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## Critical Phenomena in Gases—I

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### I—INTRODUCTION

The exact measurements of the isotherms of gases have proved extremely valuable in the determination of interatomic forces. For this purpose it has been found necessary to express the  $pv$  values of a gas as a finite power series in the density or in the pressure, and the coefficients so obtained have been compared with theoretical expressions in terms of interatomic fields. Many accounts of the method have been given and it is not necessary to give further details here (cf. Lennard-Jones 1931).

While these methods are valid for gases at low densities where binary encounters are predominant, they fail for gases at high densities such as obtain in the neighbourhood of the critical point. Michels and his collaborators (Michels and others 1937) have recently studied the isotherms of gases at pressures as high as 3000 atm., and they find that the usual method of representing isotherms as simple functions of density or pressure ceases to be useful. The equation of state of van der Waals was astonishingly successful in accounting for the critical phenomena of gases and the form of the isotherms for temperatures below the critical temperature. Other empirical equations of state, for example that of Dieterici, were even more successful in reproducing the observed relations between the critical

pressure, volume and temperature, and their very success has often obscured the fact that they were not logical theories of critical phenomena in gases, based as they were on arguments which were valid only for gases of low concentration. Thus the van der Waals equation, valuable as it has been and useful as it still is, implies that the internal energy of a vapour and its liquid phase is proportional only to the first power of the density, and this cannot be true for gases or vapours at densities comparable with those of liquids. The problem still remains of explaining why gases exhibit critical properties and of correlating the observed values of the critical temperature with the forces which atoms or molecules exert on each other.

Fowler, following the work of Bragg and Williams on order and disorder in alloys (Bragg and Williams 1935), has recently made a definite advance in the theory of the critical adsorption of atoms on surfaces. The essential step in his treatment is that he takes the heat of adsorption to be a linear function of the concentration of adsorbed atoms, and by statistical methods finds a critical temperature below which adsorbed atoms would tend to condense into a two-dimensional liquid phase (Fowler 1936). Another interesting development in the theory of condensed phases has been made by Tonks (1936), who has shown that the equation of state of a one-dimensional gas can be obtained by considering the properties of a single atom in a cell of length determined by the density. Similar considerations, applied to two- and three-dimensional assemblies, lead to equations of state valid for high concentrations, and suitable interpolation formulae are given which yield the correct form at low and high concentrations. The treatment is limited to hard elastic spheres, which exert no external forces on each other and depends on the use of the virial theorem in a manner similar to that used for gases of low concentration.

The object of this paper is to attempt to find an equation of state and other properties of gases at high concentrations in terms of interatomic forces of the same general type as has been used extensively by one of the authors in other connexions. The main idea is that an atom in a dense gas is to be regarded as confined for most of its time to a cell, and that its average environment is something like that of an atom in a liquid or a crystal. This picture can only be looked upon as a rough first approximation, for it neglects the possibility of the migration or diffusion of atoms from one cell to another, but it is probably better than attempts to deal with a dense gas by methods which depend essentially only on binary encounters. We use the methods of statistical mechanics and attempt to evaluate the partition function for a dense gas for a field in which the repulsive and attractive fields can be represented by inverse power laws, though the method is

applicable to any law of force. The resulting equation of state has the right kind of properties and in the particular cases of neon, argon, hydrogen and nitrogen, using the interatomic fields previously determined, a direct calculation of the critical temperature has been made.

## 2—GASES AT SMALL AND LARGE DENSITIES

When the density of a gas is small, its equation of state can be represented by the formula

$$pv = kNT\left(1 + \frac{B}{v}\right), \quad (1)$$

where, as usual,  $N$  is the total number of molecules in a gas of volume  $v$ , and  $B$  is the virial coefficient;  $k$  is the usual gas constant. For moderate densities it is necessary to take many more terms in the expression on the right involving higher inverse powers of  $v$ . The equation (1) is valid under the same conditions as the van der Waals equation which may be regarded as a special form of it.

For molecules of spherical symmetry, which exert on each other a field of potential  $\phi(r)$ , the theoretical formula for  $B$  is

$$B = 2\pi N \int_0^\infty r^2 \{1 - e^{-\phi(r)/kT}\} dr, \quad (2)$$

or

$$= \frac{2\pi N}{3kT} \int_0^\infty r^3 f(r) e^{-\phi(r)/kT} dr, \quad (3)$$

where  $f(r)$  is the force between two molecules.

For any given law of force  $B$  can thus be evaluated as a function of temperature, and compared with the values of  $B$  determined from the isotherms. In this way interatomic forces have been determined.

The internal potential energy of a gas can easily be derived from  $B$ , for, if  $\bar{\phi}$  is the average potential energy of any one atom in the field of the rest, we have

$$\bar{\phi} = \nu \int_0^\infty 4\pi r^2 \phi(r) e^{-\phi(r)/kT} dr, \quad (4)$$

where  $\nu$  is the average concentration of the gas. From equation (2) or (3) we then get

$$\bar{\phi} = -2(\nu/N) kT^2 (dB/dT), \quad (5)$$

and the average potential energy of the whole assembly is

$$\Phi = N\bar{\phi}/2 = -\nu kT^2 (dB/dT), \quad (6)$$

or, in terms of the volume,

$$\Phi = -\frac{NkT^2 dB}{v dT}. \quad (7)$$

This relation can also be obtained by the use of the thermodynamic formula

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p \quad (8)$$

and equation (1). This gives

$$U = -\frac{NkT^2}{v} \left(\frac{dB}{dT}\right) + U_0(T), \quad (9)$$

where  $U_0$  is a constant of integration, independent of the volume but dependent on temperature, and clearly refers to the value of  $U$  for an ideal gas.

