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A Study of the Liquid State

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A theory of holes in liquids is developed to account for the thermal and mechanical properties of the liquid state. The treatment is founded on the assumption that the thermal motion of the liquid is determined by the motion of its "surface," this surface, however, to be understood in a broader sense so as to include internal boundaries of which the liquid forms as many as its number of degrees of freedom will permit. An equation of state is obtained and applied to liquid argon, and very close agreement with the empirical data is reached.

AS Bauer, Magat and Surdin¹ have recently demonstrated, various properties of a large number of pure liquids, most strikingly perhaps their molecular volumes, can be brought into correspondence with each other when plotted on a reduced temperature scale with the triple point as zero and the critical point as unity. This suggests a simple mechanism common to pure liquids and adds new emphasis to our lack of a picture in terms of which the mechanical and thermal properties of the liquid state could be understood in as general, if idealized, a manner as we understand the rarefied gases and solid bodies. At the same time, to be accessible from the mathematical side, such a picture ought to provide some information about approximately normal modes of motion of a liquid in the same sense as the positional coordinates and momenta of gas molecules, or the amplitudes and frequencies of elastic waves in a solid, are descriptive of normal modes of motion of their respective phases. But, of course, it remains questionable whether a simple and equally convincing description of the liquid state can be given.

Here it is proposed to describe the motion of a liquid by means of a new set of variables for which the assumption seems reasonable that cross terms in the potential and the kinetic energy vanish. It is assumed that all $3N$ degrees of freedom which one mole of monatomic liquid has are divided into a large number of small groups, each group operative in maintaining a spherical cavity in the liquid, of variable position and size. A cavity, or hole, is not accessible to the center of a molecule except at the expense of

heat of evaporation, which is available only in a very few cases. It is further assumed that the liquid surrounds the holes as if it were an incompressible fluid² of volume V_0 , and that the equations of hydrodynamics are obeyed by the fluid sufficiently well to give the right kinetic energy of a configurational change.

We postulate in other words that the state of motion of the liquid is determined at any moment by the motion of its "surface," this surface, however, to be understood in a broader sense so as to include internal boundaries of which the liquid forms as many as its number of degrees of freedom will permit.

The concept of holes in solids³ and liquids⁴ is not a new one in itself; though it appears that previous authors have restricted their attention to holes of molecular size. In fact, the author's approach to the liquid state has been largely stimulated by Eyring's particularly interesting publication on viscosity. Eyring has stressed the importance of molecular holes "for all phenomena in which a part of the matter in a condensed phase moves with respect to the other parts," obtaining a theory of viscosity and related phenomena in liquids as well as a qualitative understanding of the law of the rectilinear diameter. It should be born in mind, however, that the duality which holes of fixed molecular size bear to molecules in the vapor phase, of necessity fixes their respective numbers to be very nearly equal to each other. If such is truly the case only a very small fraction of the total number of degrees of freedom can be accounted

² We shall reserve the word "fluid" for use in this sense, meaning the bulk of matter surrounding the holes.

³ J. Frenkel, *Acta Physicochimica* **4**, 567 (1936).

⁴ J. Frenkel, *Acta Physicochimica* **3**, 633, 913 (1935); H. Eyring, *J. Chem. Phys.* **4**, 283 (1936).

¹ Bauer, Magat and Surdin, *J. de phys. et rad.* **7**, 441 (1936).

for in terms of holes (about one in a thousand in the lower temperature range). In contrast with this situation the picture given here places the number of holes within the order of magnitude of liquid molecules, and in the extreme case to which the idealization will be carried here accounts for all degrees of freedom. Thus it becomes possible to extend the scope from a mere investigation of structural features to one which aims at a full statistical description of the liquid and treatment as a thermodynamical system.

Tentatively one may wish to identify the numerous holes postulated here with the inhomogeneities in density (or compressibility) which have been postulated by Lucas⁵ (to account for the high absorption of supersonic waves in liquids observed by Biquard⁶).

Perhaps it is only proper to point out that the assumptions in the form stated involve a good deal of idealization and, being meant as a first approach from a somewhat unorthodox direction, they must not be taken too literally. In the first place, clearly the whole emphasis is placed on what probably is one feature in a notoriously complex situation. The implication that lattice vibrations, or elastic waves, can be ignored in the liquid is probably not correct at lower temperatures; they may have to be considered as another alternative for disposing of part of the degrees of freedom. In view of the good agreement obtained for the temperature-volume relation on the present assumption one might feel tempted to think that lattice vibrations play a minor role in liquids.

Secondly, in connection with holes of approximately molecular size the notion of a surrounding ideal fluid must be used with very considerable caution. On the other hand, no very specific conclusions from this notion are being used; the result that the effective mass of a hole turns out to be proportional to the amount of liquid displaced may be expected to result from almost any theory, continuous or otherwise.

Thirdly, the conception of surface tension used in this paper will probably have to be adapted more rigorously to the special situation

of very small holes. The ground for this has been well prepared by the treatment which surface tension has been given by Born and Courant⁷ a long time ago, and can probably be done without change in the fundamental concepts.

