

Significant structure theory applied to liquid ^4He

(thermodynamic properties/surface tension)

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ABSTRACT The large kinetic zero-point motion of ^4He molecules has been properly taken into account in the significant structure theory of liquids in order to describe the liquidity of liquid ^4He . The Debye and the Bose-Einstein partition functions are used for the solid-like molecules of the normal fluid component and for the whole gas-like molecules, respectively. The solid-like molecules of the superfluid component are considered as ground state molecules without having positional degeneracies. The Bragg-Williams approximation of an order/disorder phase transition has been applied to the λ transition of liquid ^4He . Thermodynamic and surface properties of liquid ^4He have been calculated up to the critical point. The results are satisfactory when compared with the observed values.

Liquid ^4He is an exciting subject for the study of thermodynamic and transport properties of matter because of its remarkable properties. Although there have been numerous experimental and theoretical studies of liquid ^4He , few theories can explain its equilibrium properties quantitatively from nearly absolute zero up to the critical point. The theories of Landau and Feynman concerned with elementary excitations explain the equilibrium properties of liquid ^4He near absolute zero (1). But difficulties arise at higher temperatures because the excitation spectra become more complicated. The structure of liquid ^4He is also an interesting subject. X-ray (2–5) and neutron (6–8) scattering data show that there is a short-range correlation in liquid ^4He , in either He-I or He-II, and that there are no appreciable changes of structure during the λ transition. This fact indicates useful applicability of significant structure theory (9–11) to liquid ^4He . Hence, we attempt here to explain the equilibrium thermodynamic and surface properties of liquid ^4He by applying significant structure theory.

The significant structure theory of liquids regards a liquid as having a quasi-lattice structure in which the sites are occupied by molecules or fluidized vacancies of molecular size. It has been successfully applied to various liquids (9–11) including quantum liquids such as liquid hydrogen (12) and liquid ^3He (13). However, in the case of liquid ^3He , it was successful only at temperatures above 1 K without consideration of the kinetic zero-point motion of He molecules. It is well established that liquid He is strongly influenced by the zero-point motion (14) due to the low atomic mass and the extremely weak intermolecular attraction. This effect of zero-point motion should therefore be taken into account in treating liquid He near absolute zero. On the other hand, the peculiar λ transition of liquid ^4He is described phenomenologically as a kind of order/disorder phase transition (14, 15) such as the transition in ferromagnets near the Curie point and the order/disorder transition in binary alloys. As London (14) stressed, the order in liquid ^4He is considered to be some kind of order in momentum space, not in ordinary space. In this paper, we use the Bragg-Williams

approximation (16, 17) of order/disorder phase transition to explain the λ transition of liquid ^4He while taking into account the kinetic zero-point motion of the molecules.

We will first derive the partition function for the liquid and then evaluate the thermodynamic and surface properties from the partition function. The results will be compared with the experimental data.

PARTITION FUNCTION

The description of liquid ^4He requires another partition function for the λ transition in addition to the conventional one for the liquidity. So, the partition function is written as

$$f_N = f_{\text{conv}} \cdot f_{\text{conf}} \quad [1]$$

in which f_{conv} is a conventional partition function describing the liquidity and f_{conf} is a configurational partition function to explain the λ transition.

In order to obtain f_{conv} , the λ situation at absolute zero is considered from the viewpoint of the significant structure theory. Because all the thermal motions vanish, the solid-like molecules will be located at their own sites at absolute zero. Therefore, application of the significant structure theory at absolute zero gives a quasi-lattice structure and explains no properties of liquids. The fluidity of liquid ^4He at absolute zero is ascribed to the large kinetic zero-point motions of the molecules. A molecule at 0 K is not locked in a occupied site due to the kinetic zero-point motions. Thus, by using the basic concepts of the significant structure theory and taking into account the kinetic zero-point motion, the conventional partition function is written as

$$f_{\text{conv}} = \exp(-NK_0/RT) \cdot f_s^{NV_s/V} \cdot f_g^{N_V - V_s/V} \quad [2]$$

Here, N , V , V_s , R , and T are Avogadro's number, the molar volume of the liquid, the molar volume of the solid-like molecules, the gas constant, and the absolute temperature, respectively; K_0 is the kinetic zero-point energy per ^4He molecule; f_s and f_g are the partition functions of the solid-like and gas-like molecules, respectively.