It is instructive in passing to compare two alternative definitions of the internal pressure of gases. The *internal pressure*  $p_i$  of a gas is sometimes defined by either side of equation (8), and so is given by

$$p_i = (NkT^2/v^2)(dB/dT). \quad (10)$$

On the other hand, equation (1) can be written as

$$p = \nu kT + p_s, \quad (11a)$$

where

$$p_s = NkT B/v^2, \quad (11b)$$

and  $p_s$  has been shown (Lennard-Jones 1924) to be equal to the stress across unit area of a plane in the gas due to the interatomic forces and is positive when the stress is one of repulsion. This has been called the *statical* pressure. We see from (9) and (11) that  $p_i$  and  $p_s$  do not refer to the same thing; in fact

$$p_i = T^2 \frac{d(p_s/T)}{dT}. \quad (11c)$$

Observations of the isotherms of gases show that  $B$  is negative at low temperatures and increases to positive values at high temperatures (through the Boyle point, where it vanishes); it has a maximum and then begins to fall again. Hence from (7) we infer that  $\Phi$  behaves in a similar way. At very high temperatures it becomes positive, implying that owing to the high translational energies the atoms are penetrating deeply into each other's repulsive fields. We note also from (10) that at low temperatures  $p_i$  is positive, while from (11b)  $p_s$  is negative. This is a matter of definition;  $p_i$  is a measure of the tendency of the gas to compress itself, while  $p_s$ , as defined above, is a measure of its tendency to expand.

Returning now to the discussion of internal energy we see from (9) that  $U$  is a linear function of the density in the region in which this expression is valid, viz.

$$U = U_0 + \alpha\rho. \quad (12)$$

The curves given by Michels for the energy of  $\text{CO}_2$  gas as a function of density show clearly that while the energy is proportional to the density for small enough densities, there are considerable deviations for larger pressures (Michels 1937, fig. 1). There is no adequate theory at present to explain the observations. We can see in a general way that (12) will cease to be valid. In a dense gas an atom will be surrounded by a number of others and will be moving in the field of several at the same time. Of course at high temperatures there will be continual change of the immediate neighbours of the complex, surrounding any one atom, but the average potential energy of each will be of the same order of magnitude as that of an atom in a crystal. The potential energy of any one in its position of equilibrium is given approximately by

$$\phi_0 = c\phi(r_0),$$

where  $c$  is the number of nearest neighbours, if we neglect the effect of more distant atoms. If we adopt for  $\phi$  a form of potential which has proved to be a useful representation of the fields of inert gases, viz.

$$\phi = \frac{\lambda}{r^n} - \frac{\mu}{r^m}, \quad (13)$$

where  $n$  and  $m$  are integers, then we get for the potential energy of the assembly

$$\Phi = \frac{N}{2}\phi_0 = \frac{Nc}{2}\phi(r_0), \quad (14)$$

where  $r_0$  is the equilibrium value of the distance between nearest neighbours when all are at rest. The relation between  $\Phi$  and the density, neglecting heat motion, is then of the form

$$\Phi = \lambda'\rho^{n/3} - \mu'\rho^{m/3}. \quad (15)$$

The temperature-dependent part of  $\Phi$  the energy is given by Einstein or Debye expressions as long as the amplitude of vibration about the mean position is small, but when the amplitude becomes large it is to be anticipated that  $\Phi$  will be a more complicated function of density, temperature and the interatomic fields. Between these extremes of very low and very high densities, the theory will be more difficult. It is the object of this paper

to develop a method which may be regarded as a step towards a theory of gases at moderate densities.

### 3—A MODEL OF A GAS AT MODERATE DENSITIES

If we adopt the hypothesis that for moderate densities each atom may be considered to be enclosed by its neighbours in a box of definite dimensions, then we have the following picture. At first the box is so large that the potential within it is fairly uniform except near the boundary, where there is a region of low potential energy; the enclosure is, in fact, like a box with an adsorbing surface, and the enclosed atom will tend to be near it. As the density of the gas increases and the size of the box diminishes, the fields of the adsorbing surface will begin to overlap as in figs. 1 ( $a_1$ ) and 1 ( $a_2$ ), giving an energy barrier in the centre which diminishes with the density.

Finally, a stage is reached at which the barrier disappears, the minimum of the potential energy is at the centre and remains there for all greater densities as in fig. 1 ( $b$ ), but owing to the increasing overlap of the repulsive fields the absolute minimum of potential begins to rise with increasing concentration. We thus have two types of field, one of type ( $a$ ) and one of type ( $b$ ), depending on the density.

These features may be represented roughly by a simple model. We suppose every atom to be confined to a spherical box in which the potential energy is uniform for any given size but changes as the size changes. Thus we suppose the potential energy to vary with the radius  $R$  according to a law such that it is zero for large  $R$ , and then falls steadily as  $R$  decreases until it reaches its greatest negative value at  $R = R_0$ , when it begins to rise again, eventually becoming positive. We denote this function by  $\chi(R)$  or by  $\chi(v)$ , where  $v$  is the average volume occupied by each atom.

