

SIGNIFICANT STRUCTURES IN THE LIQUID STATE. I

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The mechanical properties of solids can be understood only by taking proper account of the imperfections present in the crystal lattice. Such lattice imperfections are so important in the liquid as to be an essential part of any description of this less ordered state. When a normal liquid such as argon melts, it expands 12 per cent. Such an expansion is typical. The atypical 10 per cent contraction of ice upon melting can be made to disappear if one first applies some 2,500-atm. pressure, at an appropriate temperature, to the hydrogen-bonded tetrahedral ice I and so transforms it into close-packed ice III, which is a fifth more dense. Ice III then melts with a normal 10 per cent expansion. Anhydrous salts such as sodium chloride melt with about the normal 10 per cent expansion. Metals such as sodium melt with about a 3 per cent expansion. This small expansion on melting of metals was long ago interpreted¹ as a consequence of the small size of the ion formed from atoms which no longer localize their conducting electrons. The ion, being only about one-third atomic size, requires only a third the expansion of normal liquids on melting to provide the same number of vacant sites and therefore the same increased disorder, which leads to melting.

To account for the properties of the liquid state in general and of melting in particular, we require a model. We shall describe our procedure for arriving at this model as the identification of significant structures. A simple example will clarify the procedure.

Suppose we wish to calculate the thermodynamics of iodine in the gaseous state at a temperature at which the diatomic molecules are partly dissociated into atoms. Clearly, there are two significant structures—diatomic molecules and atoms—and the partition function for the whole is a product of partition functions for the molecules and for the atoms. Now, since a diatomic molecule and a monatomic one contribute equally to the pressure, the pressure at any temperature measures the total number of diatomic plus monatomic molecules per cubic centimeter. A knowledge of the density, together with the pressure, fixes the composition and thereby all thermodynamic properties. For example, the energy, like the pressure, follows immediately from the composition in the iodine system. The composition is fixed by the easily formulated requirement that molecules and atoms be at the same chemical potential. Knowing the composition, the partition function is expressible in terms of the independent variables V and T , so that all the thermodynamic properties of the system become readily calculable. The key to success in this procedure is the recognition of the two significant structures—iodine molecules and iodine atoms.

We proceed to develop the method of significant structures for the liquid state. Figure 1 shows a partial dislocation extending from top to bottom through the middle of the figure. The nine molecules to the left (west) of the dislocation occupy what we will call a sites, while the nine molecules on the right (east) occupy b sites. If the distance between centers of close-packed neighboring molecules be

indicated by d , one can see that molecules on a sites bordering the dislocation can shift to adjacent empty b sites by moving northeast a distance $d/\sqrt{3}$. Similarly, molecules on b sites next to the dislocation can move to empty neighboring a sites by proceeding southwest a distance $d/\sqrt{3}$. Such molecular displacements merely shift the position of dislocations without creating or destroying them. This shifting of molecular positions we call a -to- b transitions or b -to- a transitions, as the case may be, and write for them, as for chemical reactions, the expressions $a \rightarrow b$ and $b \rightarrow a$, respectively. When an $a \rightarrow b$ or $b \rightarrow a$ transition occurs, there is an elastic readjustment of all neighbors, with a net storage or release of energy.

Long, narrow passageways in glass like the dislocation in Figure 1 have long been known to exist. Thus Pyrex leaks helium, which has a diameter of 2 Å and is impervious to H_2 with a diameter of 2.5 Å as well as larger molecules. Soft glass



FIG. 1.—Model of type dislocations present in the liquid state.

has its passageways partly obstructed, as helium does not leak through it. Water containing sulfuric acid when frozen into glass and irradiated has been observed² to give hydrogen atoms at twenty times the yield obtained from crystalline materials similarly treated. Escape passageways in the glass would explain the difference. When sulfuric acid is replaced by phosphoric and some other acids, the differences in hydrogen yield almost disappear. Since a glass is presumably a metastable liquid with the passageways frozen in, it is to be expected that such passageways would be present in the liquid.

Thus we are led to identify three significant structures in the liquid state. The first structure is that of molecules with solid-like degrees of freedom. Thus in the direction of one or more degrees of freedom the molecule is bonded and restrained to an equilibrium position much as if it were in the solid state. Second, we recognize positional degeneracy due to the presence of vacant sites accessible

to a molecule at the price of storing up more or less elastic energy due to structural distortion as the molecule shifts to the new equilibrium position. Third, we must recognize that molecules which have escaped in one direction at least from fitting into the potential well made by neighbors may, in this liberated freedom, move much like a gaslike degree of freedom. Having recognized these significant structures, as was done in the iodine case, it still remains to estimate their concentrations.

X-rays indicate that the distance between near neighbors is closely the same for liquids as for solids, in spite of the over-all expansion. Thus it is natural to attribute the bonding energy to solid-like degrees of freedom and to attribute lack of bonding energy to gaslike degrees of freedom associated with localized loosening of the structure.