Assuming that ^4He molecules are hard-spheres with diameter d , London (14) was able to derive the kinetic zero-point energy. Thus,

$$K_0 = \frac{151.3d}{(r - 0.8909d)^2(r + 0.7133d)} \text{ cal/mol} \quad [3]$$

in which

$$r = (V/N)^{1/3}$$

and r and d are expressed in angstroms. The partition function f_s is given by

$$f_s = \exp(E_s/RT) \cdot f_{\text{Debye}}^{X_n} \cdot \left[1 + n \frac{V - V_s}{V_s} \exp \left\{ \frac{-aE_s V_s}{(V - V_s)RT} \right\} \right]^{X_n} \quad [4]$$

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E_s , X_n , and f_{Debye} are the sublimation energy of the quasi-lattice, the fraction of normal fluid component, and the Debye partition function (18), respectively. In deriving Eq. 4, we have assumed that the partition function of the solid-like molecules of the superfluid component is unity because the molecules have been considered as ground state molecules. For the fraction X_n , the following empirical formulas (ref. 1, pp. 374–408) are used:

$$X_n = \begin{cases} (T/T_\lambda)^{5.6} & \text{for } T < T_\lambda \\ 1 & \text{for } T \geq T_\lambda \end{cases} \quad [5]$$

in which T_λ is the λ temperature of the liquid. The Debye partition function is given by the relationship

$$\ln f_{\text{Debye}} = \frac{\pi^4}{5} \left(\frac{T}{\theta_D}\right)^3 - 9 \sum_{n=1}^{\infty} \left\{ \frac{1}{n^2} \left(\frac{T}{\theta_D}\right) + \frac{2}{n^3} \left(\frac{T}{\theta_D}\right)^2 + \frac{2}{n^4} \left(\frac{T}{\theta_D}\right)^3 \right\} e^{-n\theta_D/T} \quad [6]$$

in which θ_D is the Debye characteristic temperature. The partition function of an ideal Bose–Einstein gas (ref. 5, pp. 292–299) with spin = 0 is used for the gas-like molecules by treating the molecules as identical independent particles having a symmetrical wave function. Accordingly,

$$\ln f_g = \frac{(2\pi mkT)^{3/2}}{h^3} \frac{V}{N} F_{5/2}(\alpha) + \alpha \quad [7]$$

in which m , k , h , α , and F are the atomic mass of ^4He , Boltzmann's constant, Planck's constant, the chemical potential divided by kT , and the Bose–Einstein integral function (ref. 14, pp. 203–205), respectively. The value of α in Eq. 7 is determined as a function of V and T by the condition prescribing the total number of molecules:

$$N = \frac{(2\pi mkT)^{3/2}}{h^3} V F_{3/2}(\alpha) + \frac{1}{e^\alpha - 1} \cdot \frac{1}{V - V_s} \quad [8]$$

For K_0 , V_s , and E_s in the conventional partition function, the two-fluid concept is applied as follows:

$$K_0 = X_n K_{0n} + X_s K_{0s}, \text{ etc.} \quad [9]$$

in which the subscripts n and s denote the normal fluid and superfluid components, respectively.

The configurational partition function is derived by the Bragg–Williams approximation of order/disorder phase transitions. Just as we picture the ferromagnets as composed of a large number of spin-reversed clusters called domains, so we picture the superfluid He as composed of a large number of He atom clusters called droplets (15). The same mathematical procedure can be used for both systems.

Assuming that there are N lattice sites for N spins, the configurational partition function is given by the following equations:

$$f_{\text{conf}} = W(Q) \cdot \exp \{-E(Q)/kT\} \quad [10]$$

$$W(Q) = N C N_+ = \frac{N!}{\left\{ \frac{N(1+Q)}{2} \right\}! \left\{ \frac{N(1-Q)}{2} \right\}!} \quad [11]$$

$$\begin{aligned} E(Q) &= N_+ V_+ + N_- V_- \\ &= \frac{N}{2} \{ (V_+ + V_-) + (V_+ - V_-) Q \} \\ &= \frac{N}{2} (U_0 - V_0 Q^2). \end{aligned} \quad [12]$$