Under the Boltzmann principle, spherical boundaries have the obvious advantage of minimum potential energy over other shapes. Consistently with Born and Courant's theory just referred to, each hole must be permitted small vibrations about the ideal sphere, and each vibration contributing through the surface tension σ to the free energy of a hole must be counted as one degree of freedom of that hole. Born and Courant's treatment accounts for the remarkable empirical relation between surface tension and temperature, first announced by Eötvös. We shall make a very explicit use of Eötvös' law but, for the present purpose, shall use a slightly different formulation by L. Brillouin.⁸ This author obtains a simpler and yet numerically satisfactory formula by considering capillary surface waves as the carriers of the thermal agitation of the surface molecules.

Thus each hole must be endowed with degrees of freedom of three kinds: One expansional degree q , which measures the radius of the hollow sphere; three translational degrees x, y, z , which describe the position of its center; and a variable number f of vibrational degrees, connected with surface vibrations. The number of the latter is proportional to the area. As the holes grow bigger with rising temperature, degrees of freedom of still another kind will enter into consideration because a small number of molecules evaporate into the bigger holes and—having escaped from the zone of influence of their neighbors—behave much like vapor molecules, i.e., as mass points with three independent degrees of freedom each. Later it will be explained how a number of circumstances cooperate in effectively reducing the frequency with which this process occurs so that it can be treated as a small correction.

1. THE DISTRIBUTION FUNCTION

We are concerned with the statistical equilibrium of a system capable of dividing its $3N$

⁵ R. Lucas, *Comptes rendus* **201**, 1171 (1935). See also: *Trans. Faraday Soc.* **33**, 130 (1937).

⁶ P. Biquard, Thesis, Paris. *Comptes rendus* **202**, 117 (1936).

⁷ Born and Courant, *Physik. Zeits.* **14**, 731 (1913).

⁸ L. Brillouin, *Comptes rendus* **180**, 1248 (1925).

degrees of freedom into $n = \sum_i n_i$ groups of $(f_i + 4)$ each, in such manner as to render the total entropy S a maximum. Defining the "molal" surface a_m

$$a_m = N^{\frac{1}{3}} V^{\frac{2}{3}} \quad (1)$$

as the area of a surface layer of N molecules, and therefore with $3N$ degrees of freedom,⁸ we have for the total number of degrees of freedom of a mole of liquid:

$$3N = \sum_i n_i (f_i + 4) = 4n + (3N/a_m) \sum_i a_i n_i = 4n + 3a(N/V)^{\frac{2}{3}} \quad (2)$$

where $a = \sum_i a_i \cdot n_i$. The subscripts i refer to holes of a particular size q_i , and the summation goes from zero to infinite size. The subscript notation will be dropped as the sums are later replaced by integrals. If we denote the entropy per unit surface area by s_a , we have the extremal condition for S at constant volume V and energy $E = \sum_i n_i E_i$:

$$0 = (1/k) \delta S \equiv \delta [n \ln n - \sum_i n_i \ln n_i + a(s_a/k)] = \delta n (\ln n + 1) - \sum_i \delta n_i (\ln n_i + 1) + \delta a (s_a/k) \quad (3)$$

subject to the conditions that:

$$\delta n - \sum_i \delta n_i = 0, \quad (4)$$

$$\delta a - 4\pi \sum_i q_i^2 \delta n_i = 0, \quad (5)$$

$$\sum_i E_i \delta n_i = 0, \quad (6)$$

$$(4\pi/3) \sum_i q_i^3 \delta n_i = 0, \quad (7)$$

$$\delta n + \frac{3}{4} (N/V)^{\frac{2}{3}} \delta a = 0. \quad (2a)$$

Multiplying (4) to (7) and (2a) with the arbitrary multipliers $(\ln A - 1)$, B , $-1/kT$, $-P/kT$ and C , respectively, and adding to (3) we obtain:

$$\delta n [\ln nA + C] + \delta a \left[B + \frac{s_a}{k} + \frac{3}{4} \left(\frac{N}{V} \right)^{\frac{2}{3}} C \right] + \sum_i \delta n_i \left[-\ln n_i A - 4\pi q_i^2 B - \frac{E_i}{kT} - \frac{4\pi q_i^3}{3kT} P \right] = 0$$

and consequently

$$C = -\ln nA,$$

$$B = -(1/k) s_a + \frac{3}{4} (N/V)^{\frac{2}{3}} \ln nA,$$

$$n_i = \frac{1}{A} \exp \left\{ 4\pi q_i^2 \left((1/k) s_a - \frac{3}{4} (N/V)^{\frac{2}{3}} \ln nA \right) - (E_i/kT) - (4\pi/3kT) q_i^3 P \right\}. \quad (8)$$

From the last equation one finds A by summing over n_i and solving. As is seen from (8), A makes its appearance both outside the exponential function and in the exponent. To avoid the complication arising from this we content ourselves with the approximation of calculating the total surface area of all holes, a , from the relation $a = \sum_i n_i a_i$ as if the total number of holes were known, striking at the same time C from our list of multipliers. With a determined as a function of n , we can then proceed to find n from Eq. (2). We thus get:

$$n_i = \frac{1}{A} \exp -1/kT [E_i - 4\pi q_i^2 s_a T + (4\pi/3) q_i^3 P],$$

$$A = \frac{1}{n} \int_0^\infty dq \int \int \int_V dx dy dz \int \int \int_{-\infty}^{+\infty} dp_x dp_y dp_z \times \exp -1/kT [E_i - 4\pi q^2 s_a T + (4\pi/3) q^3 P]. \quad (9)$$

