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A CONSISTENT-VIBRATIONS MODEL OF THE
INTERNAL DYNAMICS OF LIQUID HYDROGEN

by

H. G. Carter
General Dynamics/Port Worth
(NARP)
Contract AF 29(601)-6213

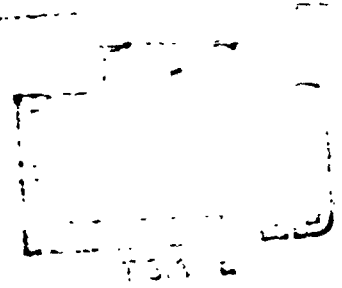
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Research and Technology Division
AIR FORCE WEAPONS LABORATORY
Air Force Systems Command
Kirtland Air Force Base
New Mexico

March 1965



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FOREWORD

The work reported in this document was performed at the Nuclear Aerospace Research Facility, General Dynamics/Port Worth, under Contract AF 29(601)-6213, Project 6773, Task 677301, Program Element 6.54.02.12.4. The document was submitted in March 1965 in accordance with Item 5 of the statement of work (FZN-2959-A), covering the period 1 October 1963 through 30 September 1964. An associated report, WL TR-64-161 (General Dynamics/Port Worth Report FZK-199), is based upon the work reported herein.

The Air Force project monitor is Lt R. G. Hawkins, AFWL (VLEB-2). The author wishes to express his full appreciation to J. B. Eggen for his assistance in the machine programming and in the analysis of calculated results.

The contractor's report number is FZK-197.

This technical report has been reviewed and is approved.



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ABSTRACT

A model describing the internal dynamics of a nonassociated liquid has been constructed for use in the calculation of cold-neutron scattering cross sections and free-radical recombination rates in liquid hydrogen. The proposed model assumes that the specification of a given temperature and density implies a quiescent state in which each molecule vibrates with random phase in a field set up by the sum of the position probability densities of its neighbors, the central sites of which comprise a close-packed quasi-lattice. A computer program has been written to calculate the consistent vibration frequency, the molecular well depth, the internal energy, the entropy, and the free energy of a liquid with a given temperature and density and with known Lennard-Jones parameters of the intermolecular interaction. Application of the program to the case of liquid hydrogen at points on the P-V-T surface ranging from 20° to 28°K along the saturation line has given predictions of thermodynamic properties which are in good agreement with experimental data. It is tentatively concluded that the model anticipates the most significant general features of motion in the liquid and may be implemented in calculations of cross sections and recombination rates which are dependent on the details of the internal dynamics and microscopic structure.

CONTENTS

	<u>Page</u>
1. INTRODUCTION	1
2. THE PROPOSED LIQUID MODEL	4
2.1 Description and Assumptions	4
2.2 Consistent Frequency and Well Depth of the Quiescent Liquid	8
2.3 Internal Energy and Entropy of the Quiescent Liquid	22
2.4 Acoustical Effects	25
2.5 Hole Concentration and the Approach to Equilibrium	34
2.6 Summary of Expressions for the Equilibrium State	35
3. THE COMPUTER PROGRAM	40
3.1 Procedure	40
3.2 Input and Output	41
4. APPLICATION TO LIQUID HYDROGEN	44
4.1 Liquid Structure and Intermolecular Potential	44
4.2 Results and Comparison with Experimental Data	45
5. RESULTS AND CONCLUSIONS	52
REFERENCES	53
DISTRIBUTION	55

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Geometry Associated with a Central Site at 0 and a Neighbor Shell of Radius a_i	19
2.	Calculated and Empirical Internal Energy of Liquid Hydrogen Along the Saturation Line	50
3.	Calculated and Empirical Entropy of Liquid Hydrogen Along the Saturation Line	51

LIST OF TABLES

1.	Neighbor-Site Distribution for Four Types of Lattice	9
2.	T-T _h Output for the State of Liquid Para-Hydrogen	46
3.	Summary of Results for Para-Hydrogen	48

1. INTRODUCTION

In the design of hydrogen-propelled, nuclear-powered rocket systems, two independent problems are encountered which require a mathematical description of the dynamics and distribution of molecules in liquid hydrogen for their solution. First, it has been shown (Ref. 1) that the molecular species produced by the attenuation of neutrons and gamma rays in liquid hydrogen may not immediately undergo the external reactions leading to a return to the H_2 ground state. The potential energy that is stored temporarily in the formation of radiation products such as H , H_2^+ and H_2^* (vibrationally or rotationally excited molecules) may not appear as heat for several seconds, even assuming that the mobility of such products in the liquid is as high as in a gas of the same density. Since a large fraction of the radiation energy goes initially into the formation of such species and since the most intensely irradiated portion of the liquid propellant is generally nearest the exit of the storage tank, it is possible that the delay in equipartition will effectively reduce the amount of heat production while the rocket is under power.

When the lattice structure of liquid hydrogen is taken into account, it may be found that the inhibition of mobility

associated with molecular ordering and cryogenic temperature results in a delay in the equipartition of energy that is much longer than seconds. In the case of one particular kind of rotationally excited molecule, namely, ortho-hydrogen, the return to the para-hydrogen ground state is known to require months. The evolution of heat over a long period presents a problem in space vehicles that must retain part of the irradiated propellant for future operations.