Here, Q is the long-range order parameter; N_+ and N_- are the

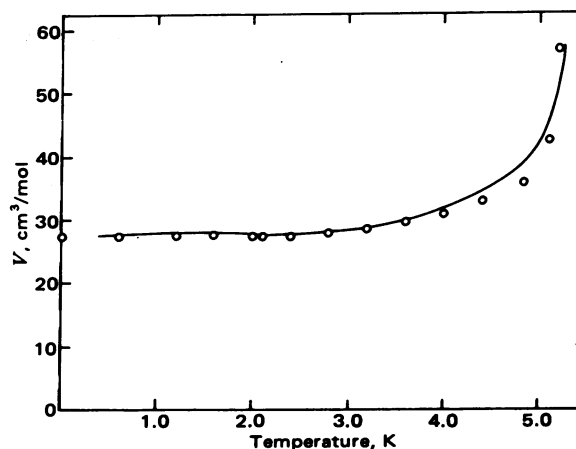


FIG. 1. Molar volume of liquid ^4He as a function of temperature. —, Calculated; O, experimental.

numbers of spins in the up and down directions, respectively. $W(Q)$ is the number of possible ways of obtaining the N_+ state of the spins; $E(Q)$ is the configurational internal energy of the system; V_+ and V_- are potential energies of the up and down directional spins, respectively; U_0 is the energy of the completely disordered state $Q = 0$; $V_- - V_+ = V_0 Q$ is assumed. The order parameter Q is obtained from

$$Q = \tanh \left(\frac{T_\lambda}{T} \right). \quad [13]$$

CALCULATION

For the calculation of thermodynamic properties, the following physical constants are used: $n = 10.38$; $V_s = 23.37 \text{ cm}^3/\text{mol}$; $\theta_D = 20.3 \text{ K}$; $E_s = 41.16 \text{ cal/mol}$ (1 cal = 4.184 joules) for the normal fluid and 42.96 cal/mol for the superfluid; and $d = 2.073 \text{ \AA}$ for normal fluid and 2.121 \AA for superfluid. The thermodynamic properties are obtained by adding the terms corresponding to the conventional and the configurational partition functions. All calculations are performed by using a CYBER-174 computer.

Molar Volume and Vapor Pressure. The Helmholtz free energy is given by $A = -kT \ln f$. If the Helmholtz energy is plotted as a function of volume at constant temperature and a common tangent to the points corresponding to the liquid and vapor phases is drawn, the vapor pressure is given by the common tangent and the abscissas of the two points indicate the respective molar volumes of the liquid and the vapor. In the

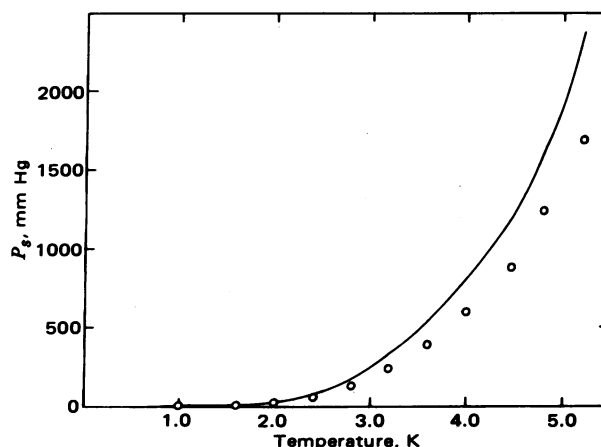


FIG. 2. Vapor pressure of liquid ^4He as a function of temperature. —, Calculated; O, experimental.

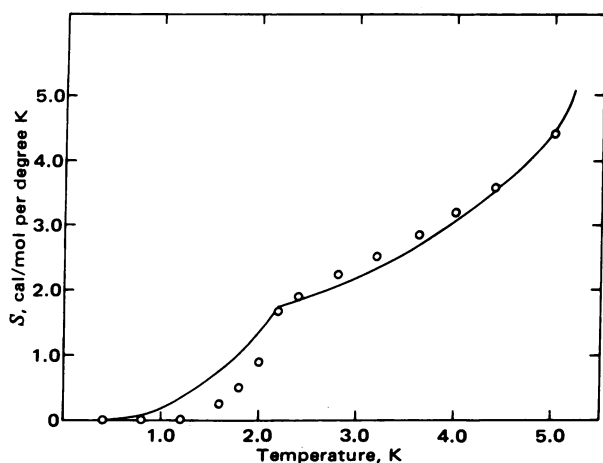


FIG. 3. Molar entropy of liquid ^4He as a function of temperature. —, Calculated; O, experimental.

calculations for He-II, it is assumed that the superfluid component is nonexistent in the vapor phase. The results of calculations are shown in Figs. 1 and 2 where they are compared with the experimental values of molar volume (19) and vapor pressure (20–22). The calculated molar volume exhibits a minimum at T_λ .