To carry out the integration we must express E_i as the sum of potential energy necessary to form a hole, and its kinetic energy of translation and expansion:

$$E_i = 4\pi \sigma_0 q_i^2 + k_i (p_x^2 + p_y^2 + p_z^2). \quad (10)$$

To find the kinetic energy of translation we use the well-known theorem of classical hydrodynamics stating that the apparent mass of a sphere moving in a frictionless liquid is increased by one-half of the mass of liquid displaced. Thus the apparent mass of translation, and the kinetic energy going with it, are given by:

$$m_i = (2\pi\mu/3) q_i^3, \quad k_{xyz} = (\pi\mu/3) q_i^3 (\dot{x}^2 + \dot{y}^2 + \dot{z}^2),$$

where μ is the density of the liquid. Similarly, the apparent mass which a hole exhibits while expanding or contracting, can be found by a simple deduction to be three times the mass of liquid displaced. We consider the kinetic energy of the liquid while receding from the hole at its surface at the rate \dot{q} , and at all larger distances at such rate as to maintain a constant density everywhere, flowing away radially. An integration over the infinitely extended liquid gives for the kinetic energy of expansion:

$$k_q = -\frac{\mu}{2} \int_q^\infty dr 4\pi r^2 \left(\dot{q} \frac{q^2}{r^2} \right)^2 = 2\pi\mu q^3 \dot{q}^2.$$

The kinetic part of (10) is next expressed in terms of the conjugate momenta: Eq. (2):

$$k = \frac{\pi \mu q^3}{3} (\dot{x}^2 + \dot{y}^2 + \dot{z}^2 + 6\dot{q}^2) \\ = \frac{3}{4\pi \mu q^3} (p_x^2 + p_y^2 + p_z^2 + \frac{1}{6}p^2). \quad (11)$$

The surface energy can be separated into the free energy $4\pi q^2 \sigma$ and an entropy term which cancels against another term in the exponent of (9). Thus the distribution law assumes the form:

$$Adn = dq dx dy dz dp_x dp_y dp_z dp \\ \times \exp - (3/4\pi \mu q^3 kT) (p_x^2 + p_y^2 + p_z^2 + \frac{1}{6}p^2) \\ - 1/kT (4\pi \sigma q^2 + (4\pi/3)Pq^3), \quad (12)$$

where

$$A = \frac{1}{n} \int_0^\infty dq \int \int \int_V dx dy dz \int \int \int_{-\infty}^{+\infty} dp_x dp_y dp_z \\ \times \exp - (3/4\pi \mu q^3 kT) (p_x^2 + p_y^2 + p_z^2 + \frac{1}{6}p^2) \\ - 1/kT (4\pi \sigma q^2 + (4\pi/3)Pq^3) \\ \text{or } A = \left(\frac{2}{27}\right)^{\frac{1}{2}} (4\pi^2 \mu kT)^2 \frac{V}{N} \int_0^\infty dq q^6 \\ \times \exp - 1/kT (4\pi \sigma q^2 + (4\pi/3)Pq^3). \quad (12a)$$

We are now in a position to identify the multiplier P with the external pressure acting on the liquid. Let us consider a hole in a given configuration (x, y, z, q) but with its remaining degrees of freedom in their average distribution. Then its free energy as represented by the expression in brackets in the exponent of (12a) consists of two parts, the first of which accounts exactly for the free surface energy of the hole. The remaining part therefore when differentiated with respect to the volume gives P as the pressure acting on the hole, or on any other hole. Therefore, P must be interpreted as the pressure at the external surface of the liquid.

To find the number n of all holes present at a given temperature T and pressure P , we must first determine the total surface a , and use

$$a = 4\pi \int \dots \int dq \dots dp_x n_i q_i^2 = 4\pi \int \dots \int dn q^2.$$

This, after introducing a new integration variable

$$x = (4\pi \sigma / kT)^{\frac{1}{2}} q \quad (13)$$

reduces to

$$\frac{a}{n} = 4\pi \frac{\left(\frac{kT}{4\pi \sigma}\right)^{9/2} \int_0^\infty dx x^8 e^{-x^2 - \alpha x^3}}{\left(\frac{kT}{4\pi \sigma}\right)^{7/2} \int_0^\infty dx x^6 e^{-x^2 - \alpha x^3}} = \frac{kT}{\sigma} \frac{I_8(\alpha)}{I_6(\alpha)}, \quad (14)$$

$$\text{where } I_n(\alpha) \equiv \int_0^\infty dx x^n e^{-x^2 - \alpha x^3};$$

$$\alpha = \left(\frac{kT}{36\pi \sigma^3}\right)^{\frac{1}{2}} P. \quad (15)$$

For ordinary pressures and at temperatures near the melting point, the numerical values of α are of the order of 10^{-3} per atmosphere or less, and the pressure has little influence on the distribution function and on the values of $I_n(\alpha)$. In the case $\alpha = 0$ the expression (14) reduces to

$$a = (7/2)(nkT/\sigma), \quad (14a)$$

and the surface free energy of all holes assumes the simple form $7/2nkT$. But with increasing temperature even quite moderate pressures correspond to values of α of the order of unity and exert a very important effect upon the distribution functions. Introducing the value (14) for a into Eq. (2), we find:

$$n = \frac{3N}{4} \left(1 + \frac{3}{4} \left(\frac{I_8(\alpha)}{I_6(\alpha)} \right) \frac{kT}{\sigma} \left(\frac{N}{V} \right)^{\frac{1}{2}} \right). \quad (16)$$