We now suppose that the partition function of the whole assembly can be expressed as a product of the partition functions of the individual atoms. We shall examine this assumption later in the paper. We assume that each atom moves on the average in the same field and is confined to the same volume. The partition function of each atom is then given by

$$\begin{aligned}
 f &= \iiint e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} \int_0^R e^{-\chi(v)/kT} 4\pi r^2 dr / h^3 \\
 &= \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{-\chi(v)/kT} \frac{4\pi R^3}{3} \\
 &= \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} v e^{-\chi(v)/kT},
 \end{aligned} \tag{16}$$

the value of  $\chi$ , as explained, being constant within the cell, and  $v$  being taken now for the volume available for one atom.

We could improve upon this model by taking into account the finite size of the atoms. Thus we could represent them by a diameter  $\sigma$  and then, supposing the centres of the surrounding atoms to be situated on the surface of the cell, the above expression must be replaced by

$$f = \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{-\chi(v)/kT} \frac{4\pi(R-\sigma)^3}{3}$$

$$= \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} e^{-\chi(v)/kT} \alpha v \left(1 - \frac{\sigma}{R}\right)^3, \quad (17)$$

where  $\alpha v = 4\pi R^3/3$  and  $\alpha$  is a numerical constant; for example, if the atoms were arranged regularly throughout space as a face-centred cubic crystal, we should have  $\alpha = 4\pi\sqrt{\frac{2}{3}}$ . For the above expression to be valid we must have  $R > \sigma$  and also the "available" regions for neighbouring atoms must not overlap; this latter condition implies that  $R < 2\sigma$ . Within these limits, however, there lies the interesting range of densities near the critical point.

Equating the partition function of the whole assembly to  $f^N$ , we then get for the free energy  $A (= U - TS)$

$$A = -NkT \log f, \quad (18)$$

and the pressure is given by

$$p = NkT \left( \frac{\partial}{\partial v} \log f \right)_T.$$

Using (16) we then get

$$p = NkT \left( \frac{1}{v} - \frac{\chi'(v)}{kT} \right), \quad (19)$$

and using (17) we get for the second model (atoms of finite size)

$$p = \frac{NkT}{v \left( 1 - \left( \frac{v_0}{v} \right)^{\frac{1}{3}} \right)} - N\chi'(v), \quad (20)$$

an equation very similar to that of van der Waals' when  $\chi(v)$  has the special form of  $-a/v$ .

It is not necessary for our purpose to deal with this more complex form of the equation of state; the simple form (19) leads to critical phenomena if a suitable form for  $\chi(v)$  be chosen. We have seen that  $\chi(v)$  must vanish

for large  $v$ , reach a minimum for a finite value of  $v$  and thereafter must increase as  $v$  decreases. A suitable function with these properties is

$$\chi(v) = \frac{\alpha}{v^\nu} - \frac{\beta}{v^\mu}, \quad (21)$$

where  $\nu > \mu$ . If the second term is to represent van der Waals attractive fields we must have  $\mu \approx 2$ .

Critical temperature, pressure and volume are given by

$$\left(\frac{\partial p}{\partial v}\right)_T = 0 = -\frac{1}{v^2} - \frac{1}{kT} \left\{ \frac{\nu(\nu+1)\alpha}{v^{\nu+2}} - \frac{\mu(\mu+1)\beta}{v^{\mu+2}} \right\}, \quad (22)$$

$$\left(\frac{\partial^2 p}{\partial v^2}\right)_T = 0 = \frac{2}{v^3} - \frac{1}{kT} \left\{ \frac{-\nu(\nu+1)(\nu+2)\alpha}{v^{\nu+3}} + \frac{\mu(\mu+1)(\mu+2)\beta}{v^{\mu+3}} \right\}. \quad (23)$$

These equations give the critical volume  $v_c$  at once as

$$v_c^{\nu-\mu} = \frac{\nu^2(\nu+1)\alpha}{\mu^2(\mu+1)\beta}, \quad (24)$$

while the critical temperature  $T_c$  is given by

$$kT_c = -v_c^2 \chi''(v_c) = \frac{\mu(\mu+1)\beta}{v_c^\mu} \frac{\nu-\mu}{\nu} \quad (25)$$

on using (24). If we denote by  $v_m$  the value of  $v$  at which  $\chi(v)$  assumes its minimum value, we have

$$v_m^{\nu-\mu} = \nu\alpha/\mu\beta, \quad (26)$$

and

$$\chi(v_m) = -\frac{\beta}{v_m^\mu} \frac{\nu-\mu}{\nu}. \quad (27)$$

Using these relations and (24) in (25), we find

$$\frac{kT_c}{|\chi(v_m)|} = \mu(\mu+1) \left[ \frac{\mu(\mu+1)}{\nu(\nu+1)} \right] \mu/(\nu-\mu). \quad (28)$$

Further, the Kamerlingh Onnes constant  $K$  is given by

$$\frac{1}{K} = \frac{p_c v_c}{NkT_c} = 1 + \frac{\chi'(v_c)}{v_c \chi''(v_c)} = \frac{\mu\nu}{(\mu+1)(\nu+1)}. \quad (29)$$

Taking  $\nu = 4$  and  $\mu = 2$ , corresponding to a repulsive potential varying



as an inverse twelfth power of the distance and attractive potential varying as an inverse sixth power, we find

$$v_c/v_m = 1.82, \quad kT_c = (1.8) |\chi(v_m)|, \quad K = 1.87. \quad (30)$$

The Kamerlingh Onnes constant is actually about 3.7 for many gases, and to obtain better agreement with experiment it would be necessary to consider the finite size of the atom in its cell as was done in equation (20). We note, however, that the model gives a simple linear relation between the critical temperature and the maximum absolute value of the potential in the cell. A somewhat similar relation is obtained by the more detailed calculations below.

