrections,  $\dots$ ,  $n_\nu$   $\nu$ -fold corrections all of which are nonzero only when all the molecules of the cluster are close to each other. That is, one expresses  $G_N^{(0)}$  as



$$G_N^{(0)} = 1 + \sum_{n_2} \sum_{n_3} \cdots \sum_n \prod_{p=1}^{p=n_2} \text{(pair corrections)} \\ \times \prod_{i=1}^{i=n_3} \text{(triple corrections)} \cdots \prod_{c_p=1}^{c_p=n} (\nu\text{-fold corrections}).$$

It is not difficult to express the  $\nu$ -fold cluster correction quite generally in terms of  $G_\mu^{(0)}$  for  $\mu \leq \nu$ . If an integral,

$$(26) \quad b_\nu = (1/\nu!V) \int \int_V \cdots \int (\nu\text{-fold corrections}) d\{\nu\},$$

is defined, one sees that at the limit  $V \rightarrow \infty$ ,  $b_\nu$  is independent of  $V$ . The combinatorial problem of the number of ways one can make  $n_\nu$  clusters of  $\nu$  each is easily solved, and the simple result,

$$(27) \quad P/kT = z + \sum_{\nu \geq 2} b_\nu z^\nu,$$

is found. The coefficient,  $b_2$ , for instance, is

$$(28) \quad b_2 = \frac{1}{2} \int 4\pi r^2 \left\{ \left[ \exp - \frac{1}{kT} u(r) \right] - 1 \right\} dr.$$

Equation (27) gives a useful expression for  $P$  for low  $z$ -values, and is valid up to the first singularity,  $z = z_0$ , on the positive real axis of  $z$ , which singularity is at the activity,  $z_0$ , of condensation. For the condensed state we are forced to use more erudite methods.

Before discussing the integral equation approach, one should at least mention the cell or free volume method, which does lead, without too great computational difficulties, to expressions for  $P$  that are reasonably good in the condensed phase range. The method may be justified in various ways. That which I prefer is as follows. One may readily prove that any thermodynamic potential is always an extremum for the equilibrium distribution of molecules. One may then assume a distribution, namely the functions  $G_N^{(0)}$  of equation (1), in some analytical form such that the integrations over the coordinates can actually be carried out, and some thermodynamic potential, say the Helmholtz Free Energy, actually computed for this nonequilibrium assumed distribution. If there are any adjustable parameters of the distribution they should be so determined as to give a minimum Free Energy for fixed  $V$ ,  $T$ , and  $N$ .

The simplest integrable distribution is that of placing the  $N$  molecules in a close-packed lattice of  $N$ -cells, with one molecule per cell constrained to a probability distribution within the cell, say a simple

Gaussian around the center, independently of the positions of the others. The single adjustable parameter is then that determining the Gaussian width. The model may be improved by adjusting the lattice parameter, permitting more cells than molecules, with some cells empty, or further by permitting a correlation which changes the probability of finding a cell empty depending on the number of neighboring empty cells.

Different variations of this method have led to reasonably respectable equations for the pressure in the condensation range. However it is fair to say that none of these various approaches has grown to the stature of distinguishing two condensed phases, crystalline and liquid in different temperature-density ranges. Essentially the method always assumes a long range crystalline order.

The most ambitious method of solution of the problem is that which leads to a system of integral equations.

Consider any linear operator,  $O$ , which operates on  $G_N^{(0)}$  to give,

$$(29) \quad OG_N^{(0)} = G_N^{(0)} \left[ \sum_{i=1}^{i=N} \psi_1^{(0)}(\mathbf{r}_i) + \sum_{N \geq i > j \geq 1} \psi_2^{(0)}(\mathbf{r}_i, \mathbf{r}_j) + \sum_{N \geq i \geq j \geq k \geq 1} \psi_3^{(0)}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) + \dots \right],$$

and on  $G_n$  to give a similar sum,

$$(30) \quad OG_n = G_n \left[ \sum_{i=1}^{i=n} \psi_1(\mathbf{r}_i) + \sum \sum + \dots \right].$$