Eq. (16) and all other formulas involving σ assume particularly simple and convenient forms when σ is expressed in terms of the Eötvös formula. Choosing the formulation by Brillouin⁸

$$\sigma = \frac{9}{4} k \left(\frac{N}{V} \right)^{\frac{1}{2}} (T_c - T) \quad (17)$$

we finally obtain the following relation for the

total number of holes:

$$n = \frac{3N}{5} \left(1 + \frac{1}{3} \frac{T}{T_c - T} \frac{I_8(\alpha)}{I_6(\alpha)} \right) \quad (18)$$

with
$$\alpha = \frac{4}{81\pi^{\frac{1}{2}}} \frac{PV}{NkT} \left(\frac{T}{T_c - T} \right)^{\frac{1}{2}} \quad (19)$$

and T_c denoting the critical temperature.

2. AN EQUATION OF STATE

Eqs. (12), (18) and (19) together with the Eötvös formula represent the formal equipment necessary for the calculation of such observable quantities as total energy, free energy and volume of the system at given temperature and pressure. In this note we shall restrict ourselves to determining the volume as a function of the other two variables of state. As an illustration the molal volume of liquid argon will be calculated over its whole temperature range and under its saturation pressure which covers the pressure range up to 48 atmos.

Proceeding in much the same way as in the calculation of the surface area, we find the volume by an integration of $(4\pi/3)q^3$ over all

holes:

$$V - V_0 = \sum n_i v_i \\ = \frac{4\pi}{3} \int \dots \int dq^3 = \frac{4\pi n}{3} \left(\frac{kT}{4\pi\sigma} \right)^{\frac{3}{2}} \frac{I_9(\alpha)}{I_6(\alpha)} = nv.$$

Here v represents the average volume per hole and can be written by use of (17):

$$v = \frac{4}{81\pi^{\frac{1}{2}}} \frac{V}{N} \left(\frac{T}{T_c - T} \right)^{\frac{1}{2}} \frac{I_9(\alpha)}{I_6(\alpha)}. \quad (20)$$

From a comparison of (19) and (20) it is found, incidentally, that

$$Pv = kT\alpha(I_9(\alpha)/I_6(\alpha)) \quad (21)$$

or
$$P(V - V_0) = nkT\alpha(I_9(\alpha)/I_6(\alpha)). \quad (22)$$

It must be considered that n and α depend on V implicitly in a complicated way; hence, solving for V is most easily accomplished by a trial method. It follows from Eqs. (18) and (20) that nv/V depends on V only through α in a less important way. Thus writing

$$V - V_0 = V_0/(V/nv - 1)$$

it is found that:

$$V - V_0 = \frac{V_0}{27\pi^{\frac{1}{2}} \frac{I_6(\alpha)}{I_9(\alpha)} \left(\frac{T_c - T}{T} \right)^{\frac{1}{2}} \left[1 + \frac{1}{3} \frac{T}{T_c - T} \frac{I_8(\alpha)}{I_6(\alpha)} \right] - 1}. \quad (23)$$

This formula was used in the following calculations of the volume of argon. Since the numerical value which one has to insert for α presupposes the knowledge of V which is being calculated, a few slightly different values for α must be tried until the calculated volume agrees with the volume first assumed. Since an increase in α must always result in a decrease of the computed V , one is certain that the true value of V must lie between the one originally assumed and the one obtained from (23).

All computations hinge on the evaluation of integrals of the type $I_n(\alpha)$. The thing that immediately suggests itself is a series expansion in powers of α at $\alpha=0$:

$$I_n(\alpha) = \sum_{k=0}^{\infty} (-1)^k \frac{\alpha^k}{k!} \Gamma\left(\frac{n+1}{2} + \frac{3k}{2}\right). \quad (24)$$

Unfortunately this series is not convergent because the gamma-functions increase faster than the factorials in the denominators (the arguments of the gamma-functions increase in steps of 3/2 whereas the factorials increase in unit steps). At first, the expansion coefficients decrease quite rapidly only to begin increasing again when a certain index k is reached. However, for a limited range of values α the first terms of the series converge toward a definite sum and this semi-convergence makes it possible to use Eq. (24) in the low temperature region where α is of the order of 0.01. In order to cover the whole temperature range it was decided to apply numerical quadrature to the integrals I_n , ($n=6, 7, 8$ and 9), for a selected number of suitably distributed values of α . The following

recursion formula can easily be seen to be valid:

$$(n+1)I_n(\alpha) = 2I_{n+2}(\alpha) + 3\alpha I_{n+3}(\alpha). \quad (25)$$

Thus one of the three, I_9 let us say, could simply be found from I_6 and I_8 . But in view of the additional check obtained with little extra labor it was thought best to calculate them all independently.