#### 4—THE EQUATION OF STATE OF A GAS AT MODERATE DENSITIES— CRITICAL PHENOMENA

Having seen that the simple considerations of the preceding section lead to an equation of state with the right kind of properties, at any rate as regards critical phenomena, we now proceed to consider the problem more closely and to try to find an equation of state in terms of interatomic forces. Instead of assuming the potential of an atom within its available volume to be constant, we must endeavour to find its potential due to all its immediate neighbours as a function of position and also as a function of the size of the available volume.

We shall use as before the approximation that the partition function of a dense gas can be expressed as a product of the partition functions of the individual members of the assembly, each member being confined to a cell from which all others are excluded. This approximation is probably the more reasonable, the greater the density. Whereas in a sparse gas binary encounters alone are important and an atom can migrate or diffuse rapidly from one part of a vessel to another, in a dense gas an atom will be imprisoned by its immediate neighbours and will make more multiple encounters than binary ones and will escape from one environment to another the more slowly the greater the density. We neglect this possibility of migration as being an infrequent event compared with the time spent in any given cell. None the less it is of interest to examine the error introduced for a case for which the approximation is least justified, that is, for a perfect gas.

Let  $N$  be the number of atoms in a gas and  $v$  the total volume. Then if we divide  $v$  into  $N$  cells, each of volume  $v/N$ , the partition function for a particle in such a cell will be given by

$$f(T) = [(2\pi m kT)^{3/2}/h^3] (v/N), \quad (31)$$

and the partition function for the whole system by

$$F(T) = [f(T)]^N, \quad (32)$$

whereas the correct partition function is given by

$$F^*(T) = [(2\pi m kT)^{\frac{3}{2}} v/h^3]^N/N!, \quad (33)$$

so that the ratio is  $\frac{F(T)}{F^*(T)} = \frac{N!}{N^N} = (2N\pi)^{\frac{1}{2}} e^{-N}$ .

When  $N$  is large the difference of the free energies is approximately

$$kT\{\log F^* - \log F\} = kT\left(\log \frac{F^*}{F}\right) = kT N,$$

and the difference of the free energies per atom is  $kT$ . This difference, depending only on  $N$  and the temperature, will thus not affect the equation of state when it is derived by the usual formula from the partition function.

We shall now suppose that the system consists of  $N$  particles moving in a volume  $v$  which is divided in some regular way into  $N$  equal cells each of volume  $v^*$ , and that each particle is confined to one of these cells. Each particle will be moving in the field of the others, which will vary with time, and to obtain the partition functions for the individual particles we must replace this field by some suitable average. The simplest assumption we can make is that the average field in which any one atom moves is that due to its immediate neighbours when each is in its equilibrium position, that is, at the centre of its own cell; and we shall consider this case as a suitable first approximation.

Since atomic fields fall off very rapidly with distance we shall consider only nearest neighbours. The problem we have to deal with, therefore, is that of a particle moving in the field of a number of other particles symmetrically arranged on the surface of a sphere. If the number of immediate neighbours is large (it will generally be about twelve), the field within the cell will have a high degree of symmetry, and it will be sufficient for our purpose to replace the actual field by one which is spherically symmetrical about the centre of the cell. This may be obtained by taking a suitable average. We may take the average field, as the atom within the cell describes a sphere about the centre. This is equivalent to the average potential produced within the cell when the nearest neighbours take up all positions with equal probability on the surface of a sphere.

Let  $a$  be the average distance between nearest neighbours and let  $\phi(a)$  be their mutual potential energy at this distance apart. We suppose one

particle kept fixed while the other is moved about a sphere of radius  $r$ , described by the vector  $\mathbf{a} + \mathbf{r}$ . The average potential of the particles is then given by

$$\bar{\phi}(r) = \frac{1}{2} \int_0^\pi \phi\{(r^2 + a^2 - 2ar \cos. \theta)^{\frac{1}{2}}\} \sin \theta d\theta. \tag{34}$$

If  $c$  is the number of nearest neighbours, the average potential energy within a cell for  $r < a$  may be written as

$$\psi(r) = c\bar{\phi}(r). \tag{35}$$

In order to make further progress it is necessary to take particular forms of  $\phi(r)$ . For a monatomic gas a convenient function is

$$\phi(r) = Ar^{-n} - Br^{-m}, \tag{36}$$

and then

$$\psi(r) = \frac{c}{2} \left[ \frac{A}{(n-2)a^n} \left(\frac{a}{r}\right) \left\{ \left(1 - \frac{r}{a}\right)^{-n+2} - \left(1 + \frac{r}{a}\right)^{-n+2} \right\} - \frac{B}{(m-2)a^m} \left(\frac{a}{r}\right) \left\{ \left(1 - \frac{r}{a}\right)^{-m+2} - \left(1 + \frac{r}{a}\right)^{-m+2} \right\} \right]. \tag{37}$$