Operate on both sides of equation (1) with  $O$ . On the right, under the integral, consider a single term of the sum of equation (29), say the term  $\psi_{\nu+\mu}^{(0)}$  with  $\{\nu\}$  consisting of some of the molecules of  $n$ , and  $\{\mu\}$  a subset of the molecules of  $N$ . Sum over all values of  $N \geq \mu$ , which will contain such a term, and integrate over the coordinates  $d\{N-\mu\}$ . One obtains just  $G_{n+\mu} \psi_{\nu+\mu}^{(0)}$  to be integrated over  $d\{\mu\}$ . One has, then, on the left the functions on the right hand side of equation (30), and on the left a sum of integrals of  $\int G_{n+\mu} \psi_{\nu+\mu}^{(0)} d\{\mu\}$ . With a little algebraic manipulation this can be brought into the form of a generalized vector-matrix equation,

$$(31) \quad \Psi = L\Psi^{(0)},$$

i.e.

$$(31') \quad \psi_n = \sum_m L_{n,m} \psi_m^{(0)},$$

in which  $\Psi$  is a vector whose components,  $\psi_n$ , are themselves functional vectors in the continuous  $3n$ -dimensional coordinate space of  $n$  molecules, and  $L$  is a matrix, whose elements,  $L_{n,m}$ , are themselves rectangular continuous matrices of  $3n$ - and  $3m$ -dimensional coordinates, that is,  $L_{n,m}\psi_m^{(0)}$  means matrix multiplication,

$$(32) \quad L_{n,m}\psi_m^{(0)} = \int \int \cdots \int L(\{n\}, \{m\})\psi_m^{(0)}\{m\}d\{m\}.$$

The elements  $L_{n,m}$  are functions that can be expressed in terms of  $\rho_{n+m}\{n+m\}$ ,  $\rho_{n+m-1}\{n+m-1\}$ , etc., that is in terms of the probability densities,  $\rho_\mu\{\mu\}$ , for  $1 \leq \mu \leq n+m$ .

$$(33) \quad L_{n,m} = L_{n,m}(\rho_{n+m}\{n+m\}, \rho_{n+m-1}\{n+m-1\}, \cdots).$$

If the elements  $L_{n,m}$  were known this could be used for a perturbation calculation. For instance, if the potential  $U_N$  were written as

$$(34) \quad U_N = U_N^{(0)} + \lambda \sum_{i=1}^{i=N} \psi_1^{(0)}(\mathbf{r}_i) + \lambda \sum_{N \geq i > j \geq 1} \psi_2^{(0)}(\mathbf{r}_i, \mathbf{r}_j) + \cdots,$$

and the operator  $O$  as  $O = -kT(d/d\lambda)_{\lambda=0}$ , then the functions  $\psi_\nu$  would give the effect, in first order, of the perturbations due to  $\psi_\nu^{(0)}$  on the functions  $G_n$ .

Actually the functions  $G_n\{n\}$  composing the elements  $L_{n,m}$  are exactly the unknowns that we wish to determine. Equation (31), then, is only of value if the operator  $O$  is so chosen that there is a functional relationship between the functions  $\psi_n$  and the  $\rho_n$ , and this is the trick which has been used by Yvon, and by Kirkwood. I will discuss this in more detail later.

One remark may be inserted here. The determination of  $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$  as a function of  $z$  and  $T$  is adequate also for a determination of  $P$ , and hence all other thermodynamic functions, since  $P$  is given by the virial theorem as an integral involving the forces between pairs of molecules multiplied by the pair density.

However, equation (1) can be solved for the functions  $G_N^{(0)}$  in terms of the functions  $G_n$ , and the solution is,

$$(35) \quad G_n^{(0)} = \sum_{N \geq 0} \frac{(-z)^N}{N!} \int \int_V \cdots \int_V G_{n+N}\{n+N\}d\{N\},$$

which can be readily checked by using one expression in the other and obtaining an identity, and which is adequate proof since the condition (6) requires that both series (1) and (35) are absolutely

convergent for finite  $V$ . The operation  $\mathbf{O}$  on both sides of (35) results in the expression,

$$(36) \quad \Psi^{(0)} = \mathbf{L}^{(0)}\Psi,$$

where the elements,  $L_{n,m}^{(0)}$ , of  $\mathbf{L}^{(0)}$  are expressible in terms of  $(-z)^\mu e^{U_\mu/kT}$  for  $1 \leq \mu \leq n+m$ , in the same way that  $L_{n,m}$  depends on  $\rho_\mu$ . Thus the elements  $L_{n,m}^{(0)}$  are now known functions.