A second problem requiring the use of a liquid-hydrogen model is the production of hydrogen-capture gamma rays by cold-neutron absorption. Owing to interference effects, the neutron scattering cross section of the free hydrogen molecule falls off drastically below 0.023 eV (Ref. 2). Under the assumption that the cross section of molecules in the liquid is the same as for free molecules, the cold-neutron mean free path in the liquid becomes comparable to the fast-neutron penetration distance, and the probability of leakage from the propellant tank may become greater than the probability of neutron capture. This establishes the importance of cold-neutron transport, since hydrogen-capture gammas are important from both the heating and the dose-rate standpoints. It follows that the influence of liquid forces on the cold-neutron scattering cross section, an effect which

is sure to be significant but is at present of unknown magnitude, has an important bearing on shield and pressure-vessel design.

The treatment of the two problems cited above requires a mathematical description of both the neighbor distributions for a typical molecule and the state of motion (or possible states of motion) of the molecule itself. With this information the magnitude of the energy barriers which inhibit the free migration of radiation-induced molecular species can be determined and the effect of liquid binding forces and lattice structure on the molecular cross section can be calculated.

The present report describes a model for the internal dynamics and microscopic structure of a nonassociated liquid which will lend itself to calculations of the types required in the consideration of an irradiated hydrogen propellant. Evidence for the validity of the model is given in the form of a comparison between predicted thermodynamic properties, calculated with the aid of an IBM 7090 computer, and published experimental results. Applications of the model to the problem of cold-neutron scattering and recombination rates are the subjects of another NARF report (Ref. 3).

2. THE PROPOSED LIQUID MODEL

2.1 Description and Assumptions

Any theory of the liquid state with a claim to rigor must be derived from a general statistical mechanics formulation and must be amenable to the inclusion of quantum mechanical effects. In such a first-principle approach, exemplified in the nonquantum-mechanical case by the work of Kirkwood (Ref. 4), the structure of the liquid is determined from the free interactions of many molecules and is not assumed to be locally similar to that of a corresponding solid. However, the integral equations which result are difficult to solve without the introduction of mathematical approximations that tend to offset the rigor of the physical foundation. Hence, nonrigorous models based on a prior assumption of a "quasi-crystalline" liquid structure continue to be used because of their heuristic value in describing the general features of internal liquid motion and because of their adaptability to the correlation of experimental data. It is a model of this sort that is introduced here as a basis for specialized types of calculations.

In the theory of Lennard-Jones and Devonshire (Refs. 5 and 6) each molecule in a liquid is assumed to move in the intermolecular potential field that would be set up if its

nearest neighbors were smeared uniformly over a spherical surface passing through their central lattice sites. An extended form of the L-J-D model takes vacancies into account by minimizing the Helmholtz free energy. However, the ratios of vacancies to molecules predicted in this way are found to be much smaller than those obtained from X-ray determinations of the liquid structure (Refs. 7 and 8). It is inferred that the latter model cannot be relied upon to provide a liquid description adequate for the calculations of quantities which are dependent on the details of the internal dynamics and microscopic structure. The same conclusion is reached in regard to the currently eminent "significant structure" theory (Ref. 9), which provides good thermodynamic results but which relies on the use of an empirical Debye temperature and prescribes no method of determining the potential energy of the quasi-lattice at points off the vapor-point line.

The object of the present effort is to adumbrate a tractable liquid model which is more or less in the spirit of the L-J-D model but which takes into account both neighbor displacements and quantum mechanical effects. As in the L-J-D model, a specific quasi-crystalline structure with local order extending out to the third or fourth nearest neighbor is assumed. However, in the method offered here the motion of each molecule

is determined by the state of motion of its neighbor, so that factors such as the change in molecular environment with temperature variation at constant density are taken into account.

The particulars of the present model will be formulated on the basis of the following set of assumptions:

1. The liquid structure is quasi-crystalline, with local order of central sites extending for at least several molecular separations.
2. At constant temperature and density, increases in the vacancy fraction (hole concentration) result in a scale compression of the lattice dimensions so that the form of the site distribution is preserved with none of the molecules occupying off-site positions.
3. The interactions are due to central, isotropic, two-molecule forces (thus, the model is limited to "nonassociated" liquids).
4. Each molecule moves quantum-mechanically about its own central site: in the vicinity of this site the molecule moves "harmonically" in discrete energy states characteristic of a three-dimensional harmonic oscillator.
5. Each molecule vibrates in a field set up by a "molecular cloud" defined by the sum of the position probability densities of its neighbors that are averaged over all modes of vibration; the "consistent" frequency thus defined is common to all of the molecules, as in the Einstein model, but is, in this case, determined uniquely by the common neighbor environment.
6. The foregoing assumptions define a quiescent liquid in which there is no correlation

between the phases of vibration of neighboring molecules.

