

An Elementary Theory of Condensation

F. Cernuschi and H. Eyring

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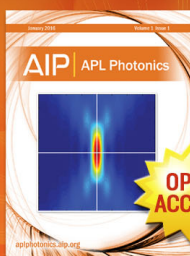
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hood of the transition point. It seems that for the explanation of these phenomena appeal must be made to the discontinuous pretransition mechanism discussed in the present paper. This mechanism can be likened to that which is advocated in the case of electrolytic dissociation, say, by the old chemical theories of Arrhenius, Van't Hoff and Ostwald, whereas the quantitative mechanism corresponds to the Debye-Hückel theory of complete dissociation and co-operative interaction. In the case of concentrated electrolytic solutions both mechanisms must be taken into account a part of the dissolved molecules dissociating into ions according to Ostwald's theory, and these ions acting on each other according to the Debye-Hückel

theory. A similar condition is found in the study of the premelting phenomena. It is clear that the gradual dilatation and dissociation of the crystal lattice must speed up the beginning of the premelting process, and that, on the other hand, this premelting must accelerate the dissociation of the remaining portion of the crystal lattice, which is seriously disturbed by the appearance of liquid droplets within it.

It would be possible to improve our theory by taking into account the internal pressures produced by these drops because of their larger molecular volume. The scarcity of the available experimental data does not warrant, however, a more detailed treatment of these secondary effects.

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An Elementary Theory of Condensation

F. CERNUSCHI* AND H. EYRING

Princeton University, Princeton, New Jersey

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A theory of liquids is presented based on the assumption of the presence of holes in a lattice-like structure and using a method analogous to that used in treating order and disorder in alloys. This treatment provides an elementary theory of condensation and a clear and simple treatment of the critical phenomena of liquids and also yields a theoretical curve for the density of vapor and liquid as a function of temperature in agreement with the experimental curve. The existence of more than one phase arises as a consequence of the theory.

INTRODUCTION

WE shall develop an elementary theory of the critical phenomena in liquids. For that purpose we shall assume the simplest possible model which can give us a clear interpretation of that phenomena. We believe that our model may be considered as a good first approximation and that the theory developed in this paper can be further developed on the basis of these assumptions.†

* On a fellowship from the Argentine Association for the Progress of Science.

† *Historical Note.*—As far as we are aware Ising (*Zeits. f. Physik* **31**, 253 (1925)) was the first to apply a statistical method of order and disorder. He applied it to the one-dimensional theory of ferromagnetism. Some clear ideas about the subject are found in the paper by Gorsky (*Zeits. f. Physik* **50**, 64 (1928)). Later came the papers by Bragg and Williams about order and disorder for long range interactions (*Proc. Roy. Soc. A145*, 699 (1934); *A151*, 540 (1935)). Bethe (*Proc. Roy. Soc. A150*, 553 (1935)) gives a

Let us assume: (1) that the particles (atoms or molecules) are moving in a regular array of holes,

modified method applicable to short range interactions. For the one-dimensional case Ising's method is more rigorous. More recently the methods of order and disorder have been applied by many writers to a great variety of problems involving critical conditions. Fowler has applied a somewhat modified method to critical conditions on a surface (Fowler's *Statistical Mechanics* (1936), pp. 832–839). Peierls (*Proc. Camb. Phil. Soc.* **32**, 477 (1936)) has applied Bethe's method to analyze the critical conditions of the adsorbed particles on a surface. Cernuschi (*Proc. Camb. Phil. Soc.* **34**, 392 (1938)), using the quantum analog of Gibbs's canonical equations (Fowler, *Proc. Camb. Phil. Soc.* **34**, 282 (1938)) and two layers of adsorbed particles, discusses the critical conditions of the adsorption isotherm. It would require too much space to give a complete list of the papers dealing with critical conditions. We shall only mention two of the most recent papers because they deal with similar problems; a paper by Kirkwood (*J. Phys. Chem.* **43**, 97 (1939)) in which order and disorder is applied to the problem of liquid solutions; and the paper by Lennard-Jones (*Proc. Roy. Soc. A169*, 317 (1939)), in which a theory of melting is developed using order and disorder. Critical phenomena for a single liquid,

such that each hole, considered as a central one, is surrounded by a shell of Z holes.