As has been pointed out before, it is necessary to vary α by small amounts until a self-consistent value V is found from Eq. (23). This can very conveniently be done by means of a Taylor expansion about a suitably chosen α . The first and second derivatives can be calculated by the combined use of

$$\begin{aligned} (d/d\alpha)I_n &= -I_{n+3}, \\ (d^2/d\alpha^2)I_n &= I_{n+6} \end{aligned}$$

and continued application of (25), until all derivatives are reduced to expressions in I_7, I_8, I_9 . We find:

$$\begin{aligned} \frac{dI_6}{d\alpha} &= -I_9, \quad \frac{dI_7}{d\alpha} = -\frac{1}{3\alpha}[8I_7 - 2I_9], \\ \frac{dI_8}{d\alpha} &= \frac{16}{9\alpha^2}I_7 - \frac{3}{\alpha}I_8 - \frac{4}{9\alpha^2}I_9, \\ \frac{dI_9}{d\alpha} &= -\frac{32}{27\alpha^3}I_7 + \frac{2}{\alpha^2}I_8 - \left(\frac{10}{3\alpha} - \frac{8}{27\alpha^3}\right)I_9, \\ \frac{d^2I_6}{d\alpha^2} &= -\frac{dI_9}{d\alpha}; \quad \frac{d^2I_8}{d\alpha^2} = I_7 \left[-\frac{368}{27\alpha^3} + \frac{128}{243\alpha^5} \right] \\ &\quad + I_8 \left[\frac{12}{\alpha^2} - \frac{8}{9\alpha^4} \right] + I_9 \left[\frac{44}{9\alpha^3} - \frac{32}{243\alpha^5} \right], \\ \frac{d^2I_9}{d\alpha^2} &= I_7 \left[\frac{128}{9\alpha^4} - \frac{256}{729\alpha^6} \right] + I_8 \left[-\frac{50}{3\alpha^3} + \frac{16}{27\alpha^5} \right] \\ &\quad + I_9 \left[\frac{130}{9\alpha^2} - \frac{368}{81\alpha^4} + \frac{64}{729\alpha^6} \right]. \end{aligned} \quad (26)$$

A few sets of the integrals I_n and their derivatives were computed and are listed in Table I. Thanks to the possibility of computing intermediate points by means of the Taylor expansions this was found amply sufficient to cover all practical needs. It might appear from

the table as if a higher accuracy than necessary has been accomplished in the integrations; actually in some cases this accuracy turns out just sufficient for the calculation of the derivatives. For instance when $(d^2/d\alpha^2)I_9(0.100)$ is calculated with the use of (27), one has to form the difference of very big numbers and the result turns out to be about a thousand times smaller than the individual terms contributing to it.

3. CORRECTION FOR "INTERNAL VAPOR PRESSURE"

When the size of holes becomes sufficiently big so that molecules can evaporate into them, the effective pressure acting on a hole ceases to be equal to the external pressure but is reduced by the back pressure exerted by the molecules inside of holes. Hence, the average number of holes of a given size q is increased just as if an average back pressure, or internal vapor pressure, were exerted in all holes. If molecules were just as free to evaporate into holes as they are to evaporate into outside space the saturation pressure inside a hole would just counter-balance the external pressure, and a liquid under its own saturation pressure would exhibit no change of volume under its own saturation pressure.

Actually there are various reasons why this is not the case. In the first place, the effective free volume which a molecule acquires when evaporating into a big volume which it shares with a great many other molecules is bigger by a factor e than its share if this same volume were equally divided into compartments, with the exclusive use of one compartment for each molecule.⁹ Planck, on page 370 f.,⁹ points out the difference between the partition functions of the two cases: The transition from the system of N molecules in their respective compartments of size V/N to the other system where the volume V is shared by N molecules, involves division by $N!$. At the same time the volume accessible to each molecule is increased by a factor N . With the use of the Stirling formula, this introduces a factor $(Ve/N)^N$ into the partition function of the vapor, replacing the factor $(V/N)^N$ which one obtains in the case of N separated

⁹ Planck, *Ann. d. Physik* **66**, 365 (1922). See also, K. Herzfeld, *Kinetische Theorie der Wärme*, Eleventh Edition, p. 150.

TABLE I.

α	$I_n(\alpha)$				$(d/d\alpha)I_n(\alpha)$			$(\alpha^2/d\alpha^2)I_n(\alpha)$		
	$n=6$	7	8	9	6	8	9	6	8	9
0.000	3.3233	6.000	11.631	24.000	-24.000	-120.00	-287.88	287.88	1871.2	5040.0
.100	.91565	1.4703	2.5197	4.5709	-4.5709	-17.34	-36.75	36.75	191.0	317.00
.500	.2391	.3027	.4065	.5743	-.5743	-1.309	-2.085	2.085	5.877	10.243
1.200	.070643	.073318	.080455	.09268	-.09268	-.1392	-.18007	.18007	.33049	.46668
2.173	.026031	.023123	.021665	.021296						

