

SIGNIFICANT STRUCTURES IN LIQUIDS. II.

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In the first paper of this series,¹ a procedure was described for arriving at a model of the liquid state. The procedure identifies three significant structures in the liquid state. First, solid-like degrees of freedom result from binding of a molecule to an equilibrium position by its neighbors. The second significant structure arises from possible position degeneracy in the solid-like structure. If additional vacant sites are available to a molecule in addition to its equilibrium position, some strain energy is stored in the lattice as the molecule shifts position. Finally, gaslike degrees of freedom occur as a molecule escapes in at least one direction from the solid lattice.

Bonding energy is attributed to solid-like degrees of freedom. The concentrations of the significant structures are estimated in the following way. The bonding energy is taken as $E_s(V_s/V)$, where E_s is the energy of sublimation of the solid at the melting point, V_s is the molar volume of the solid at the melting point, and V is the liquid volume. Then V_s/V is assumed to be the fraction of solid-like degrees of freedom and $(V - V_s)/V$ is the gaslike fraction.

The partition function, f , of a normal liquid such as argon is then

$$f = \left[\frac{e^{\frac{E_s}{RT}}}{\left(1 - e^{-\frac{\theta}{T}}\right)^3} \left(1 + n_h e^{-\frac{a}{n_h RT}}\right) \right]^{\frac{NV_s}{V}} \left[\frac{(2\pi mkT)^3}{h^3} \frac{eV}{N} \right]^{\frac{N(V - V_s)}{V}} \quad (1)$$

In the above, n_h is the number of equilibrium sites accessible to a molecule in addition to the 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. θ is the Einstein characteristic temperature. 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.

For the energy of distortion of argon:

$$a/n_h = 0.00534 E_s V_s / (V - V_s) \quad (2)$$

The linear dependence of strain energy on the inverse of the concentration of holes is a reasonable relationship.

The partition function (1) permits the calculation of all thermodynamic properties for normal liquids.

The first square brackets of Equation (1) enclose that part of the partition function to be attributed to solid-like degrees of freedom. Gaslike degrees of freedom are represented by the expression inside the second set of square brackets. The gaslike part of the partition function in the general case contains f_{vib} and f_{rot} for any internal vibration or rotational degrees of freedom which the molecule may possess. If the motion is present in the solid state also, the appropriate terms appear as a factor in the over-all expression.

The parameters n_h and a have been studied to see how they vary from liquid to liquid when the best fit between calculated and experimentally observed properties

is obtained. n_h is calculated by $n(V - V_s)/V_s$. The pressure effect on viscosity would predict a value for n of about 7. It is probable that a temperature variation of θ would allow $n = 7$, but this study takes θ as constant since such a temperature variation is not theoretically calculable at present. The quantity, a , is related to E_s by the relation

$$\frac{a}{n_h} = \frac{aE_sV_s}{n(V - V_s)} = \frac{a'E_sV_s}{V - V_s}$$

In Tables 1 and 2, the values of n and a' and the solid parametric values, respectively, are listed which were used in this paper.

TABLE 1
VARIATION OF PARAMETERS

	n	a'
Neon	11	0.00802
Argon	10.8	0.00534
Krypton	11.7	0.00590
Xenon	12.27	0.00563

TABLE 2
SOLID PARAMETERS USED

	Neon	Argon	Krypton	Xenon
Melting point, °K	24.55	83.85	116.0	161.3
E_s , cal.	447.4	1,888.6	2,710.4	3,897.7
V_s , ml	13.98	24.98	28.4	36.5
θ , °K	44.7	60.0	45.0	39.2

The calculation of the best fitting values of n and of a' produced calculated properties of the rare gases differing slightly from those reported earlier.^{1,2} The results obtained are compared with experiment in Table 3.