7. The quiescent system thus defined is disturbed by longitudinal acoustical waves with a velocity determined by the "consistent" frequency of vibration and with wavelengths restricted to integral multiples of twice the lattice dimensions.
8. Owing to absorption, only those acoustical waves are possible whose energies are less than that required for the excitation of "consistent" quantum levels in the quiescent liquid; the "ground state" energies of all such waves taken together are identified with those of the stationary, consistently vibrating modes.
9. For constant temperature and density, the hole concentration tends toward a value corresponding to the lowest Helmholtz free energy; the hole concentration is the only significant independent variable in the minimization of the Helmholtz free energy.

Each of the above assumptions can be supported by arguments based either on empirical considerations or on thermodynamical verities. However, the ultimate argument for such a construct rests in its pragmatic validity, i.e., its general utility in the satisfactory prediction of empirical data. Hence, the above assumptions will be incorporated into mathematical statements without individual analysis, and the results of a subsequent application to the case of liquid hydrogen will, for the present, be taken as an indication of their collective validity.

2.2 Consistent Frequency and Well Depth of the Quiescent Liquid

According to Assumption 1, the neighbor sites of each molecule lie on concentric spherical surfaces (shells), with the number of sites per shell determined by the type of quasi-lattice. Let r_i and z_i be the radius and number of neighboring molecules, respectively, corresponding to the i^{th} shell.

Let the density of the liquid be ρ and let the hole concentration, defined as the fraction of sites which are unoccupied, be f . Then, according to Assumption 2, r_i is proportional to $[\rho/(1-f)]^{-1/3}$ and z_i is proportional to $(1-f)$. The neighbor-site distributions out to the fourth neighbor shell have been derived for four types of lattice structure and are given in Table 1. The neighbor-shell radii computed from the table are in cm when M is the molecular mass in amu and N_A is Avogadro's number.

As a matter of mathematical convenience, the approximation is made (as in the L-J-D method) that the central neighbor sites are "smeared" over the neighbor shell; thus the environment of each molecule is formed by a radially symmetric cloud made up of contributions from the stationary wave functions of various neighbor molecules whose central sites are smeared over the shells to which they are attached. Figure 1 shows the geometry associated with a central site at 0 and a neighbor

Table 1

NEIGHBOR-SITE DISTRIBUTION FOR FOUR TYPES OF LATTICE

Simple Cubic

i	1	2	3	4
z_i	$6(1-f)$	$12(1-f)$	$8(1-f)$	$6(1-f)$
a_i	$\left[\frac{M}{N_A} \right]^{1/3} \left[\frac{\rho}{1-f} \right]^{-1/3}$	$\sqrt{2} a_1$	$\sqrt{3} a_1$	$2 a_1$

Body-Centered Cubic

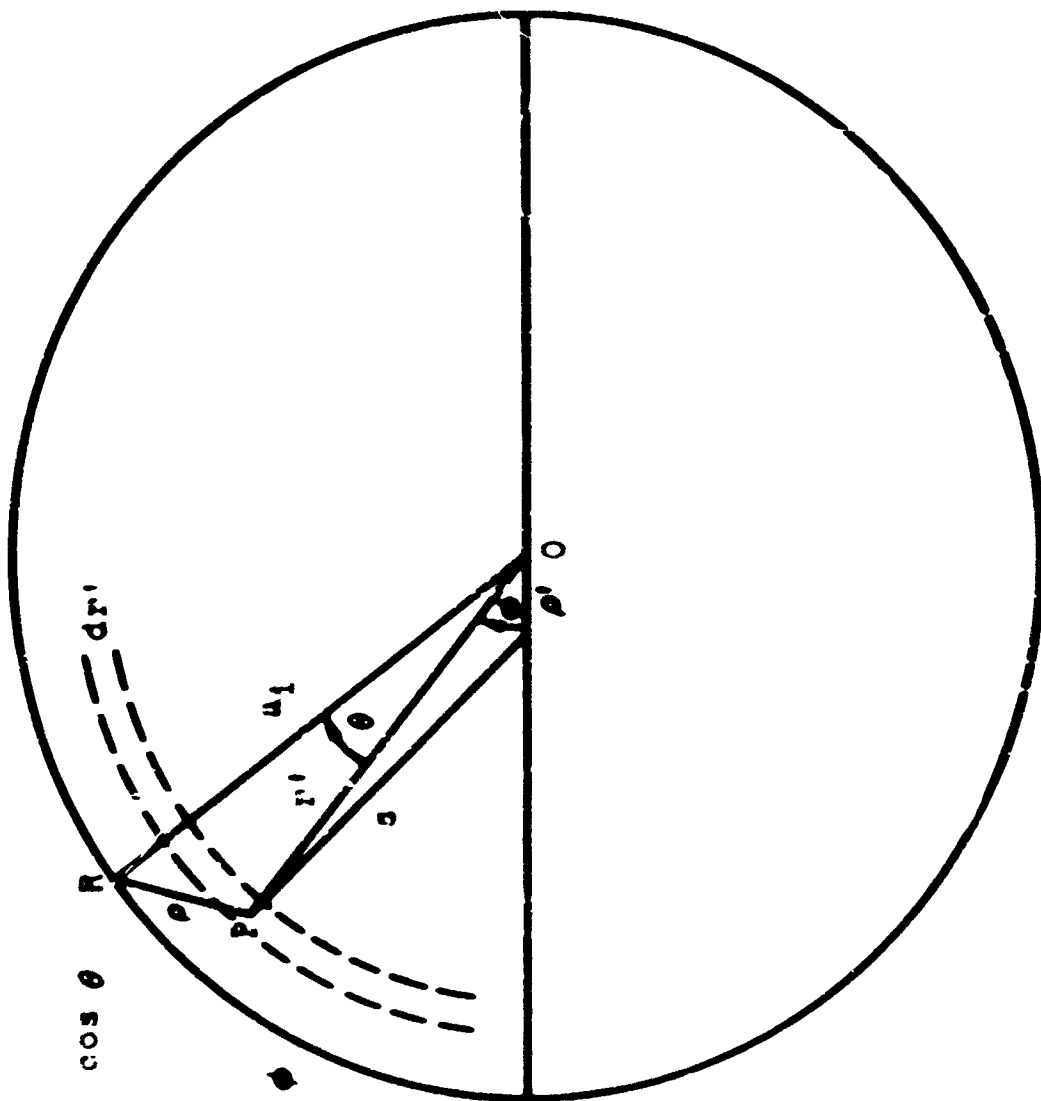
i	1	2	3	4
z_i	$8(1-f)$	$6(1-f)$	$12(1-f)$	$24(1-f)$
a_i	$\left[\frac{3}{4} \left(\frac{M}{N_A} \right) \right]^{1/3} \left[\frac{\rho}{1-f} \right]^{-1/3}$	$\sqrt{\frac{4}{3}} a_1$	$2 \sqrt{\frac{2}{3}} a_1$	$\sqrt{\frac{11}{3}} a_1$