For the special case of  $n = 12, m = 6$ , which has been found to represent the fields of some of the inert gases satisfactorily (Lennard-Jones 1931), we get

$$\psi(r) = \frac{c}{2} \left[ \frac{A}{a^{12}} \left(\frac{a}{10r}\right) \left\{ \left(1 - \frac{r}{a}\right)^{-10} - \left(1 + \frac{r}{a}\right)^{-10} \right\} - \frac{B}{a^6} \left(\frac{a}{4r}\right) \left\{ \left(1 - \frac{r}{a}\right)^{-4} - \left(1 + \frac{r}{a}\right)^{-4} \right\} \right],$$

which may be written in the form

$$\psi(r) - \psi(0) = c[ Aa^{-12} l(y) - Ba^{-6} m(y) ], \tag{38}$$

where

$$y = r^2/a^2, \tag{39}$$

$$l(y) = [1 + 12y + (25 \cdot 2)y^2 + 12y^3 + y^4] (1 - y)^{-10} - 1, \tag{40}$$

and

$$m(y) = (1 + y)(1 - y)^{-4} - 1. \tag{41}$$

Since  $a^3$  is proportional to  $v^*$  the specific volume, we may write the equation for  $\psi(r)$  in the form

$$\psi(r) - \psi(0) = A\{(v_0^*/v^*)^4 l(y) - 2(v_0^*/v^*)^2 m(y)\}, \tag{42}$$

where  $A$  and  $v_0^*$  are constants, chosen so that

$$A(v_0^*/v^*)^4 = cAa^{-12}, \quad 2A(v_0^*/v^*)^2 = cBa^{-6}. \tag{43}$$

Putting  $v_0 = Nv_0^*$ , and  $v = Nv^*$ , we also have

$$\psi(r) - \psi(0) = A\left\{(v_0/v)^4 l(y) - 2(v_0/v)^2 m(y)\right\}. \quad (43a)$$

Some representative curves for  $\psi(r)$  for certain values of  $(v_0/v)$  are shown in fig. 1. Curves  $(a_1)$  and  $(a_2)$  have a potential barrier at the centre while  $(b)$  has not. It is found that the field ceases to have this central hump when  $(v/v_0)$  is of the order of 1.6. At the critical volume  $(v/v_0 = 2.2)$ , the height of the hump is approximately  $kT_c/2$ ; at  $v/v_0 = 3.16$  it is  $(0.9) kT_c$ .

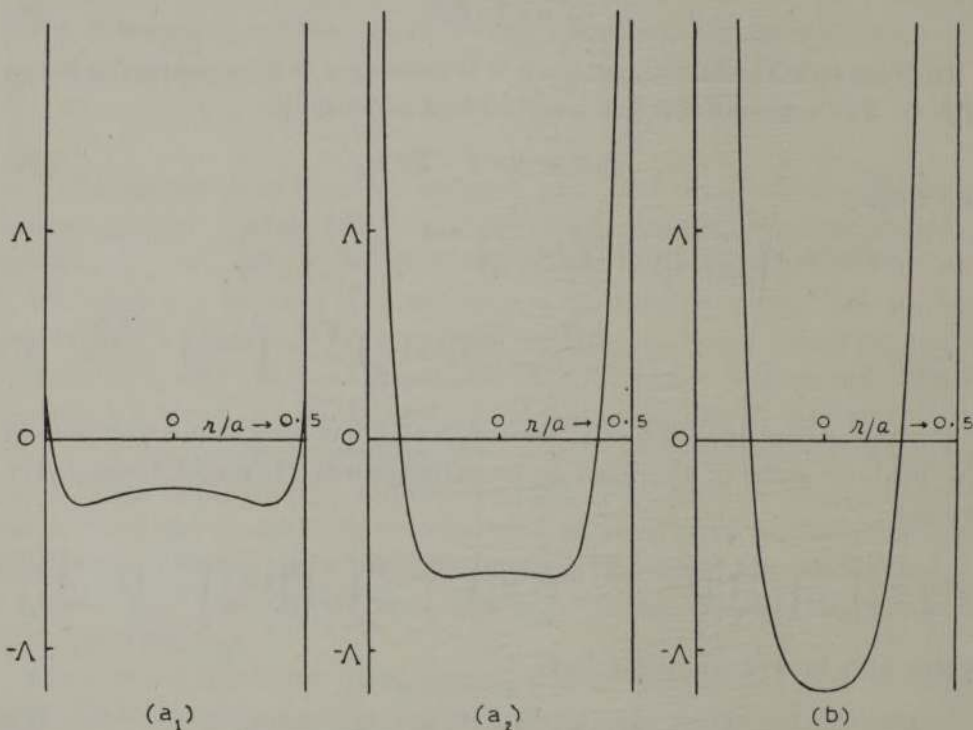


FIG. 1—The potential field within a cell; curves  $(a_1)$ ,  $(a_2)$  and  $(b)$  correspond to  $(v_0/v)^2 = 0.10, 0.30, \text{ and } 0.70$  respectively.