Combining equations (31) and (36) one sees that

$$(37) \quad \mathbf{L}\mathbf{L}^{(0)} = \mathbf{L}^{(0)}\mathbf{L} = \mathbf{1}$$

with  $\mathbf{1}$  the unit matrix. The sums

$$(37') \quad \sum_m L_{km} L_{mk}^{(0)} = \sum_m L_{k,m}^{(0)} L_{m,k} = \mathbf{1},$$

can now also be seen to converge for relatively small  $m$  values, for instance if  $k=1$  and  $m > 13$  there is no range of the coordinates  $\{m\}$  for which both  $L_{1,m}(\mathbf{r}_1, \{m\})$  and  $L_{m,1}^{(0)}(\{m\}, \mathbf{r}_1)$  differ significantly from zero.

A specialized form of equation (31) was first derived by Yvon in France, and a similar one by Kirkwood. Later Born and Green independently derived the Yvon form. In all these cases the operation  $\mathbf{O}$  involved one unique molecule, whose coordinates could be placed at the origin. Some renumbering of the matrix elements is necessary, and one then has,

$$(38) \quad L_{n,m} = L_{n,m}[\rho_{n+m+1}\{n+m+1\}, \rho_{n+m}, \dots],$$

instead of (33), in particular  $L_{1,1}$  depends on  $\rho_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$ . However the operator was so chosen that the functions  $\psi_\nu^{(0)}$  and  $\psi_\nu$  bore known relations to  $G_n^{(0)}$  and  $G_n$ , respectively. In the Yvon (and Born-Green) case,

$$(39) \quad \mathbf{O} = -kT\nabla_0$$

with  $\nabla_0$  operating on the coordinate of the unique molecule whose coordinate can be taken at the origin, so that,

$$(40) \quad \psi_1^{(0)} = \nabla u(|\mathbf{r}|), \quad \psi_1 = -kT\nabla \ln \rho_2(|\mathbf{r}|).$$

If the total potential,  $U_N$ , is purely a sum of pair terms, equation (20), one has

$$(41) \quad \psi_\nu^{(0)} \equiv 0, \quad \nu > 1.$$

The equations become, in our notation,

$$(42) \quad \psi_n = L_{n,1} \psi_1^{(0)}$$

of which only the first,

$$(42') \quad \psi_1 = L_{1,1} \psi_1^{(0)},$$

is actually considered. The matrix element,  $L_{1,1}$ , now depends on  $\rho_3$  as well as  $\rho_2$ . Some assumption is necessary. The Kirkwood assumption,

$$(43) \quad \rho_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \rho^{-3} \rho_2(|\mathbf{r}_1 - \mathbf{r}_2|) \rho_2(|\mathbf{r}_2 - \mathbf{r}_3|) \rho_2(|\mathbf{r}_3 - \mathbf{r}_1|),$$

that the number density of triples is the product of that for the three pairs, properly normalized, leads to a definite equation in (42').

The actual equation becomes

$$(44) \quad -kT \nabla \ln \rho_2(\mathbf{r}_1) = \nabla u(\mathbf{r}_1) + \rho^{-1} \int \rho_2(\mathbf{r}_{13}) [\rho_2(\mathbf{r}_3) - \rho^2] \nabla u(\mathbf{r}_3) d\mathbf{r}_3.$$

The similar equation with the Kirkwood operator has been solved numerically by Kirkwood, and the results are fair, in the sense of looking very much like the experimentally known function,  $\rho_2$ .