Face-Centered Cubic (Close-Packed Cubic)

i	1	2	3	4
z_i	$12(1-f)$	$6(1-f)$	$24(1-f)$	$12(1-f)$
a_i	$\left[\sqrt{2} \frac{M}{N_A} \right]^{1/3} \left[\frac{\rho}{1-f} \right]^{-1/3}$	$\sqrt{2} a_1$	$\sqrt{3} a_1$	$2 a_1$

Close-Packed Hexagonal

i	1	2	3	4
z_i	$12(1-f)$	$6(1-f)$	$2(1-f)$	$18(1-f)$
a_i	$\left[\sqrt{2} \frac{M}{N_A} \right]^{1/3} \left[\frac{\rho}{1-f} \right]^{-1/3}$	$\sqrt{2} a_1$	$2 \sqrt{\frac{2}{3}} a_1$	$\sqrt{3} a_1$



$$\rho^2 = a_1^2 + r_1^2 - 2a_1 r_1 \cos \theta$$

$$s^2 = r_1^2 + \rho^2 - 2r_1 \rho \cos \phi$$

Figure 1 Geometry Associated with a Central Site a_1 , ϕ and a Neighbor Shell of Radius a_1

shell of radius a_i . The associated position probability density at a distance r' from 0 is designated as $z_i(r')$. Then for a small displacement ρ' of the central molecule, the potential energy due to molecules in a shell of thickness dr' associated with the i^{th} neighbor shell is

$$\phi_i(\rho', r') dr' = z_i(r') dr' \int_{\theta=0}^{\pi} v(s) 2\pi r'^2 \sin\theta d\theta \quad (2-1)$$

where

$$s = \sqrt{r'^2 + a_i^2 - 2r'a_i \cos\theta} \quad (2-2)$$

and where $v(s)$ is the intermolecular interaction. In most cases of interest $v(s)$ is expressible in the Lennard-Jones form, viz.,

$$v(r) = -v_c r^{-6} + v_c r^{-12} \quad (2-3)$$

Carrying out the integration, expanding the result in terms of ρ' , and discarding terms of order higher than ρ'^2 (by Assumption 4) gives

$$\phi_i(\rho', r') dr' = 4\pi r'^2 z_i(r') dr' \left\{ \left[-\frac{v_c}{6} r'^{-6} + \frac{v_c}{6} r'^{-12} \right] + \left[\frac{5v_c}{3} r'^{-9} + 22\frac{v_c}{3} r'^{-14} \right] \rho'^2 \right\} \quad (2-4)$$

Differentiation with respect to ρ' gives the restoring force per unit central molecule per unit displacement due to the

molecules in the differential shell between r' and dr' :

$$\begin{aligned} K_i(r')dr' &= \left[\frac{\partial \theta_i(\rho', r')}{\partial \rho'} \right] / \rho' \\ &= 8\pi r'^2 z_i(r') dr' \left[5v_c r'^{-8} + 22v_c r'^{-14} \right] \end{aligned} \quad (2-5)$$