The partition function for a particle moving in this field, when the energy zero is taken to be that of a particle at  $r = 0$ , is given by

$$\begin{aligned} f(T) &= (2\pi mkT)^{\frac{3}{2}} h^{-3} \int_0^{a/2} 4\pi r^2 \exp\{[\psi(r) - \psi(0)/kT]\} dr \\ &= (2\pi mkT)^{\frac{3}{2}} h^{-3} 2\pi a^3 \int_0^{\frac{1}{2}} y^2 \exp\left[\frac{A}{kT} \left\{-\left(\frac{v_0}{v}\right)^4 l(y) + 2\left(\frac{v_0}{v}\right)^2 m(y)\right\}\right] dy, \quad (44) \end{aligned}$$

where we have neglected the contribution to the partition function from portions of the cell outside the sphere of radius  $a/2$ , but this is certainly small

owing to the repulsive field except at high temperatures. The partition function for the whole system, when the energy zero is that of an atom at rest at infinity, is then

$$F(T) = f(T)^N \exp \left[ \frac{N}{kT} \frac{1}{2} \left\{ 2A \left( \frac{v_0}{v} \right)^2 - A \left( \frac{v_0}{v} \right)^4 + \alpha(v) \right\} \right], \quad (45)$$

where  $\alpha(v)$  is an extra term inserted to take account of the interaction of particles which are not nearest neighbours. For a face-centred cubic structure the interaction between such particles increases the attractive term in the potential energy by about 20 % and has a negligible effect on the repulsive term (Lennard-Jones and Ingham 1925, Table I). We have therefore

$$F(T) = f(T)^N \exp \left[ \frac{N}{kT} \left\{ 1.2A \left( \frac{v_0}{v} \right)^2 - 0.5A \left( \frac{v_0}{v} \right)^4 \right\} \right]. \quad (46)$$

The expression 
$$\psi^*(0) = \left\{ -2.4A \left( \frac{v_0}{v} \right)^2 + A \left( \frac{v_0}{v} \right)^4 \right\} \quad (47)$$

is the potential energy of each atom when the atoms are at the centres of their cells. It has a maximum value equal to 1.44 when  $\left( \frac{v_0}{v} \right)^2 = 1.2$ ;  $v_0^* (= v_0/N)$  is thus approximately 1.1 times the specific volume  $v^*$  of the crystal at the absolute zero, and  $A$  is 1.39 times the heat of sublimation at the absolute zero.

The equation for the partition function may be written

$$\frac{1}{N} \log F(T) = \frac{A}{kT} \left\{ 1.2 \left( \frac{v_0}{v} \right)^2 - 0.5 \left( \frac{v_0}{v} \right)^4 \right\} + \log \left( 2\pi \frac{\sqrt{2}v}{N} \right) + \log g + \frac{3}{2} \log \left( \frac{2\pi m kT}{h^2} \right), \quad (48)$$

where  $g$  is a function of  $(A/kT)$  and of  $(v_0/v)$  only, viz.

$$g = \int_0^1 y^{\frac{1}{2}} \exp \left[ \frac{A}{kT} \left\{ - \left( \frac{v_0}{v} \right)^4 l(y) + 2 \left( \frac{v_0}{v} \right)^2 m(y) \right\} \right] dy. \quad (49)$$

We have used the relation  $a^3 = \sqrt{2}v^*$  for a face-centred cubic structure. All the equilibrium properties of the system may now be readily derived. For example, the pressure is given by

$$p = kT \frac{\partial}{\partial v} \log F(T) \\ = \frac{NkT}{v} \left[ 1 - \frac{A}{kT} \left\{ 2.4 \left( \frac{v_0}{v} \right)^2 - 2 \left( \frac{v_0}{v} \right)^4 \right\} - \frac{4A}{kT} \left\{ \left( \frac{v_0}{v} \right)^2 \frac{g_m}{g} - \left( \frac{v_0}{v} \right)^4 \frac{g_l}{g} \right\} \right], \quad (50)$$

where  $g_m$  and  $g_l$  are also functions of  $(A/kT)$  and  $(v_0/v)$  only, given by

$$g_m = \int_0^{\frac{1}{2}} y^{\frac{1}{2}} m(y) \exp \left[ \frac{A}{kT} \left\{ - \left( \frac{v_0}{v} \right)^4 l(y) + 2 \left( \frac{v_0}{v} \right)^2 m(y) \right\} \right] dy \quad (51)$$

and 
$$g_l = \int_0^{\frac{1}{2}} y^{\frac{1}{2}} l(y) \exp \left[ \frac{A}{kT} \left\{ - \left( \frac{v_0}{v} \right)^4 l(y) + 2 \left( \frac{v_0}{v} \right)^2 m(y) \right\} \right] dy. \quad (52)$$

Similarly the mean energy per atom is given by

$$\begin{aligned} \bar{E} &= \frac{k}{N} T^2 \frac{\partial}{\partial T} \log F(T) \\ &= A \left\{ 0.5 \left( \frac{v_0}{v} \right)^4 - 1.2 \left( \frac{v_0}{v} \right)^2 + A \left( \frac{v_0}{v} \right)^4 (g_l/g) - 2A \left( \frac{v_0}{v} \right)^2 (g_m/g) + \frac{3}{2} kT \right\}, \quad (53) \end{aligned}$$

and the specific heat by

$$\begin{aligned} c_v = \frac{\partial E}{\partial T} &= k \left[ \frac{3}{2} + \left( \frac{A}{kT} \right)^2 \left\{ \left( \frac{v_0}{v} \right)^8 \left( \frac{g_{ll}g - g_l^2}{g^2} \right) - 4 \left( \frac{v_0}{v} \right)^6 \left( \frac{g_{lm}g - g_l g_m}{g^2} \right) \right. \right. \\ &\quad \left. \left. + 4 \left( \frac{v_0}{v} \right)^4 \left( \frac{g_{mm}g - g_m^2}{g^2} \right) \right\} \right], \quad (54) \end{aligned}$$

where 
$$g_{ll} = \int_0^{\frac{1}{2}} y^{\frac{1}{2}} l^2(y) \exp \left[ \frac{A}{kT} \left\{ - \left( \frac{v_0}{v} \right)^4 l(y) + 2 \left( \frac{v_0}{v} \right)^2 m(y) \right\} \right] dy, \quad (55)$$

and  $g_{lm}$ ,  $g_{mm}$  are given by similar expressions.