(2) that between an occupied central hole and an occupied hole of the first shell an interaction energy ϵ_1 exists, due to an attractive force.

(3) that the interaction between two occupied neighboring holes in the first shell be neglected. If this interaction is taken explicitly into account considerable mathematical difficulties are encountered without any important change in the physical results.¹

(4) that holes as used here are simply unoccupied lattice points. The total number of lattice points n_l in a phase of volume V is $n_l = V/\tau$, where τ is the volume of a lattice point. Consequently the number of unoccupied lattice points n_h has the value $n_h = V/\tau - n$ where n is the total number of particles. If there were no interaction between the particles the chance that any lattice point would be occupied divided by the chance of being empty would just equal the ratio n/n_h . From our definition of holes it follows that with increasing pressure the number of holes decreases monotonously at constant temperature. We therefore can write $n/n_h = f(p)$ where $f(p)$ increases monotonously with p . We define a quantity θ as the probability of a lattice point being occupied; so that θ is proportional to the density. For fixed values of n and τ we have V inversely proportional to the density.

(5) that the average interaction on an occupied hole in the first shell due to the outside particles and the nearest neighbors in the first shell itself is represented in the partition function by a factor ζ which is to be determined by the equilibrium conditions. In all previous treatments of order and disorder ζ has been assumed independent of the density. But since in this model interactions between neighbors in the first shell is not explicitly considered and only the first shell is taken into account this factor ζ must increase monotonously with θ . However, as has always been done heretofore, we neglect this dependence of ζ on θ .

(6) that there are n particles at equilibrium under a pressure p and a temperature T .

(7) that whenever in our results two different values of θ , i.e., two different densities are found in equilibrium at the same temperature and pressure these are to be interpreted as two phases. The higher value of θ represents the liquid phase and the smaller represents the gas phase. We want to emphasize that in this treatment the existence of two phases is not assumed but as we shall see arises automatically from the above assumptions.

It is known from x-ray diffraction experiments that the liquid state has a semi-crystalline structure.² Such experiments provide a method of determining both Z and τ for any particular type of particles.

These same quantities may be determined theoretically by choosing particular completely filled lattice structures, using the well-known quantum-mechanical methods to deduce the interaction potential between all possible pairs, and finally choosing that structure for which the energy is lowest. This has been done in an interesting though as yet incomplete way by Lennard-Jones and collaborators.³

To develop statistically the model defined by the given assumptions, we shall use a slightly different method than the one developed by Bethe⁴ in dealing with order and disorder in alloys and later applied by Peierls⁵ to the problem of adsorption of gases on surfaces.

THEORY

If $\bar{\theta}$ is the average probability (in a long period of time) for the central hole to be occupied, the probability for the same hole to be empty will be $1 - \bar{\theta}$. The partition function when the central hole is occupied will be:

$$F_{0,0} = f \cdot (1 + f\eta\zeta)^Z. \quad (2)$$

The first subscript has the value 0 or 1 according to whether the partition function refers to a central hole or to one in the first shell, respectively. The second subscript is 0 or ϵ depending

with which we are here concerned, have been discussed by Mayer (J. Chem. Phys. **5**, 67 (1937)) by an interesting but intricate method. Lennard-Jones and Devonshire (Proc. Roy. Soc. **A163**, 53 (1937)) have treated the critical phenomena by a simpler but less rigorous method.

¹ F. Cernuschi, Ph.D. Thesis, Cambridge (1938).

² H. Menke, Physik. Zeits. **33**, 593 (1932); O. Kratky, *Ibid.* **34**, 482 (1933).

³ Lennard-Jones, Proc. Roy. Soc. **A129**, 598 (1930). Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930); **27**, 66 (1931).

⁴ Bethe, Proc. Roy. Soc. **A150**, 552 (1935).