molecules. This reduces the internal vapor pressure by a factor e^{-1} compared with the saturation pressure observed at that temperature. Besides, the heat of evaporation from the plane external boundary surface is less than that from a strongly concave surface. This is the exact analog of the well-known increase in vapor pressure at the surface of small drops; only that the curvature of our internal boundaries is of the opposite sign, besides being infinitely stronger than the curvature of the drops which usually serve as an illustration of this phenomenon. Except for the reversed sign, however, the thermodynamical argument proceeds in the same way as for small drops.¹⁰ Taking the relation usually derived, but with inverted sign and inserting an e factor, we write:

$$RT \ln (ep/P) = -2\sigma/sq, \quad (28)$$

where p and P are the vapor pressures inside the holes and outside the liquid respectively, s the density of the liquid and q the radius of the hole considered. Multiplying both sides of (28) with d_0 , the density of the outside vapor, and invoking the approximate validity of the ideal gas law for the vapor we obtain:

$$P \ln (ep/P) = d_0 RT \ln (ep/P) = -(2\sigma/q)(d_0/s).$$

Here a distinction between α and α_0 becomes necessary. Henceforth we shall denote by α_0 the quantity as defined by (19) which was associated with the external pressure P , and reserve the letter α for a quantity similarly associated with $(P-p)$:

$$\alpha = \alpha_0 - \alpha'; \quad \alpha' = \frac{4}{81\pi^{\frac{1}{2}}} \frac{pV}{NkT} \left(\frac{T}{T_c - T} \right)^{\frac{3}{2}}.$$

Introducing α_0 and the integration parameter x previously used, we can write the equation for

the internal pressure p :

$$p = P \exp - (1 + (2\sigma/Pq)(d_0/s)) \\ = P \exp - (1 + \frac{2}{3}(d_0/s)(1/d_0x)). \quad (29)$$

This reduction of the internal vapor pressure should be clearly distinguished from another fact which we have to discuss, namely, that the volume accessible to a molecule which has evaporated into a hole is not the volume of that hole. Owing to the fact that its own volume occupies a considerable portion of the hole in which it is moving, the center of the molecule is restricted to move within a sphere whose radius is smaller than the radius of the hole by one molecular diameter $2q_0$. Consequently, the internal pressure is taken into consideration by the addition of a term $\alpha'(x-x_0)^3$ to the exponent of $I_n(\alpha_0)$; this term counteracts the other one, $-\alpha_0 x^3$, only within the small volume to which the center of the molecule has access.

$$I_n(\alpha) = \int_0^\infty dx x^n \exp -x^2 - \alpha_0 x^3 + \alpha'(x-x_0)^3, \quad (30)$$

where

$$x_0 = 2q_0 \left(\frac{4\pi\sigma}{kT} \right)^{\frac{1}{2}} = 3(\pi)^{\frac{1}{2}} \left(\frac{N}{V} \right)^{\frac{1}{2}} \left(\frac{T_c - T}{R} \right)^{\frac{1}{2}} (2q_0).$$

Expressions of the form (30) must be used as the temperature goes to high values. At the same time the number n of holes must be adjusted for the loss of degrees of freedom resulting from the escape of a small fraction of molecules from the fluid. This correction, though small, becomes quite noticeable within a few degrees of the critical temperature. The number of molecules escaped is found by integration over the product of their density $d(q)$ —a function of the diameter of the hole—and their accessible volume; the integration extending over all holes.

¹⁰ W. Thomson, Phil. Mag. 42, 448 (1881); H. v. Helmholtz, Wied. Ann. 27, 508 (1886).

A simple way to perform this integration is by means of an average density defined as

$$d_{Av} = \frac{1}{I_9(\alpha)} \int dx d(x) (x-x_0)^3 x^6 e^{-x^2-\alpha x^3} \quad (31)$$

with $d(x) = d_0 \exp - (1 + \frac{2}{3}(d_0/s)(1/\alpha_0 x))$.

The fractional number of molecules escaped—which is equal to the fractional number n'/n of holes lost in this process—is given by

$$\frac{n'}{n} = \frac{d_{Av}}{s} \frac{V - V_0}{V}. \quad (32)$$

For large values of α_0 , formulas (29), (30) and (31) can be approximated by a series expansion of the exponential function. Since this case arises at higher temperatures, and thus for bigger holes where a distinction between x and $(x-x_0)$ becomes less important, we approximate (30) by

$$I_n(\alpha) = \int_0^\infty dx x^n \times \exp -x^2 - \alpha_0(1-1/e)x^3 - \frac{2}{3}(d_0/es)x^2, \quad (30')$$

which is easily transformed into

$$I_n(\alpha) = \left(1 + \frac{2}{3e} \frac{d_0}{s}\right)^{-(n+1)/2} I_n(\alpha_{eff}) \quad (33)$$

with α_{eff} independent of x :

$$\alpha_{eff} = \alpha_0 \left(1 - \frac{1}{e}\right) \left(1 + \frac{2}{3e} \frac{d_0}{s}\right)^{-1}. \quad (34)$$

It is of particular advantage to use the approximation offered by these last formulas—which is increasingly close as the critical temperature is approached—because the numerical values which α_{eff} assumes in the high temperature range are a repetition of those which α_0 assumes at much lower temperatures where no correction for internal back pressure is necessary. Thus we are able to make a two-fold use of every set of integrals I_n listed in Table I, first at that temperature where the particular parameter value α for which it was determined coincides with α_0 , and again at the higher temperature where the same value results for α_{eff} .