We note that the *average* value of the potential energy of each atom in its cell is

$$\begin{aligned} \bar{\psi}(v, T) &= \int_0^{a/2} \psi(r) 4\pi r^2 \exp[-\psi(r)/kT] dr / \int_0^{a/2} 4\pi r^2 \exp[-\psi(r)/kT] dr \\ &= -k \frac{\partial \log g}{\partial (1/T)} + \psi(0) \\ &= A \left[ \left( \frac{v_0}{v} \right)^4 \frac{g_l}{g} - 2 \left( \frac{v_0}{v} \right)^2 \frac{g_m}{g} \right] + \psi(0). \quad (56) \end{aligned}$$

Hence the average potential energy in a cell, referred to the potential at the centre as zero, is

$$\chi(v, T) = \bar{\psi}(v, T) - \psi(0) = A \left[ \left( \frac{v_0}{v} \right)^4 \frac{g_l}{g} - 2 \left( \frac{v_0}{v} \right)^2 \frac{g_m}{g} \right]. \quad (57)$$

We see from (53), using (47) and (57), that the mean energy per atom is

$$E = \frac{1}{2} \psi^*(0) + \chi(v, T) + \frac{3}{2} kT, \quad (58)$$

and the total energy is  $NE$ . The factor  $\frac{1}{2}$  in the first term is due to the fact that this term arises from the mutual potential energy of atoms, and it might be expected that a similar factor should appear in the second term, since this also is due to the extra mutual potential when the atoms are disturbed from the centres of their cells. Some justification for the non-appearance of this factor may be made as follows.

Let  $P$  and  $Q$  be the mean positions of two atoms and  $P'$  and  $Q'$  be simultaneous positions of the atoms near  $P$  and  $Q$  respectively. Let  $PQ = a$ ,  $PP' = r_1$ , and  $QQ' = r_2$ . Then we have for the mean potential of the two atoms as they describe spheres of radii  $r_1$  and  $r_2$  about  $P$  and  $Q$  respectively (to the second order)

$$\begin{aligned} \overline{\phi(P'Q')} &= \phi(a) + \overline{\Sigma(x_1 - x_2) \phi_x} + \overline{\Sigma \frac{1}{2}(x_1 - x_2)^2 \phi_{xx}} \\ &= \phi(a) + \frac{1}{2} \{ \overline{x_1^2} \phi_{xx} + \overline{y_1^2} \phi_{yy} + \overline{z_1^2} \phi_{zz} \} + \frac{1}{2} \{ \overline{x_2^2} \phi_{xx} + \overline{y_2^2} \phi_{yy} + \overline{z_2^2} \phi_{zz} \} \\ &= \phi(a) + \frac{1}{6} (r_1^2 + r_2^2) \left( \frac{\partial^2 \phi}{\partial a^2} + \frac{2}{a} \frac{\partial \phi}{\partial a} \right) \\ &= \phi(a) + \chi_1 + \chi_2, \end{aligned} \tag{59}$$

where  $\chi_1$  is the extra average energy of one atom due to its disturbance from the centre and  $\chi_2$  the corresponding energy of the other atom. Hence we get two  $\chi$  terms for each  $\phi$  term.

The values of  $g$ ,  $g_l$  and  $g_m$  calculated by numerical integration for two values of  $\Lambda/kT$  and a range of values of  $v/v_0$  are given in Table I. The isotherms, deduced from them, are shown in fig. 2.

TABLE I—THE FUNCTIONS OF  $g$ ,  $g_l$  AND  $g_m$

$v/v_0$	$(v_0/v)^2$	$\Lambda/kT = 9$			$\Lambda/kT = 10$		
		$g$	$g_l$	$g_m$	$g$	$g_l$	$g_m$
1.195	0.7	0.00180	0.000910	0.000173	0.00161	0.000747	0.000139
1.291	0.6	0.00295	0.002042	0.000372	0.00269	0.001723	0.000316
1.414	0.5	0.00515	0.00511	0.000875	0.00478	0.00441	0.000762
1.581	0.4	0.00964	0.01462	0.00228	0.00916	0.01315	0.00208
1.826	0.3	0.01957	0.0495	0.00670	0.01920	0.0468	0.00643
2.236	0.2	0.0437	0.2211	0.02366	0.0445	0.2156	0.02347
2.575	0.15	0.0676	0.543	0.0482	0.0700	0.546	0.0493
3.162	0.1	0.1069	1.635	0.1084	0.1125	1.667	0.1126