⁵ Peierls, Proc. Camb. Phil. Soc. **32**, 477 (1936).

on whether the hole indicated by the first subscript is occupied or empty.

Where $\eta = e^{\epsilon_1/kT}$ is the factor which represents the interaction between the occupied central hole and an occupied hole in the first shell; ζ , as it was defined before, takes into account the influence of the outside particles and the nearest particles in the first shell on an occupied hole in the first shell. It may be useful to clarify in some detail relation (2). If the central hole is occupied the partition function, neglecting the action of the nearest neighbors, is by definition f ; but when the central hole is occupied each one of the holes in the first shell may be occupied or empty; if a hole is empty its contribution in the partition function is given by a factor equal to unity; if a hole is occupied its contribution is given by a factor $f\eta\zeta$, which is easily understood with the given definitions; and as each one of the Z holes of the first shell may be independently occupied or empty one gets, when the central hole is occupied, the expression (2).

For similar reasons, the partition function when the central hole is empty will be:

$$F_{0,e} = (1+f\zeta)^Z. \quad (3)$$

The ratio of the probabilities of the central hole being occupied or empty is given by the ratios of the corresponding partition functions; thus we obtain

$$\frac{\bar{\theta}_0}{1-\bar{\theta}_0} = \frac{f \cdot (1+f\eta\zeta)^Z}{(1+f\zeta)^Z}, \quad (4)$$

which gives the density as a function of the variables just defined.

The particular position chosen as the central hole is arbitrary. Due to the regularity of the array, any one of the holes of the first shell can be chosen as a central hole. Therefore the probability of a first shell hole being occupied, $\bar{\theta}_1$, must be equal to $\bar{\theta}_0$. Let us call this common probability $\bar{\theta}$.

Figure 1 represents a regular array in a plane with $Z=4$. We see that, e.g. the hole 1 belonging to a first shell about the center 0, may be considered as the central hole of another shell. When the hole 0 is occupied, the hole 1 may be occupied or empty. In both cases if we consider the hole 0 as belonging to the shell with center 1 and hole 1 as belonging to the shell with center 0

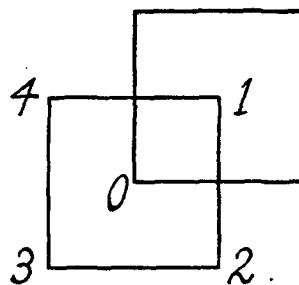


FIG. 1.

then we get for the partition function:

$$F_{1,o} = f \cdot \zeta \cdot (1+f\eta\zeta). \quad (5)$$

In a similar way, when the hole 0 is empty, the partition function will be:

$$F_{1,e} = 1+f\zeta. \quad (6)$$

It is easily seen that our reasoning to obtain Eqs. (5) and (6) is independent of Z and that it is equally true in three-dimensional space.

If we define

$$\delta = f\zeta \quad (7)$$

from (5) and (6) we obtain:

$$\frac{\bar{\theta}}{1-\bar{\theta}} = \delta \frac{1+\eta\delta}{1+\delta} \quad (8)$$

from (8) and (4), remembering (7):

$$f = \delta \left(\frac{1+\delta}{1+\eta\delta} \right)^{Z-1}. \quad (9)$$

If we suppose f (in our 4th assumption) to be a slowly varying function of the density, Eqs. (9) and (8) for a given temperature, i.e., for a given η , determine the values of p and θ as functions of the parameter δ .