If we represent the energy of sublimation of the solid at the melting point by E_s , then the energy of vaporization of the liquid should be $E_s V_s/V$, where V_s is the volume of the solid at the melting point and V is the volume of the liquid. This follows because V_s/V is the average fraction of the space around a molecule filled by other molecules and is therefore the fractional degree of bonding of the liquid compared to the solid.

Just as in the iodine case the total bonding energy measures the fraction of the atoms which are present in molecular degrees of freedom, so in the liquid, we assume, the bonding energy measures the fraction, V_s/V , of solid-like degrees of freedom. The remaining fraction $(V - V_s)/V$ we take to be gaslike.

As a result of these considerations, we write for the partition function, f , of a normal liquid such as argon thus:

$$f = \left\{ (1 - e^{-\theta/T})^{-3} e^{E_s/RT} (1 + n_h e^{-a/n_h RT}) \right\}^{N V_s/V} \left\{ \frac{(2\pi m k T)^{3/2}}{h^3} eV/N \right\} \frac{N(V - V_s)}{V}. \quad (1)$$

Here n_h is the number of equilibrium sites accessible to a molecule in addition to its single most stable position; a/n_h is the strain energy stored in the system as the molecule shifts to one of the n_h sites. Undoubtedly, a/n_h should be written as $a/(n_h + \delta)$ since the strain energy when n_h is zero is very large but not infinite. However, to evaluate δ experimentally would involve a detailed knowledge of the glassy state not presently available.

The term eV/N in equation (1) comes from dividing the volume $(V - V_s)$, available to gaslike molecules, by the number of gaslike molecules, $N(V - V_s)/V$, and multiplying by the factor e , yielding the communal entropy associated with gaslike degrees of freedom. Such considerations involve making the assumption that gaslike degrees of freedom distribute themselves in such a way as to share communally the available volume, $V - V_s$. The factor eV/N in equation (1) likewise follows from the equality:

$$\left(\frac{(2\pi m k T)^{3/2}}{h^3} (V - V_s) \right)^{N(V - V_s)/V} (N(V - V_s)/V)!^{-1} = \left(\frac{(2\pi M k T)^{3/2}}{h^3} eV/N \right)^{N(V - V_s)/V}$$

θ , E_s , and V_s are the Einstein characteristic temperature, the energy of sublimation, and the volume of the solid, all measured at the melting point. We can regard these three quantities as parameters calculated from a quantum-mechanical treat-

ment of the solid state or as experimental solid-state parameters. The two new parameters characteristic of the liquid state are the extra sites per molecule, n_h , added in the liquid and the strain energy, a/n_h , required to occupy these sites. The pressure effect on viscosity would lead us to expect the formula

$$n_h = n(V - V_s)/V_s = 7(V - V_s)/V_s \quad (2)$$

for the number of holes, whereas

$$n_h = 10(V - V_s)/V_s \quad (3)$$

gives a better account of thermodynamic properties. Equations (2) and (3) would arise if seven and ten new equilibrium positions, respectively, arose each time the liquid volume, V , was increased by an amount V_s . A consideration of Figure 1 will convince one that these numbers are about right.

For the energy of distortion we require

$$a/n_h = 0.00285 E_s V_s / (V - V_s), \quad (4)$$

where again it can be said that the linear dependence of strain energy on the inverse of the concentration of holes is a reasonable, if oversimplified, relationship, as is the magnitude of the proportionality factor 0.00285.

Returning to equation (1), one justifies the assumption that the extra volume $V - V_s$ is available to gaslike motions in spite of the degeneracy of solid-like degrees of freedom because all structures exclude the same volume, V_s . The strain energy, a/n_h , becomes negligible in its effect as volume and temperature increase. Thus in the neighborhood of the critical point, the term $n_h \exp(-a/n_h RT)$ reduces to n_h .

The partition function (1), with the values for the parameters n_h and a given by equations (3) and (4), permits the calculation of all thermodynamic properties for a normal liquid. The solid parameters used for the rare gases are listed in Table 1.

Some properties calculated for argon are tabulated in Tables 2-4.

TABLE I
SOLID PARAMETERS AT MELTING POINT

	Neon	Argon	Krypton	Xenon
Energy of sublimation, E_s (cal.)	447.4	1,888.6	2,710.4	3,897.7
Solid volume, V_s (cc.)	13.98	24.98	28.4	36.5
Einstein characteristic temperature	44.7	60.0	45.0	39.2

TABLE 2
MELTING-POINT DATA FOR LIQUID ARGON

	Calculated	Observed
Volume (cc.)	28.00	28.03
Vapor pressure (atm.)	0.662	0.674
Temperature ($^{\circ}$ K.)	(83.85)	83.85
Melting entropy (e.u.)	3.66	3.35