Entropy. The entropy is calculated by

$$S = S_{\text{conv}} + S_{\text{conf}} = \left\{ \frac{\partial}{\partial T} (kT \ln f_{\text{conv}}) \right\}_V + Nk \left\{ \ln 2 + \frac{1}{2} (1 + Q) \ln(1 + Q) + \frac{1}{2} (1 - Q) \ln(1 - Q) \right\} \quad [14]$$

in which S_{conv} and S_{conf} are the entropies corresponding to the conventional and configuration partition functions, respectively. The results are compared with the experimental data (23, 24) in Fig. 3. At the λ point, the entropy due to the configurational partition function is about 80% of the total calculated entropy.

Heat Capacities. In order to check on the accuracy of the second derivatives of the partition function, the heat capacities are evaluated. The heat capacity at constant volume and the heat capacity at constant pressure are related to the partition function by the equations

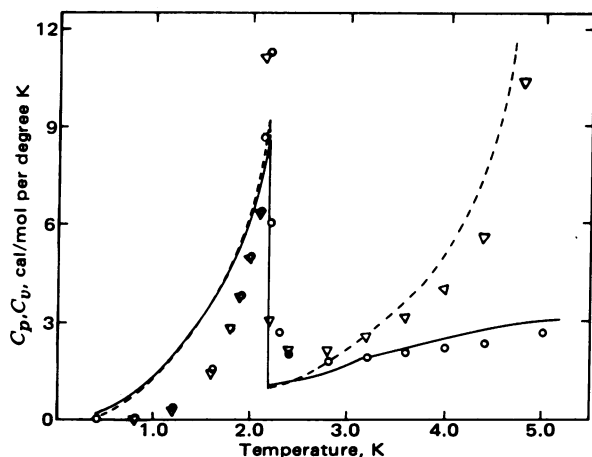


FIG. 4. Heat capacities of liquid ^4He as a function of temperature. —, Calculated C_v ; O, experimental C_v ; ---, calculated C_p ; ▽, experimental C_p .

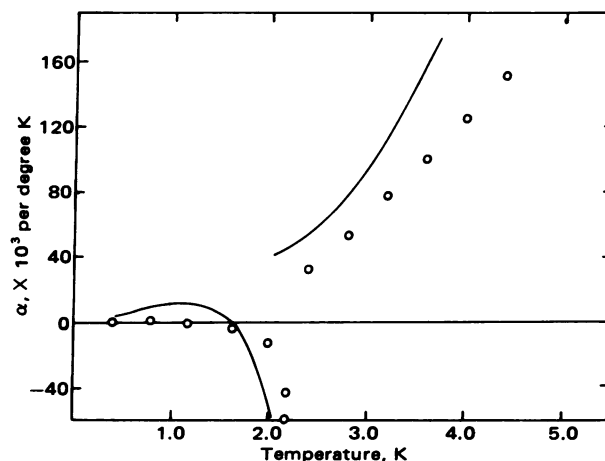


FIG. 5. Thermal expansion coefficient of liquid ^4He as a function of temperature. —, Calculated; O, experimental.

$$C_v = C_{v \text{ conv}} + C_{v \text{ conf}} = \left\{ \frac{\partial}{\partial T} \left(kT^2 \frac{\partial}{\partial T} \ln f_{\text{conv}} \right) \right\}_V - NV_0 Q \left(\frac{\partial Q}{\partial T} \right)_V \quad [15]$$

and

$$C_p = C_v - k \left[\frac{\partial}{\partial T} \left\{ T \left(\frac{\partial}{\partial V} \ln f_{\text{conv}} \right)_T \right\} \right]_V^2 / \left(\frac{\partial^2}{\partial V^2} \ln f_{\text{conv}} \right)_T \quad [16]$$

in which $C_{v \text{ conv}}$ and $C_{v \text{ conf}}$ are the heat capacities at constant volume corresponding to the conventional and configurational partition functions, respectively. In Fig. 4, the calculated results are compared with the experimental data taken from refs. 25 and 26.

Thermal Expansion Coefficient. The thermal expansion coefficient is related to the partition function by

$$\alpha = - \frac{1}{V} \left[\frac{\partial}{\partial T} \left\{ T \left(\frac{\partial}{\partial V} \ln f \right)_T \right\} \right]_V / \left\{ T \left(\frac{\partial^2}{\partial V^2} \ln f \right)_T \right\} \quad [17]$$

The calculated results, together with the experimental values (19), are shown in Fig. 5.