Finally, the "restoring coefficient" due to all of the neighbors around a central molecule is

$$K_R = \sum_i \int K_i(r') dr' \quad (2-6)$$

All that is needed to evaluate the restoring coefficient, and hence the frequency imposed on a central molecule by its neighbors in their own quantum mechanical distributions, is an expression for $z_i(r')$, the radial density associated with neighbors whose central sites lie on the i^{th} cell. This is obtained by integrating the density contributions from all neighbors with central sites smeared on the i^{th} shell at an arbitrary point in the vicinity of the shell. Such an integration requires the knowledge of the position probability density of neighbors about their central sites, which in turn depends on the "restoring coefficient" (or classical frequency) of the neighbors. Let $\rho^2(\rho)$ represent the position probability density, averaged over all modes of vibration, of a neighbor molecule at a distance ρ (Fig. 1)

from its central site. (ρ will not be confused with the liquid density, designated by the same symbol. An i subscript to ρ is indicated but is omitted for convenience.) $\rho^2(\rho)$ is equal to the sum of contributions $\rho_j^2(\rho)$ corresponding to energy state Σ_j weighted by the population fraction of such states. Solution of the Schrödinger equation with a three-dimensional harmonic potential gives for the normalized wave function of a state characterized by the quantum numbers l , π , and n

$$\psi_{l,\pi,n}(x,y,z) = \sum_{l,\pi,n} N \sum_{l,\pi,n} H_l(ax) H_\pi(ay) H_n(az) e^{-1/2a^2(x^2+y^2+z^2)} \quad (2-7)$$

where separation into the Hermite polynomials H_n has easily been effected by the use of Cartesian coordinates defined by

$$\rho^2 = x^2 + y^2 + z^2 \quad (2-8)$$

The parameter a is related to the stiffness coefficient K_x of the neighbor molecules by

$$K_x = \hbar^2 a^2 / M k \quad (2-9)$$

where M is the molecular mass and k is the Boltzmann constant;

the normalization factors are given by

$$N_n = \left(\frac{a^3}{\pi^{1/2} 2^n n!} \right) \quad (2-10)$$

For a molecule in the j^{th} energy state

$$l+r+n = j \quad (2-11)$$

and the normalized position probability density is

$$\rho_j^2(\rho) = \frac{1}{g_j} \sum_{\substack{l,r,n \\ l+r+n=j}} U_{l,r,n}^2 \quad (2-12)$$

where

$$g_j = (1/2)(j+1)(j+2) \quad (2-13)$$

is the degeneracy (or number of terms in the summation) for a three-dimensional harmonic oscillator. Then, if F_j is the fraction of molecules in the j^{th} energy state, the average position probability density is

$$\bar{\rho}^2(\rho) = \sum_j \frac{F_j}{g_j} \sum_{l,r,n} U_{l,r,n}^2 \quad (2-14)$$

where for a temperature T

$$F_j = (j+1)(j+2)e^{-E_j/kT} / \sum_j (j+1)(j+2)e^{-E_j/kT} \quad (2-15)$$

The energy levels E_j are given by

$$E_j = \left(\frac{3}{2} + j \right) k\theta \quad (2-16)$$

where θ is uniquely related to a by

$$\theta = h^2 a^2 / 2mk \quad (2-17)$$

The quantity θ is related to the classical frequency ν by

$$\theta = \frac{h\nu}{k} \quad (2-18)$$

If all of the molecules vibrate with frequency ν , then θ may be described as the characteristic (or "Einstein") temperature of the system. In terms of θ ,

$$\begin{aligned} F_j &= (j+1)(j+2)e^{-j\theta/T} / \sum_j (j+1)(j+2)e^{-j\theta/T} \\ &= \frac{1}{2} (j+1)(j+2)e^{-j\theta/T} (1 - e^{-\theta/T})^{-3} \end{aligned} \quad (2-19)$$

Let

$$u = e^{-\theta/T} \quad (2-20)$$

Then

$$F_j / g_j = u^j (1-u)^3 \quad (2-21)$$

and

$$\begin{aligned} \psi^2(c) &= \frac{a^3}{\pi^{3/2}} e^{-a^2 \theta^2} (1-u)^3 \sum_j u^j \sum_{l,m,n} \frac{H_l^2(ax)}{2^{l+l}} \\ &\cdot \frac{H_m^2(aY)}{2^m m!} \frac{H_n^2(az)}{2^n n!} \end{aligned} \quad (2-22)$$

If m and n are fixed in the second summation so that $l = j - m - n$, then

$$\begin{aligned} \psi^2(\rho) &= \frac{a^3}{r^{3/2}} e^{-a^2 \rho^2} (1-\omega)^3 \sum_j \frac{H_m^2(a\gamma)}{2^m m!} \frac{H_n^2(az)}{2^n n!} \\ &\quad \cdot \sum_{j=m+n}^{\infty} \omega^j \frac{H_{j-m-n}^2(ax)}{2^{j-m-n} (j-m-n)!} \\ &= \frac{a^3}{r^{3/2}} e^{-a^2 \rho^2} (1-\omega)^3 \sum_j \frac{H_m^2(a\gamma)}{2^m m!} \frac{H_n^2(az)}{2^n n!} \sum_{l=0}^{\infty} \omega^{l+m+n} \frac{H_l^2(ax)}{2^l l!} \end{aligned} \quad (2-23)$$

$$\begin{aligned} &= \frac{a^3}{r^{3/2}} e^{-a^2 \rho^2} (1-\omega)^3 \sum_{m,n} \omega^{m+n} \frac{H_m^2(a\gamma)}{2^m m!} \frac{H_n^2(az)}{2^n n!} \\ &\quad \cdot \sum_{l=0}^{\infty} \left(\frac{\omega}{2}\right)^l \frac{H_l^2(ax)}{l!} \end{aligned} \quad (2-24)$$