Let us now see when we may expect two different values of θ to be in equilibrium with the particles at the same temperature and pressure. Those values of pressure and temperature which lead to a double value for θ at equilibrium, i.e., two phases, we call the "two phases condition." Therefore, when we have the "two phases condition" the relationship

$$\partial p / \partial \theta = 0 \quad (10)$$

must have two different solutions, one of which corresponds to a maximum in the p, θ curve and the other to a minimum. The two different values of θ corresponding to the two phases are obtained

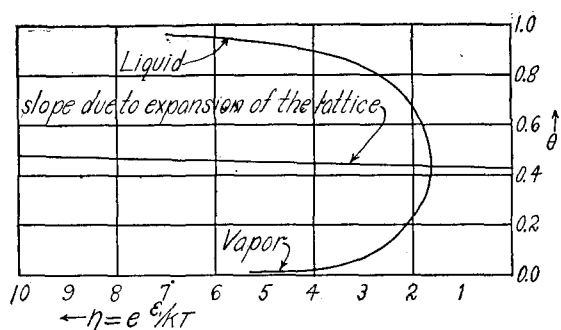


FIG. 2. $\eta = \frac{(\theta + \frac{1}{8})(1 - \theta + \frac{1}{8})}{\theta(1 - \theta)}$.

by the intersection of a line $p = \text{constant}$ with the curve in which p is plotted against $1/\theta$ and such that the two areas completely enclosed by these two curves are equal. This result follows from the usual well-known thermodynamic considerations ordinarily applied to the pressure-volume curves, since $1/\theta$ is directly proportional to V at any particular temperature. The critical point corresponds to the state in which these two solutions for θ coincide; this condition also permits us to calculate the critical temperature and pressure.

Since f is a monotonous function of pressure for a given temperature and since θ , Eq. (8), with the already mentioned restriction, is another monotonous function of δ , we see that (10) is equivalent to:

$$\partial f / \partial \delta = 0. \quad (11)$$

Using (9) and (11) we obtain:

$$(Z-1)\delta\eta(1+\delta) = (1+\eta\delta)(1+\delta) + (Z-1)\delta(1+\eta\delta). \quad (12)$$

Eliminating δ from (8) and (12) we obtain:

$$\eta = \frac{\left(\theta + \frac{1}{Z-2}\right)\left(1 - \theta + \frac{1}{Z-2}\right)}{\theta(1-\theta)}. \quad (13)$$

This equation has two solutions θ' and θ'' . The difference between these solutions is greater than—but of the same order of magnitude as—the difference between the values θ_1 and θ_2 corresponding to the two phases.

From the form of (13) it is obvious that the two solutions are related by:

$$\theta' = 1 - \theta''. \quad (14)$$

According to our definition these two solutions must coincide, not only with each other, but with θ_1 and θ_2 at the critical point. Therefore from (14) we obtain

$$\theta_c = \frac{1}{2}, \quad (15)$$

which means that for the critical point the density of the liquid and vapor are the same as experiment requires.

Inserting the value (15) in (13) we have

$$(Z/(Z-2))^2 = e^{\epsilon_1/kT}. \quad (16)$$

The first member of this equation is always greater than one; therefore if the forces between the particles were repulsive (as is the case in an electronic gas) there is no critical point as in this case, the exponential in (16) being negative, the expression (16) can't be satisfied. We may conclude that the existence of two different phases at equilibrium is a direct consequence of the attractive forces between the particles. It is interesting to notice from Eq. (16) that in a one-dimensional model ($Z=2$) it is not possible to expect two phases at equilibrium.

From Eq. (16) we obtain for the critical temperature:

$$T_c = \frac{\epsilon_1}{2k} \left[\log \left(\frac{Z}{Z-2} \right) \right]^{-1}. \quad (17)$$

Inserting this value of T_c in the partition function, $f(\theta, p, T)$, of the free particle, we get the corresponding critical pressure. For temperatures lower than the critical there are two different phases in equilibrium, given by the two roots of Eq. (13).

For $Z=8$, corresponding to a cubic body-centered array, we have:

$$T_c = \frac{\epsilon_1}{2k} \left(\log \frac{8}{6} \right)^{-1} \sim 1.74 \frac{\epsilon_1}{k}. \quad (18)$$

Reciprocally, knowing the critical temperature with the help of Eq. (18) we can calculate the energy of interaction for every case.