TABLE 3
CALCULATED AND OBSERVED PROPERTIES

	Neon			Argon			Krypton			Xenon		
	Calc.	Obs.	Δ , %	Calc.	Obs.	Δ , %	Calc.	Obs.	Δ , %	Calc.	Obs.	Δ , %
V_m	16.43	16.15	+1.71	28.90	28.03	+3.11	33.11	34.13	-2.98	42.30	42.68	-0.88
ΔS_m	3.244	3.259	-0.44	3.263	3.35	-2.61	3.456	3.35	+3.16	3.415	3.40	+0.44
P_m	0.437	0.417	+4.81	0.732	0.674	+8.55	0.756	0.722	+4.68	0.399	0.804	-50.4
V_b	17.17	16.80	+2.19	29.33	28.69	+2.22
ΔS_b	15.68	15.81	-0.83	19.04	17.85	+6.68	19.27	17.99	+7.13	19.43	18.29	+6.24
T_b	27.13	27.26	-0.48	87.29	87.29	0	119.28	119.93	-0.54	167.5	165.1	+1.45

Here, V_m , ΔS_m , and P_m are the liquid volume, the entropy change, and the vapor pressure at the melting point, respectively. V_b , ΔS_b , T_b are the analogous properties at the normal boiling point.

Application of the partition function to more complicated molecules was made. Nitrogen, methane, and benzene were studied with the results shown in Tables 4, 5, and 6. Here, the parametric values, which were used in the calculations, are given in the beginning of each table.

In the benzene calculation, two values of the Einstein θ were required; one for the solid and another, θ' , for the solid-like part of the liquid partition function. This result, and the benzene calculation in general, is in good agreement with that reported earlier by Walter and Eyring.³

TABLE 4

METHANE

Melting point, °K.....	90.65	<i>n</i>	13.3
E_2 , cal.....	2200	a'	0.00296
V_2 , ml.....	30.94	θ	75.33
ΔS , fusion, e.u.....	2.48		
	V		
$T^\circ\text{K}$	Calc.	Obs.	Δ , %
90.65(T_m)	34.111	33.63	+1.43
99.67	35.024
111.67(T_b)	36.354	37.816	-3.86
112	36.447
	Vapor Pressure		
	Calc.	Obs.	Δ , %
	0.1172	0.115	+1.95
	0.3265	0.3282	-0.51
	0.9736	1.0000	-2.64
	1.0054
	ΔS_{vap} , e.u.		
	Calc.	Obs.	Δ , %
	17.399	17.51	-0.63
	T_{vap} at 1 atm. °K		
	Calc.	Obs.	Δ , %
	112.0	111.67	+0.29
	Critical Properties		
	Calc.	Obs.	Δ , %
P_c , atm.....	63.305	45.8	+38.2
V_c , ml.....	103.90	99.02	+4.30
T_c , °K.....	214	191.04	+12.0

TABLE 5

NITROGEN

Melting point, °K.....	63.14	<i>n</i>	12.9
E_2 , cal.....	1529.9	a'	0.00343
V_2 , ml.....	29.31	θ	55.94
ΔS , fusion, e.u.....	2.73		
	V, ml		
$T^\circ\text{K}$	Calc.	Obs.	Δ , %
63.14(T_m)	32.622	31.95	+2.10
68.41	33.560	33.09	+1.42
77.34(T_b)	35.055	34.70	+1.02
99.52	41.034	40.51	+1.29
$\Delta S_{\text{vap}} = 17.433$ e.u. calc.,		17.24 e.u. obs.,	+1.12%
	Vapor Pressure, atm		
	Calc.	Obs.	Δ , %
	0.1244	0.1237	+0.55
	0.3014	0.3005	+0.29
	0.9945	1.0000	-0.55
	7.17	7.37	-2.7
	Critical Properties		
	Calc.	Obs.	Δ , %
P_c , atm.....	40.471	33.49	+20.85
V_c , ml.....	98.482	90.1	+9.30
T_c , °K.....	135.3	126.0	+7.38