Boiling Point Properties. The boiling point is the temperature at which a common tangent, $-(\partial A / \partial V)_T$, on the two points corresponding to the liquid and vapor volumes yields a slope of 1 atmosphere (1.013×10^5 pascals). This procedure determines the molar volumes and temperature of both liquid and vapor at the boiling point. Only the properties for the liquid are listed in Table 1 because good agreements are to be expected for the vapor.

Critical Constants. The critical temperature T_c , the critical pressure P_c , and the critical volume V_c are calculated from the partition function by using the usual iteration technique,

$$\left(\frac{\partial P}{\partial V} \right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0, \quad [18]$$

in conjunction with the expression $P = -(\partial A / \partial V)_T$. The calculated results are summarized in Table 2 and compared with the experimental values (26).

Table 1. Boiling point properties of liquid ^4He

	T_b , K	V_b , cm ³ /mol
Calculated	3.904	31.61
Observed	4.224	32.02
Error, %	7.6	1.3

Table 2. Critical constants of liquid ^4He

	T_c , K	P_c , mm Hg	V_c , cm^3/mol
Calculated	5.258	2363	57.69
Observed	5.201	1706	57.47
Error, %	1.1	38.5	0.4

Surface Tension. The iteration method developed by Chang *et al.* (27) is used in order to calculate the surface tension. If a simple close-packed structure is assumed, it is expected that each molecule has six nearest neighbors in the same layer, three neighbors below and three above. The sublimation energy E_{st} of a molecule in the i th surface molecular layer is then given by

$$E_{st} = E_s \left(\frac{6}{12} \frac{\rho_i}{\rho_i} + \frac{3}{12} \frac{\rho_{i+1}}{\rho_i} + \frac{3}{12} \frac{\rho_{i-1}}{\rho_i} \right) \quad [19]$$

in which ρ_i , ρ_{i+1} , and ρ_{i-1} are the respective densities of the i th layer and the layers immediately below and above it. When the i th layer is the top layer, the $(i-1)$ th layer is the first gas layer. In this case, one may write

$$\frac{\rho_{i-1}}{\rho_i} = \exp \left\{ - \frac{E_s}{2RT} \left(1 - \frac{T}{T_c} \right) \right\} \quad [20]$$

considering the extrabinding energy of liquid over that of the first gas layer. The corresponding molar volume of the i th layer, V_i , is determined by plotting A_i with E_{st} replacing E_s and by drawing a tangent whose slope is the vapor pressure; then V_i is the volume at the tangential point. In the actual calculations, successive iterations are performed for obtaining V_i and A_i .

The surface tension γ is the excess Gibbs free energy per unit area over that of the bulk liquid. Therefore, the surface tension may be calculated from

$$\gamma = \sum_i (G_i - G_l)(d/V_i) \quad [21]$$

in which $G_i - G_l$ is the difference in Gibbs free energy of the i th surface layer and the bulk liquid, and d becomes $0.9165(V_s/N)^{1/3}$ for a close-packed structure. The calculated results together with the experimental data taken from ref. 28 are given in Fig. 6. The density changes of surface layers at several temperatures are also analyzed in Fig. 7.

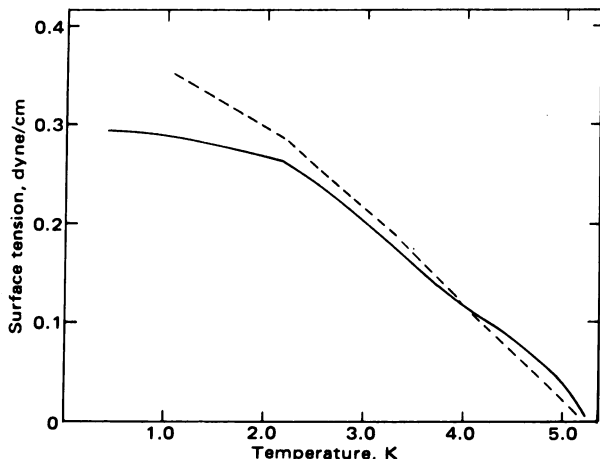


FIG. 6. Surface tension of liquid ^4He as a function of temperature. —, Calculated; ---, experimental.