4. LIMITING VALUES AT THE CRITICAL POINT

While it is too much to expect that our formulas should remain valid right up to the critical point, it is interesting that they remain finite and lead to simple limiting forms as T approaches T_c . This can be demonstrated by expanding $I_n(\alpha_0)$ in inverse powers α_0^{-k} :

$$\begin{aligned} \int_0^\infty dx x^n e^{-x^2-\alpha x^3} \\ = \frac{1}{3} \sum_{k=0}^\infty (-1)^k \frac{1}{k! \alpha^{\frac{1}{3}(n+2k+1)}} \Gamma\left(\frac{n+2k+1}{3}\right), \end{aligned}$$

from which it is immediately seen that

$$\lim_{\alpha \rightarrow \infty} \frac{I_9(\alpha)}{I_6(\alpha)} = \frac{7}{3\alpha}$$

$$\text{and} \quad \lim_{\alpha \rightarrow \infty} \frac{I_8(\alpha)}{I_6(\alpha)} = \alpha^{-\frac{1}{3}} \frac{\Gamma(9/3)}{\Gamma(7/3)} = \frac{1.679}{\alpha^{\frac{1}{3}}}.$$

The first of these equations furnishes the limiting form of Eq. (21):

$$\lim_{T \rightarrow T_c} v = \frac{kT_c}{P_c} \lim_{\alpha \rightarrow \infty} \alpha \frac{I_9(\alpha)}{I_6(\alpha)} = -k \frac{T_c}{P_c}.$$

The second when introduced into (18) gives:

$$\begin{aligned} \lim_{T \rightarrow T_c} n &= \frac{3N}{4} \frac{1}{1 + \frac{1}{3} \left[\frac{81(\pi)^{\frac{1}{3}} N k T_c}{4 P_c V_c} \right]^{\frac{1}{3}} \lim_{\alpha \rightarrow \infty} \left(\alpha^{\frac{1}{3}} \frac{I_8(\alpha)}{I_6(\alpha)} \right)} \\ &= \frac{3N}{4} \frac{1}{1 + 1.159 \times 10^6 (T_c/P_c V_c)^{\frac{1}{3}}}. \end{aligned}$$

Similarly, applying the correction for back pressure as expressed by Eqs. (33) and (34), we find:

$$\lim_{T \rightarrow T_c} v = \frac{7}{3} \frac{e}{e-1} \frac{kT_c}{P_c}, \quad (35)$$

$$\lim_{T \rightarrow T_c} n = \frac{3N}{4} \frac{1 - n'/n}{1 + 1.159(e/e-1)(T_c/V_c P_c)^{\frac{1}{3}} \times 10^6}. \quad (36)$$

The volume V_c at the critical point is then obtained by forming $(nv)_c$:

$$V - V_0 = \frac{7NkT_c}{4P_c} \frac{1 - n'/n}{1 - 1/e + 1.159 \times 10^6 (T_c/V_c P_c)^{\frac{1}{3}}}$$

with

$$\frac{n'}{n} \sim \frac{1}{e} \frac{V - V_0}{V}.$$

Actually, the volume at the critical point is much larger than the one obtained from our last formula. This disagreement is not surprising since Eötvös' law cannot be expected to hold near the critical temperature at the interface between liquid and vapor; it is derived for the interface between liquid and vacuum.

5. THE VOLUME OF LIQUID ARGON UNDER ITS SATURATION PRESSURE

Using the equation of state derived in a preceding section, the volume of one mole of liquid argon has been calculated over the temperature range from the freezing point to the critical temperature; in this temperature range the saturation pressure of the vapor varies from zero to 48 atmos. In different parts of this temperature range Eq. (23) must be used in different