Application of Mehler's formula on Hermite polynomials (Ref. 10) gives

$$\begin{aligned} \psi^2(\rho) &= \frac{a^3}{r^{3/2}} e^{-a^2 \rho^2} (1-\omega)^3 (1-\omega^2)^{-1/2} \exp\left[\frac{2a^2 x^2 \omega - 2a^2 x^2 \omega^2}{1-\omega^2}\right] \\ &\quad \cdot \sum_{m,n} \omega^{m+n} \frac{H_m^2(a\gamma)}{2^m m!} \frac{H_n^2(az)}{2^n n!} \end{aligned}$$

(Equation continued on next page)

$$\begin{aligned}
&= \frac{\alpha^3}{\pi^{3/2}} e^{-\alpha^2 \rho^2} (1-u)^3 (1-u^2)^{-1/2} \exp\left[\left(\frac{u}{1+u}\right) 2\alpha^2 x^2\right] \sum_n u^n \frac{H_n^2(\alpha z)}{2^n n!} \\
&\quad \cdot \sum_{n=0}^{\infty} \left(\frac{u}{2}\right)^n \frac{H_n^2(\alpha y)}{n!} \\
&= \frac{\alpha^3}{\pi^{3/2}} e^{-\alpha^2 \rho^2} (1-u)^3 (1-u^2)^{-1/2} \exp\left[\left(\frac{u}{1+u}\right) 2\alpha^2 (x^2 + y^2)\right] \\
&\quad \cdot \sum_{n=0}^{\infty} \left(\frac{u}{2}\right)^n \frac{H_n^2(\alpha z)}{n!} \\
&= \frac{\alpha^3}{\pi^{3/2}} (1-u)^3 (1-u^2)^{-3/2} e^{-\alpha^2 \rho^2} \exp\left[\left(\frac{u}{1+u}\right) 2\alpha^2 \rho^2\right] \quad (2-25)
\end{aligned}$$

Thus, the position probability density of a neighbor molecule with a classical frequency defined by α , averaged all modes of vibrations, is simply

$$\psi^2(\rho) = \pi^{-3/2} \lambda^3 e^{-\lambda^2 \rho^2} \quad (2-26)$$

where

$$\lambda^2 = \left(\frac{1-u}{1+u}\right) \alpha^2 \quad (2-27)$$

The radial density distribution around a central molecule can now be calculated from Equation 2-26. Reference to Figure 1 shows that the density due to the i^{th} shell at a point P which

is located a distance r' from 0 is

$$z_i(r') = \frac{z_i}{4va_i^2} \int_0^\pi v_i^2 [\rho(\theta, r')] 2va_i^2 \sin \theta d\theta$$

$$= \frac{1}{2} \int_0^\pi v_i^2 [\rho(\theta, r')] \sin \theta d\theta \quad (2-28)$$

where

$$\rho = \sqrt{a_i^2 + r'^2 - 2a_i r' \cos \theta} \quad (2-29)$$

By setting

$$t = \rho^2$$

$$z = \left[\frac{1}{2} z_i \left(\frac{v_i^{-3/2}}{2a_i r'} \right) \lambda^3 \right] \int_{(a_i - r')^2}^{(a_i + r')^2} e^{-\lambda^2 t} dt \quad (2-30)$$

$$= - \left[\frac{1}{2} z_i \left(\frac{v_i^{-3/2}}{2a_i r'} \right) \lambda \right] \left\{ \exp \left[-\lambda^2 (a_i + r')^2 \right] - \exp \left[-\lambda^2 (a_i - r')^2 \right] \right\} \quad (2-31)$$

it can easily be shown that the first item in Equation 2-31

is negligible for all cases of interest. Hence

$$z_i(r') = v_i^{-3/2} \left(\frac{z_i}{4a_i r'} \right) \lambda \exp \left[-\lambda^2 (a_i - r')^2 \right] \quad (2-32)$$

The combination of Equation 2-5, Equation 2-32, and Equation 2-6

gives for the "stiffness coefficient" of a central molecule

$$K_R = \sum_i z_i \left[a_i^{-8} k_a(\gamma_i) + a_i^{-14} k_r(\gamma_i) \right] \quad (2-33)$$

where

$$v_i = \lambda a_i = \left[\frac{1 - \exp(-\theta/T)}{1 + \exp(-\theta/T)} \right]^{1/2} a_i \quad (2-34)$$

$$k_a(v_i) = -5v_c \left(\frac{2}{\sqrt{v}} \right) v_i^7 \int_{L(v_i)}^{\infty} u^{-7} e^{-(v_i-u)^2} du \quad (2-35)$$

$$k_r(v_i) = 22v_c \left(\frac{2}{\sqrt{v}} \right) v_i^{13} \int_{L(v_i)}^{\infty} u^{-13} e^{-(v_i-u)^2} du \quad (2-36)$$

and where $u = \lambda r'$. $L(v_i)$ is a suitably chosen lower limit which must be greater than zero owing to the error in the neighbor wave functions, assumed to be harmonic, at points distant from the central neighbor sites.