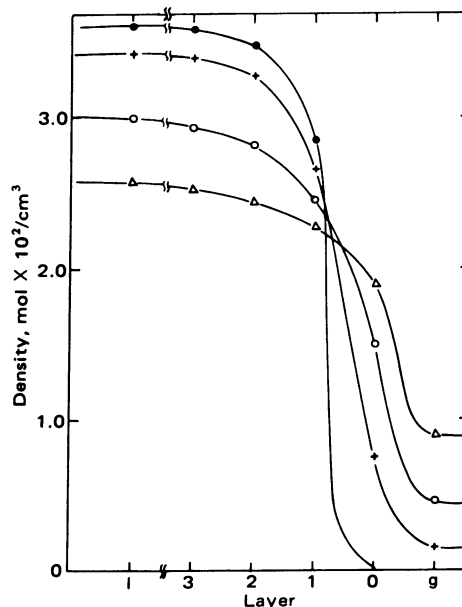


FIG. 7. Density change in going from the liquid phase through the transition layers into the gas phase for ^4He at four temperatures: ●, 0.4 K; +, 3.2 K; ○, 4.2 K; △, 4.8 K.

DISCUSSION

The values of molecular diameter d used in the calculation are a little different from the available data. According to London (14), the value is 2.3 \AA . The other available values (29) of d are 1.48, 2.00, 2.48, and 2.576 \AA from the measurement of molecular refraction, the measurement of gas viscosity, the van der Waals radius, and the Lennard-Jones σ -value, respectively. Hence, the values of d in this work are reasonable. Usually, the values of θ_D for solid-like structures in liquids have been found to be smaller than the values for solids. The θ_D used in the calculation is also slightly less than that for the hcp phase determined experimentally by Gardner *et al.* (30). The values of n usually lie between 10 and 12 (9). Thus, the value $n = 10.3$ is satisfactory. The number of nearest neighbors determined by Henshaw (7, 8) from the neutron diffraction data lies between 8.5 and 9.7 atoms, depending on the methods of analysis. The number from the x-ray measurement by Gorden *et al.* (3, 4) is 10.6 atoms. The value of V_s used in this work is somewhat greater than the molar volume of solid ^4He . In many liquids, the molar volume of the solid-like molecules is taken as greater than the molar volume of the solid due to the structural changes upon melting (9–11). The value $a = 12.0$ is much greater than the value $a = 0.0058$ (9) for simple liquids. Because the value of a is very large, the positional degeneracy term gives only a small contribution to the partition function. It is considered that the jumping motion of molecules into vacancies is not likely compared with the kinetic zero-point motion. In this respect, one may consider reasonably that the value of a is very large compared with the values for other simple liquids.

The significant structure theory of liquids is here applied to the quantum liquid ^4He , by using the quantum statistical partition function of gas-like and solid-like molecules and taking into account the kinetic zero-point energy of the molecules. The agreement between the calculated and observed values of thermodynamic properties is quite satisfactory. The theory can be applied down to near absolute zero very well because we have chosen $d = 2.121 \text{ \AA}$ and $E_s = 42.96 \text{ cal/mol}$ for the superfluid component so that the energy minimum $A_0 = -14.3 \text{ cal/mol}$ occurs for the experimental molar volume (19) $V_0 = 27.58 \text{ cm}^3/\text{mol}$ extrapolated to 0 K. However, at near absolute

zero, where the vapor pressure is less than 10^{-8} mm Hg, very accurate calculations are required for obtaining the molar volumes of liquid and vapor and the vapor pressure. Such calculations are not carried out at temperatures below 0.4 K.

The discrepancies between the calculated and experimental values of S , C_v , and C_p in the λ transition region are mostly due to the oversimplification of using the order/disorder phase transition of the Bragg-Williams approximation. Better numerical results should be obtainable by applying the more advanced treatments of order/disorder transitions such as the Kirkwood method (31) or the Frankel model (15).

Fig. 6 shows that there is a remarkable agreement between the calculated and observed surface tension above the λ point. The discrepancy at the lower temperatures arises at least partly from the assumption of a close-packing lattice structure of the surface layers. Some structural change is expected during the formation of the supersurface film (14) from bulk liquid ^4He below the λ point. Furthermore, the calculation has shown that only the top two of three molecular layers of the liquid contribute to the surface tension at 3 K. At higher temperatures, more layers contribute significantly—i.e., the transition zone between the gas and liquid phases becomes broader with increasing temperature.

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