In the above no explicit account has been taken of lattice expansion. The lattice or, in other words, the distance between the nearest neighbors must expand with increasing temperature; therefore the density due to this cause, even for θ constant must decrease with increasing temperature. Since the density is proportional to

θ and inversely proportional to the lattice constant, if we plot Eq. (13) using as the axis of abscissa a curve parallel to the decreasing one representing the change in density due to the lattice expansion with increasing temperatures, we obtain the curve representing the densities of liquid and vapor up to the critical temperature.

To illustrate the behavior of the critical curve according to this theory, we have plotted in Fig. 2 $\eta (=e^{\epsilon_1/kT})$ against θ as given by Eq. (13), for $Z=8$, on the assumption that the density, due to the expansion of the lattice, is a linear function increasing with η .

This theoretical curve shows the same behavior as do the experimental ones.⁶ This we consider the best justification of the assumptions made.

The anomalous specific heats of solids due to the rotations of the molecules can be treated by an analogous method.

FUSION

From the data it can be proved that the process of fusion for monatomic substances involves a decrease in coordination number. The partition functions for liquids considered in this laboratory have always been assumed to have a lower coordination number than the one known to apply to the crystalline state, and the same point of view has been held by Lennard-Jones and Devonshire in their theory of melting and by O. K. Rice⁷ among others.

Since for any change of phase the Gibb's free energy change, ΔF , is zero, we have for melting $\Delta H_m - T\Delta S_m = \Delta F_m = 0$ or $T_m = \Delta H_m / \Delta S_m$. In the same way we have for the boiling temperature the expression $T_b = \Delta H_b / \Delta S_b$. Now for monatomic substances ΔS_m is around 2 E.U. and according to Trouton's rule ΔS_b is about 21 E.U., so that if the melting temperature and the

boiling temperature were to coincide, the heat of fusion would have to be to the heat of vaporization as 2 : 21. This would be the case for example if melting consisted simply in emptying every tenth lattice point, since introducing a hole the size of the molecule corresponds to increasing the energy by an amount sufficient to vaporize a molecule. Since in general the melting temperature lies lower than the boiling point at atmospheric pressure $\Delta H_m / \Delta H_b$ must be somewhat less than a tenth, i.e., about a twelfth for non-metals and considerably less than a twelfth for the metals. If an expansion equivalent to vacating every twelfth lattice point in a substance did permit the lattice to collapse so that most of the communal entropy came in we would have a roughly quantitatively correct theory of melting since it also indicates about the right volume expansion, i.e., eight percent. The thermodynamic equation $dp/dT = \Delta S_m / \Delta V_m$ insures that a theory which correctly gives the expansion on melting ΔV_m and the entropy of melting ΔS_m will give the proper dependence of melting temperature on pressure. However, let us examine the matter more closely. Table I gives data for three substances. The subscript m indicates melting and b indicates boiling. If the only process that happened in melting were the occasional vacating of a lattice point as discussed above then the last two columns should be equal. The fact that the last column is smaller is proof that in addition to any decrease in bonding due to an emptying of lattice points in melting, the binding is also weakened due to a decrease in the average number of neighbors. The fractional decrease in the number of neighbors is at least as great as the difference between the last two columns. This shows that in all such cases the coordination number must decrease. Actually most of the expansion is probably due to a decrease in the numbers of neighbors, rather than gross inhomogeneities such as would be represented by so many empty lattice points. Spheres packed in tetrahedral array have a pore space of only 25.96 percent, as compared with 47.64 percent pore space for cubic close packed. Cubic close packing could permit collapse of the structure in any direction and so would provide complete communal sharing. Actual solids and liquids are probably intermediate between these extremes.

TABLE I.

SUBSTANCE	T_m	ΔS_m	T_b	ΔS_b	$\Delta H_m / \Delta H_b$	$\Delta V / V$
Ar	83.8	3.35	87.4	17.2	0.19	0.12
N ₂	63.2	2.73	77.2	17.3	0.13	0.09
Hg	234	2.38	629.9	22.5	0.039	0.0025

⁶ See for example Fowler, *Statistical Mechanics* (Cambridge Press, 1936), p. 846.

⁷ O. K. Rice, *J. Chem. Phys.* 7, 136 (1939).