TABLE 3
BOILING-POINT DATA FOR ARGON

	Calculated	Observed
Liquid volume (cc.)	28.48	28.69
Pressure (atm.)	1.05	1.00
Temperature ($^{\circ}$ K.)	(87.44)	87.44
Vaporization entropy (e.u.)	19.33	17.85

In Tables 2 and 3 the properties were calculated for the observed melting and boiling temperatures rather than for atmospheric pressure, which would have been only somewhat more laborious. To find the phases in equilibrium with each other, we plot $A = -kT \ln f$ for any desired T as a function of V and find the multiple tangent. The volumes at the various points of tangency are the volumes of the corresponding phases at the pressure given by the slope of the tangent. The tangent intercepts the axis A at the common Gibbs free energy for the various phases. Except at the triple point, a tangent line has, at most, two points of tangency. Tangents which cut the curve, A versus V , at any point correspond to a metastable state at the point of tangency which is not realizable as an equilibrium state but may be realizable kinetically.

TABLE 4
CRITICAL-POINT DATA OF ARGON

	CALCULATED		CALCULATED (WALTER)	OBSERVED
	$n = 6$	$n = 10$		
Volume (cc.)	77.7	81.0	78.7	75.26
Temperature ($^{\circ}$ K.)	154.4	150.5	154.2	150.66
Pressure (atm.)	58.7	58.1	59.4	48.0

In Table 4 the values $n = 6$ and $n = 10$ refer to the respective values chosen for n in equation (2). The calculated critical properties depend only on the single liquid parameter n , since the distortional energy has become negligible at these volumes and temperatures. Calculated values in this and subsequent tables under the heading "Walter" come from one of two publications with that author and A. E. Stearn.^{3,4} The Walter-Eyring partition function is conceptually similar to the partition function developed here and has been very successfully used in calculating the thermodynamic properties of liquids. The present development, however, represents a definite formal and conceptual simplification and improvement.

In Tables 5, 6, and 7 our calculated critical properties for neon, argon, krypton, and xenon are compared with Walter, Stearns, and Eyring's values and with the observed values. In these cases n in equation (2) was taken equal to 6, and the solid parameters used are given in Table 1. The slight changes obtained when $n = 10$ did not seem of sufficient interest to calculate at this time.

TABLE 5
CRITICAL TEMPERATURES ($^{\circ}$ K)

	$n = 6$	(Walter)	Observed
Neon	55.41	48.0	44.47
Argon	154.44	154.2	150.66
Krypton	208.33	215.0	210.6
Xenon	287.8	303	289.8

TABLE 6
CRITICAL PRESSURES (atm.)

	$n = 6$	(Walter)	Observed
Neon	37.65	32.7	26.86
Argon	58.72	59.4	48.00
Krypton	69.68	69.1	54.24
Xenon	74.89	75.6	58.2

TABLE 7

	CRITICAL VOLUMES (cc.)		Observed
	$n = 6$	(Walter)	
Neon	43.48	49.0	41.74
Argon	77.69	78.7	75.26
Krypton	88.32	81.0	...
Xenon	113.52	112.0	113.8

The critical properties above were calculated algebraically in the usual way, using

$$\left(\frac{\partial A}{\partial V}\right)_T = -p, \left(\frac{\partial p}{\partial V}\right)_T = 0, \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0.$$

The method of significant structures thus leads to a simple and surprisingly successful reduced equation of state for normal liquids. The deviations from experiment, particularly in the pressure, are such as would arise from insufficient account of clusters of molecules in the saturated vapor. Such clusters are known to exist. Extension of our partition function to abnormal liquids and to metals and molten salts are in progress along lines that have previously been found successful, using the Walter-Eyring partition function.

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¹ R. H. Ewell and H. Eyring, *J. Chem. Phys.*, **5**, 726, 1937.

² Ralph Livingston, private communication.

³ J. Walter and H. Eyring, *J. Chem. Phys.*, **9**, 393, 1941.

⁴ H. Eyring, J. Walter, and A. E. Stearn, in *Surface Chemistry*, (Washington, D. C.: American Association for the Advancement of Science, 1943), No. 21, p. 88.

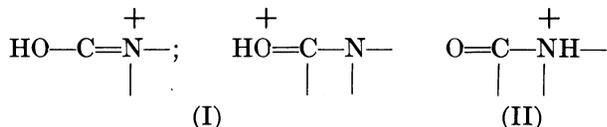
THE MODE OF PROTONATION OF AMIDES

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The relative basicities of oxygen versus nitrogen in amides is a problem which has not been satisfactorily resolved. However, it might be anticipated from considerations of resonance and structural parameters that in strongly acidic solutions the proton will attach to oxygen rather than to nitrogen, to give I rather than II:



It is generally recognized that amides are monoprotinated in 100 per cent sulfuric acid. For example, O'Brien and Niemann¹ reported *i*-factors of 2.0, 2.7, 2.0,