TABLE 6

BENZENE

Melting point, °K.....	278.6	<i>n</i>	20
E_2 , cal.....	10,383.8	a'	0.006
V_2 , ml.....	77.00	θ	80.24
ΔS , fusion, e.u.....	8.46	θ'	55.2
	V, ml		
$T^\circ\text{K}$	Calc.	Obs.	Δ , %
278.6(T_m)	87.01	87.28	-0.31
298.1	88.94	89.36	-0.47
328.1	92.01	92.80	-0.85
353.3(T_b)	94.94	95.92	-1.06
373.1	97.25	98.46	-1.23
423.1	104.72	106.8	-1.95
$\Delta S_{\text{vap}} = 21.311$ e.u. calc.,		20.848 e.u. obs.,	+2.22%
	Vapor Pressure, atm		
	Calc.	Obs.	Δ , %
	(0.0474)	0.0474
	0.1261	0.124	+1.50
	0.4337	0.4293	+1.03
	1.007	1.0000	+0.74
	1.724	1.757	-1.91
	5.738	5.704	+0.60
	Critical Properties		
	Calc.	Obs.	Δ , %
P_c , atm.....	74.39	47.9	+55.3
V_c , ml.....	268.7	256	+4.97
T_c , °K.....	644	562	+14.6

A method of procedure for more complicated molecules such as ethane is to use the following expression as the solid part of the liquid partition function:

$$\left[\frac{e^{\frac{E_s}{RT}}}{\left(1 - e^{-\frac{\theta_1}{T}}\right)^3} \left\{ \frac{1}{1 - e^{-\frac{\theta_2}{T}}} \left(1 - e^{-\frac{\delta E_s}{(V-V_s)RT}}\right) + f_{1, \text{rot}} e^{-\frac{\delta E_s}{(N-V_s)RT}} \right\} \times \right. \\ \left. \left(1 + n_h e^{-\frac{a}{n_h RT}}\right) \right]^{\frac{NV_s}{V}} \quad (3)$$

The curled brackets enclose the partition function for an oscillator which gradually turns to a free rotator at higher temperatures. This function was not given extensive testing since the necessary data for solid ethane were not available. Here, δE_s is an activation energy for free rotation, δ being a fractional number.

At the critical point, the liquid partition function (1) is seen to predict values which differ substantially from those observed (Table 7).

TABLE 7
CRITICAL DATA FOR ARGON

	Calc.	Obs.	Δ , %
T_c , °K	149.7	150.66	-0.637
V_c , ml	83.68	75.26	+11.2
P_c , atm	52.93	48.00	+10.3

It was felt that the pressure would be lowered if the partition function reflected the clustering of molecules in the gas phase at the critical point. Accordingly, the partition function becomes

$$f = \left\{ \frac{e^{-\frac{E_s}{RT}}}{\left(1 - e^{-\frac{\theta}{T}}\right)^3} \left[1 + n_h e^{-\frac{a}{n_h RT}} \right] \right\}^{\frac{NV_s}{V}} \left\{ \left[\frac{(2\pi mkT)^2}{h^3} \frac{eV}{N} \right]^2 + \right. \\ \left. \frac{(2\pi(2m)kT)^3}{h^3} \frac{eV}{N} \frac{\left(e^{\frac{D}{RT}} - 1\right)}{1 - e^{-\frac{\theta}{T}}} \frac{8\pi^2 I kT}{2h^2} \right\}^{\frac{V-V_s}{V} \frac{N}{2}} \quad (4)$$

for a liquid such as argon with no ordinary internal degrees of freedom. The contribution made by diatomic gas molecules is seen to depend upon the size of the coefficient $\left(e^{\frac{D}{RT}} - 1\right)$. This factor corrects for the energy difference between the monatomic and diatomic gas molecules. I is the moment of inertia of the diatomic molecule. If the vibration frequency is taken equal to the lattice vibration frequency and the two atoms in the molecule are assumed to be separated by a distance of two van der Waals radii, then the dissociation energy of the diatomic molecule, D , is the only arbitrary number. Various values of D were chosen and the differences, Δ , between calculated and observed values of the critical point data were obtained. It was found that the pressure may indeed be lowered in this way but that the value of Δ for the critical volume now is too large.