From these functions we deduce the equation of state from equation (50), the values of  $pv/NkT$  being given in Table II. The isotherm for  $\Lambda/kT = 9$

appears to be close to the critical one, so far as can be judged from its graph. From the relations (43) we have

$$A = cB^2/4A, \quad (60)$$

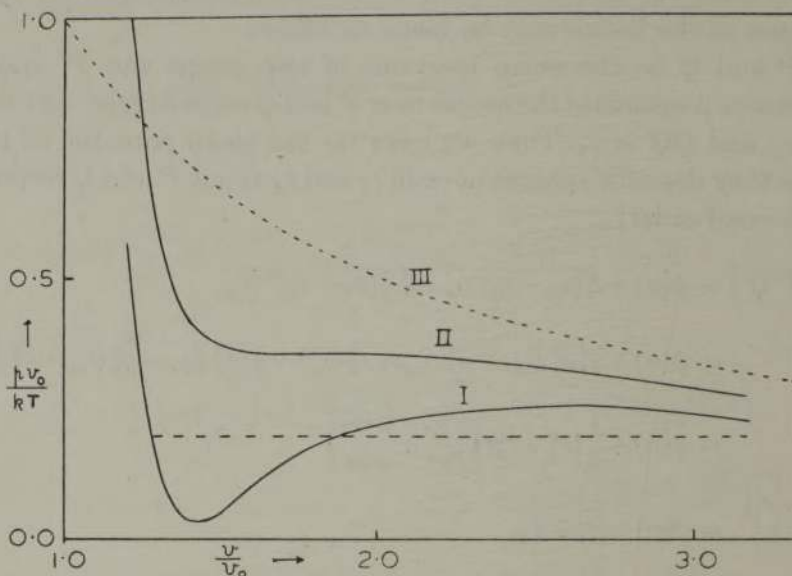


FIG. 2—Calculated isotherms. Curve I corresponds to  $kT=A/9$ , and curve II to  $kT=A/10$  with the saturated vapour phase shown dotted. The upper curve is the isotherm of a perfect gas.

TABLE II—CALCULATED ISOTHERMS OF GASES  
IN THE CRITICAL REGION

$v/v_0$	$(v_0/v)^2$	$A/kT=10$		$A/kT=9$	
		$pv/NkT$	$pv_0/NkT$	$pv/NkT$	$pv_0/NkT$
1.195	0.7	0.675	0.565	1.202	1.006
1.291	0.6	0.218	0.169	0.765	0.593
1.414	0.5	0.046	0.033	0.573	0.406
1.581	0.4	0.149	0.094	0.568	0.359
1.826	0.3	0.348	0.191	0.644	0.353
2.236	0.2	0.531	0.237	0.788	0.352
2.575	0.15	0.642	0.249	0.825	0.320
3.162	0.1	0.721	0.224	0.877	0.277

and so, adopting the value  $c = 12$  for a face-centred cubic arrangement, we can derive the critical temperature from the formula

$$kT_c = cB^2/36A = B^2/3A. \quad (61)$$



Now from the potential function given in (36) for two atoms for  $n = 12$ ,  $m = 6$  we have

$$|\phi(r)|_{\max} = B^2/4A, \quad (62)$$

and so

$$kT_c = (4/3) |\phi(r)|_{\max}, \quad (63)$$

which is similar to the result obtained in equation (30) by the simple model. The values of the critical temperature, calculated from this formula using the force fields given elsewhere by Lennard-Jones (1931, p. 475, Table I or p. 476, fig. 3), are given in Table III, and they are remarkably close to those observed.

TABLE III—CRITICAL TEMPERATURES

	$ \phi _{\max}/k$	$T_c(\text{calc.})$	$T_c(\text{obs.})$
H <sub>2</sub>	31	41	34
Ne	36	48	44
N <sub>2</sub>	96	128	126
Ar	121	161	150

It is difficult to determine the critical volume accurately from the calculated curves without excessive labour, but it seems to be about  $2v_0^*$ , which is equal to 2.2 times the specific volume at the absolute zero. This value is rather too small. The calculated value of  $p_c v_c / kT_c$  is about 0.7, whereas the experimental value for many gases is about 0.27.

We have not included helium in this table because throughout this paper we have used classical statistics, and quantum effects are likely to be appreciable in this case. The formula does, however, give the order of magnitude of the critical temperature even for helium. The method used in this paper could be extended to include quantized vibrations. We may conclude that the method reproduces the essential features of gases at high concentrations and encourages further investigations on similar lines. It is hoped in a later paper to calculate by similar methods the critical temperature of a film or two-dimensional gas with a view to finding whether it is higher or lower than that of the three-dimensional gas.

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#### SUMMARY

An attempt is made to find an equation of state of a gas at large densities in terms of interatomic forces. The main idea is that an atom in a dense gas is to be regarded as confined for most of its time to a cell, and that its average

environment is something like that of an atom in a liquid or crystal. This method abandons the attempt to calculate the properties of a dense gas from binary encounters only but considers an atom as subject to a multiple encounter all the time. The methods of statistical mechanics are used to derive an equation of state and the formulae are applied to the inert gases, for which the interatomic fields are known. The calculated values of the critical temperature are found to be close to those observed.

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## Reaction Kinetics in Films. The Hydrolysis of Long-Chain Esters

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## INTRODUCTION

The hydrolysis of the simple esters of the short-chain fatty acids in the bulk phase has been investigated under a variety of conditions (Moelwyn-Hughes 1933, pp. 87, 245). This has now been extended to the insoluble esters of the long-chain acids and alcohols. These are also of interest biologically, since the natural breakdown and resynthesis of fats are probably interfacial reactions.

The work of Hughes and Rideal (1933) on the oxidation of the unsaturated fatty acids, and of Fosbinder and Rideal (1933) on the alkaline hydrolysis of  $\gamma$ -stearolactone, has shown that these interfacial or two-dimensional reactions may differ from those in homogeneous solution; chiefly in the