The well depth of the central molecule, ψ , is calculated in analogy to K_R , using Equation 2-4 with ρ' set equal to zero. Multiplying the result by Avogadro's number gives the "molar well depth," which turns out to be

$$W = \sum_i z_i \left[a_i^{-6} u_a(v_i) + a_i^{-12} u_r(v_i) \right] \quad (2-37)$$

where

$$u_a(v_i) = -\frac{5}{A} v_c \left(\frac{1}{\sqrt{v}} \right) v_i^5 \int_{L(v_i)}^{\infty} u^{-5} e^{-(v_i-u)^2} du \quad (2-38)$$

and

$$u_r(r_i) = -\frac{1}{A^2} \left(\frac{1}{r} \right) r_i \int_{L(r_i)}^{\infty} u^{-11} e^{-|r_i-u|^2} du \quad (2-39)$$

The integrals in Equation 2-35, Equation 2-36, Equation 2-38, and Equation 2-39 become infinite if $L(r_i)$ is chosen to be zero. This is due to the fact that the neighbor wave functions, which in keeping with Assumption 4 are harmonic near the neighbor shell, are finite even at the site of the central molecule. The actual neighbor wave functions, of course, must vanish at this point. In practice, as long as Assumption 4 holds, this effect creates no difficulty. It is found that all of the significant contributions to k_a , k_r , u_a , and u_r come from portions of the neighbor distributions which are relatively close to the neighbor shell and far from the central site. In all realistic cases the contributions decrease rapidly with decreasing $u(=r')$, with a large portion of the space inside the neighbor shell contributing a negligible amount to the integral. A minimum is eventually reached after which the contributions increase drastically with decreasing r' . Assumption 4 implies that the harmonic wave functions are accurate down to values of r' corresponding to negligible contributions to the integrals. Hence, for the sake of definiteness, $L(r_i)$ can be defined as the largest of the four values

of u corresponding to the minima of the integrands in Equation 2-35, Equation 2-36, Equation 2-38, and Equation 2-39. The lower limit is thus defined as

$$L(\gamma_i) = \frac{1}{2} \left[\gamma_i - \sqrt{\gamma_i^2 - 26} \right] \quad (2-40)$$

The salient feature of the present model is the requirement that Assumption 5 be satisfied; that is, the frequency at which all the neighbors of a central molecule vibrate must correspond to a density distribution which imposes that same frequency on the central molecule. Let the "stiffness coefficient" implicit in a frequency of neighbor vibration ν (uniquely related to α through Equation 2-17 and Equation 2-18) be

$$K_N = h^2 \alpha^4 / M \quad (2-40A)$$

Then the state of the quiescent liquid is completely defined by a numerical determination of α such that

$$K_N = K_R \quad (2-41)$$

The value of α for which this condition is satisfied may be defined as the consistent-vibrations parameter, α_c . Once α_c has been determined by using trial values of α in the evaluation of Equations 2-33 and 2-40, the well depth can be computed by use of 2-37. Expressions for the remaining

quantities which are required in the evaluation of thermodynamic properties according to the present model are derived below.

2.3 Internal Energy and Entropy of the Quiescent Liquid

In a system of N molecules the total energy of vibration (including the "zero-point" energy) is

$$E = N \sum_{j=0}^{\infty} F_j E_j \quad (2-42)$$

where E_j and F_j are given by Equation 2-16 and Equation 2-19, respectively. A series identity gives for one mole of liquid ($N=N_A$)

$$E = RV(\theta, T) \quad (2-43)$$

where R is the universal gas constant and where

$$V(\theta, T) = 3\theta \left[\frac{1}{2} + \left(e^{\theta/T} - 1 \right)^{-1} \right] \quad (2-44)$$

In the present mode, θ is, of course, computed by substituting the consistent α , α_c , into Equation 2-17.

If the liquid were composed of N stationary molecules confined to their central lattice sites by wells of depth u , the internal energy of the system would be $(1/2) Nu$. This result follows from the fact that the energy which belongs to each molecule uniquely is only $\frac{1}{2} u$, the remaining half figuring into the potential energies of neighboring molecules.