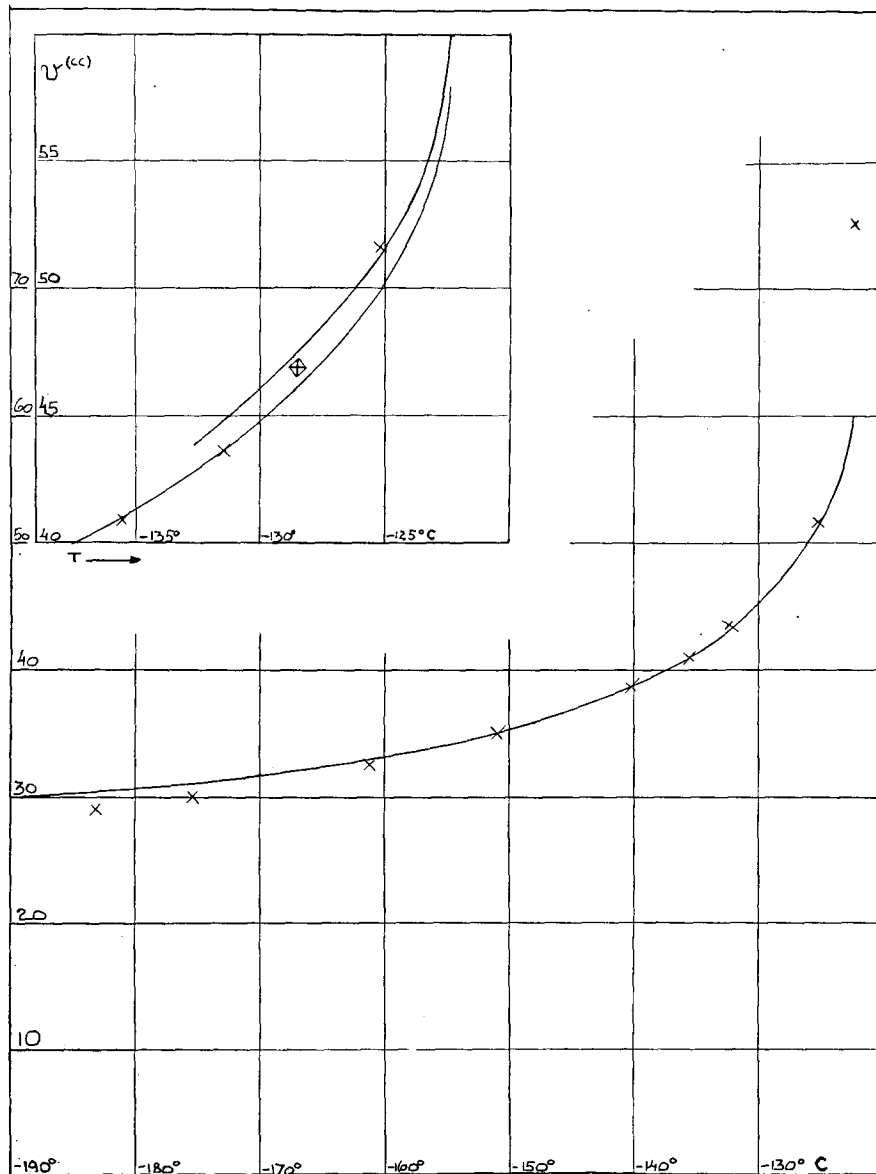


FIG. 1.

ways, in accordance with what has been said in Section 3. It was found that in the lower temperature range up to about 140°K the corrections resulting from internal back pressure can be neglected entirely, and that α can be identified with α_0 . For the remaining temperature range the back pressure becomes increasingly important and it was taken into consideration in the approximation represented by (33), (34). To ignore it would result in too small volumes as computed from (23). On the other hand, by considering it in the approximation indicated one is led to slightly too large volumes. In fact, (33) and (34) provide an upper limit rather than the true volumes; these latter being rigorously expressed by formulas (23), (30) and (32). Only for one temperature was the volume computed in the rigorous manner; namely for 144.7°K which lies in the very region where the back pressure is not negligible yet is not big enough to be approximated by formulas (33) and (34).

Results are listed in Table II, and are also summarized in Fig. 1 together with the empirical values (represented by crosses) measured by Mathias, Kamerlingh Onnes and Crommelin.¹¹ The saturation pressures given in the second column of Table II were taken from the measurements of Crommelin, and of Holst and Hamburger.¹² The values for V as given in the table were computed assigning to V_0 a value of 27.40 cc/mole. The results obtained when neglecting the effect of internal back pressure, as listed under column A in Table II, are plotted in the lower curve of inset of Fig. 1. The upper curve repre-

TABLE II.

$T^\circ\text{K}$	$P \cdot 10^{-7}$	A: No back pressure			C: Back pressure approximated by (33), (34)		
		α_0	V/V_0	V	α_{eff}	V/V_0	V
84	.089	$0.5 \cdot 10^{-7}$	1.095	30.000			
100	.325	$9.48 \cdot 10^{-8}$	1.145	31.37			
110	.675	.00299	1.191	32.64			
120	1.16	.0054	1.262	34.60			
125	1.58	.01638	1.308	35.83			
138	2.94	.10753	1.512	41.42			
140.45	3.24				0.1026	1.614	43.8
144.6	3.78	.4805	1.692	46.35			
144.68	3.79	.5000 ^B	1.7113 ^B	46.89 ^B			
146.3	4.00				.5092	1.810	49.6
148.0	4.25	2.075	1.82	50.2	1.1764	1.881	51.53

sents the results of column C ; this curve provides an upper limit for the final curve which should gradually approach it from below. The point for $T = -128.3^\circ\text{C}$, listed as (B) in column A of Table II, is represented in the inset as a little square; it indicates more definitely how the final curve changes gradually from the lower to the upper curve. Interpolating in this manner, the final curve was obtained as drawn in the main diagram of Fig. 1.

The agreement throughout the range is surprisingly close, considering how little attention has been given in this treatment to the more intimate effects which the discontinuous character of the liquid must exert on the processes we are dealing with. Minor deviations occur near the freezing point where some of our assumptions are most certainly to be replaced by more appropriate ones. This remains an object for further study.

This work was planned, and carried out in part, at the University of Vienna where it was reported at the I. Chemisches Institut in the early part of November 1936. From the latter part of that month the work has been continued at the Frick Chemical Laboratories of Princeton University.

¹¹ Mathias, Kamerlingh Onnes, Crommelin, Comm. Phys. Lab. Leyden No. 131 a. See also, Landolt-Börnstein, *Physikalische Tabellen*, Vol. I, p. 273.

¹² Crommelin, and Holst and Hamburger. See Landolt-Börnstein II, p. 1332.