One would like to believe that this solution represents the first approximation to a method which could be carried out, in principle at least, to any degree of approximation. Some light on this has been shed by the work of Liliane Sarolea. She has examined the reciprocal set of equations, which with  $\psi_2^{(0)} = 0$ ,  $\nu > 1$  become,

$$(45) \quad \psi_1^{(0)} = \sum_m L_{1,m} \psi_m,$$

$$(45') \quad 0 = \sum_m L_{n,m} \psi_m.$$

The diagonal elements,  $L_{n,n}$ , contain a diagonal part, the Dirac  $\delta$ -function, so that it is convenient to define,

$$(46) \quad K = L_1 - 1,$$

in which case we can write,

$$(47) \quad \psi_1 = \psi_1^{(0)} - K_{1,1} \psi_1 - \sum_{m>1} K_{1,m} \psi_m,$$

$$(47') \quad \psi_m = -K_{m,1} \psi_1 - \sum_{n>1} K_{m,n} \psi_n.$$

Now the Kirkwood approximation of equation (43), if taken literally, also would require that  $\psi_n = 0$  for  $n > 1$ . One might thus consider

the sum which is the last term on the right of (47) to be at least small. If this sum were neglected entirely equation (47) becomes a linear integral equation of the Fredholm type in the one unknown function  $\psi_1$ .

Sarolea has attempted to find the contribution due to this sum. She uses equation (47') to iterate the sum, and writes:

$$(48) \quad \psi_1 = \psi_1^{(0)} - \left\{ K_{1,1}^{(0)} - \sum_{m>1} K_{1,m}^{(0)} K_{m,1}^{(0)} \right. \\ \left. + \sum_{n>1} \sum_{m>1} K_{1,m}^{(0)} K_{n,m}^{(0)} K_{m,1}^{(0)} - \dots \right\} \psi_1 = \psi_1^{(0)} - M_{1,1}^{(0)} \psi_1.$$

One then finds that the matrices  $L_{1,1}$  and  $\mathbf{1} - M_{1,1}^{(0)}$  are reciprocal,

$$(49) \quad L_{1,1}(\mathbf{1} - M_{1,1}^{(0)}) = (\mathbf{1} - M_{1,1}^{(0)})L_{1,1} = \mathbf{1}.$$

Dr. Sarolea has completed the cycle by showing that the relation (49) is trivially satisfied, namely that the series represented by  $M_{1,1}^{(0)}$  of equation (48) is actually a power series in  $z$  whose analytical continuation beyond its first singularity does obey equation (49). However, in showing this, and using arguments similar to those outlined in our discussion of the virial method, equation (27), she has also shown that the series of equation (48) diverges at the values of  $z$  corresponding to the condensed phase. This most obvious method of attempting to improve the Kirkwood assumption seems to indicate that it is, at best, the first step in what one may term an asymptotic approximation.

There is little reason to doubt that the Kirkwood solutions are approximately correct solutions to the problem. They are, however, difficult to obtain, and apparently not of very high accuracy to compute the pressure or other thermodynamic properties adequately. In view of the Sarolea conclusions it is not easily apparent how they can be improved. In view of the generality of the matrix-integral equation approach one might hope that other methods of attack might possibly be found. However a new idea seems to be needed. Although the many particle number density functions,  $\rho_n\{n\}$ , seem to be the most natural functions to choose for the description of the liquid structure they are difficult to visualize, and apparently impossible to measure experimentally for  $n > 2$ . Although the Kirkwood assumption of equation (43) that  $\rho_3$  is proportional to the product of the three pair functions sounds highly plausible, it seems that all attempts to improve the justification for it lead only to new demon-

strations that it is far from being exact. The cell method concept, although simple to visualize, and relatively simple for numerical computation, seems to be inherently limited by its assumption at the outset of a long range order in the liquid.

It may be that some entirely new set of logically defined functions might be more fruitful than the number density functions  $\rho_n$ , and might lead to both a more readily visualizable concept of liquid structure, and to a convergent analytical method of computation. At least one attempt of this nature shows some hope in simplification of the equations, although using even less easily visualized functions. This is to employ the Fourier transforms of the number density functions. An operation similar to that used in obtaining the integral equations leads to a set of purely algebraic equations. However it is not clear that the equations obtained have any superiority over the integral equation method.

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