The results we have presented here show that the method of significant structures may be applied to more complicated molecules than those treated in an earlier paper.¹

APPENDIX

(1) *Partition Function for the Solid-like Part of Liquids.*—Experimental evidence, e.g., the curve of specific heat versus temperature, and simple theoretical

calculations of volume indicate that methane and nitrogen molecules rotate in the solid state. Thus in the calculations of Table 4 and 5, the following formulas, respectively, were used for the solid part of the liquid partition function

$$(1 - e^{-\theta/T})^{-3} e^{\frac{E_s}{RT}} \frac{\pi^{1/2}}{12} \left(\frac{8\pi^2 I k T}{h^2} \right)^{3/2} \prod_{i=1}^9 \frac{1}{1 - e^{-h\nu_i/kT}} \quad (5)$$

and

$$(1 - e^{-\theta/T})^{-3} e^{\frac{E_s}{RT}} \frac{8\pi^2 I k T}{2h^2} \frac{1}{1 - e^{-h\nu/RT}} \quad (6)$$

Here, I is the moment of inertia and ν is the internal frequency of the molecule. These molecular parameters are considered to be equal to those for gas molecules, and the data found in the literature⁴ were used in the calculations.

For the solid part of the liquid partition function of benzene, we used the following expression:

$$(1 - e^{-\theta/T})^{-6} e^{\frac{E_s}{RT}} \frac{\pi^{30}}{1} \frac{1}{1 - e^{-h\nu_i/kT}} \quad (6)$$

Here, it is assumed that a three-dimensional torsional vibrator oscillates with the frequency which is equal to that for the lattice vibrator.

(2) *Determination of E_s and θ .*—The θ values in the solid-like part of the liquid partition function of complex molecules are in general the Einstein characteristic temperatures fitted to the solid at the melting point. These values do not necessarily agree with the literature values which are usually the values obtained at temperatures considerably below the melting point. The procedures, by which the values θ and E_s were obtained, are given below.

For methane, the solid vapor pressure data⁵ with the Clapeyron-Clausius equation gives the value of E_s used. Using the equilibrium condition between gas and solid at the melting point, i.e.,

$$F_{\text{solid}} = F_{\text{gas}}$$

We obtain

$$A_{\text{solid}} \simeq A_{\text{gas}} + RT_m \quad (7)$$

Here, it has been assumed that the PV product for the solid is negligibly small and that the gas is ideal (which is reasonable for the low vapor pressure observed at the melting point). Now A_{gas} is readily calculated from the partition function. Then

$$A_{\text{solid}} = -RT_m \ln f_{\text{solid}} \simeq A_{\text{gas}} + RT_m \quad (8)$$

where f_{solid} is given by expression (5). It is seen that θ is now the only unknown quantity in (8) and can be readily calculated.

An alternate method is illustrated by the determination of E_s and θ for the nitrogen calculation. Use was made of the solid entropy, calculated by graphical integration of the (C_p/T) vs. T curve. This entropy, if equated to that calculated from the partition function by $S = -(\partial A/\partial T)_v$, allows an approximation of the value of θ , since E_s does not appear in the entropy expression.

Admittedly, the two results differ by

$$\int_0^{T_m} \frac{C_p - C_v}{T} dT$$

but the correction will be small. Once θ is estimated in this way, equations (7) and (8) give the value of E_s used.

Solid benzene at the melting point may be fitted well by the methods summarized for methane and nitrogen, but the parameters E_s and θ so obtained were found inapplicable to the solid-like structure in the liquid. Conceivably the solid-like degrees of freedom in benzene undergo a change as melting occurs. This is certainly indicated by the high entropy of fusion (8.46 e.u.) as compared with that of, say, argon (3.35 e.u.). Accordingly, the partition function was fitted to the liquid at the melting point and the values of E_s and θ were chosen to give the calculated solid-like contribution.

(3) *Partition Function including Clustered Molecules.*—Some comments may be necessary to understand equation (4). If $D = 0$, the gaslike part of the equation becomes the partition function corresponding to the monatomic gas as it should be, while if the first term inside the second curled brackets is negligible compared to the second, the expression becomes the partition function of the diatomic molecule.

A similar consideration is applied to equation (3), which includes the sum of states of an oscillator which transforms to a free rotator at higher temperatures.

Summary.—The method of significant structures applied to the liquid state is summarized. The theory is applied to methane, nitrogen, and benzene as well as to the rare gases, with good success. The numerical values of the parameters which give the best fit of the various liquids at the melting point are obtained. An attempt to fit the partition function to the critical point, by introducing diatomic clusters, is described.

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