In other words, when one adds up the potential energy of the system, the interaction between each pair should be counted only once. Hence, the molar internal energy of the quiescent liquid is

$$U_2 = \frac{1}{2} [U + NV(\phi, r)] \quad (2-45)$$

The entropy of a lattice composed of N harmonically bound molecules and n vacancies is given by

$$S_L = S_c + S_t \quad (2-46)$$

where S_c and S_t are the configurational and thermal entropies, respectively. According to the Boltzmann postulate these are given by

$$S_c = k \ln W_c \quad (2-47)$$

and

$$S_t = k \ln \Omega_t \quad (2-48)$$

where W_c is the number of distinguishable ways that the N molecule may occupy to $N+n$ lattice sites and Ω_t is the number of distinguishable ways that the N molecules may populate the permissible quantum levels in a system of temperature T . Thus, Ω_c is the number of ways that n identical pegs can occupy $N+n$ holes, namely,

$$W_c = \frac{(N+n)!}{N!n!} \quad (2-49)$$

For a hole concentration, f , defined by

$$f = \frac{E}{N+2} \quad (2-50)$$

use of the dominant terms of Stirling's approximation gives for the configuration entropy of one mole of liquid

$$S_c = -R \left[\ln(1-f) + \frac{f}{1-f} \ln f \right] \quad (2-51)$$

The quanta which determine the number of distinguishable "energy arrangements," Ω_t , correspond to the total internal energy in excess of the ground-state energy. In other words, Ω_t cannot include permutation involving depletions of the ground states. From Equation 2-16, Equation 2-43, and Equation 2-44 it is seen that the number q of quanta which contribute to the energy in excess of that of the ground states must satisfy the relation

$$q k \theta = 3Nk\theta \left(e^{\theta/T} - 1 \right)^{-1} \quad (2-52)$$

from which

$$q/3N = g = \left(e^{\theta/T} - 1 \right)^{-1} \quad (2-53)$$

where g has been introduced for simplicity. The number of distinguishable ways that the q quanta can be distributed among the $3N$ oscillators is the same as the number of dis-

tinguishable ways that g identical balls may be put in $3N$ boxes with no restriction on the number of balls per box, namely,

$$\Omega = (3N+g)! / (3N)! g! \quad (2-54)$$

Then, by Stirling's approximation the thermal entropy per mole is

$$S_t = 3R [(1+g) \ln(1+g) - g \ln g] \quad (2-55)$$

The foregoing equations define the thermodynamic properties of the proposed quiescent liquid with a hole concentration f .

2.4 Acoustical Effects

According to Assumption 7, the quiescent system is disturbed by acoustical waves with a velocity determined by the "consistent" frequency of vibration and with wavelengths restricted to integral multiples of twice the lattice dimension. The average time required for a molecule to communicate the approach of a disturbance across the distance $2a$, which separates its nearest neighbor on opposite sides, is $1/\nu$, where ν is the consistent-vibration frequency. The propagation velocity in a consistently vibrating liquid (and in a region devoid of holes) is thus taken to be

$$w = 2a\nu = 2ak\theta/h \quad (2-56)$$

where a is identical to the nearest-neighbor separation a_1 and where θ is obtained by substituting the consistent vibration parameter, a_c , into 2-17.

The permissible wave lengths are given by

$$\lambda_n = n(2a) \quad (2-57)$$

where $n = 1, 2, 3, \dots$. The permissible acoustical frequencies are therefore given by

$$\nu_n = w/\lambda_n = ke/hn \quad (2-58)$$

Since it is to be expected that the acoustical disturbances do not extend over domains which include vacancies in the quasi-lattice, the number of waves of a given length should decrease rapidly with increasing hole concentration f . The situation can be approximately represented by a simple cubic lattice consisting of N sites of which fN are unoccupied. The length of a linear column of molecules is $N^{1/3}a$, which means that, in the absence of holes, the number of one-dimensional waves of length λ_n that can exist along the column is $N^{1/3}/2n$. However, if each site has a probability f of being unoccupied, the average number of one dimensional waves that can exist along the column is only $(1-f)^{2n} N^{1/3}/2n$. Considering that there are $N^{2/3}$ columns for each of three mutually orthogonal

directions, the number of one-dimensional acoustical oscillators of frequency ν_n in one mole of liquid is (taking into account the increase in the number of sites per mole due to the vacancy fraction f)

$$N_n = 3 \left[\frac{N_A}{(1-f)} \right] \left[\frac{(1-f)^{2n}}{2^n} \right] \quad (2-59)$$

According to Assumption 7, the acoustical contribution to the internal energy is obtained by multiplying N_n by the energy of a one-dimensional oscillator of frequency ν_n averaged over states with energies less than $k\theta$ and not including the ground state energy. Since the assured absorption of waves of energy $k\theta$, or greater, merely changes the form of the available kinetic energy, the level population of oscillators of frequency ν_n should not be affected by the process of truncation. Hence, the average energy, including the ground state energy, is

$$u_n = \left\{ \sum_{j=0}^{\infty} F_{nj} E_{nj} - \sum_{j=J}^{\infty} F_{nj} E_{nj} \right\} / \left\{ 1 - \sum_{j=J}^{\infty} F_{nj} \right\} \quad (2-60)$$

where F_{nj} is the fraction of oscillators of frequency ν_n which are in the j^{th} level in an ordinary quantized distribution characteristic of a temperature T , E_{nj} is the energy of the j^{th} level, and J is the level corresponding to an excitation $k\theta$. For a one-dimensional oscillator,

$$F_{nj} = e^{-j h \nu_n / k T} \left(1 - e^{-h \nu_n / k T} \right) \quad (2-61)$$

and

$$E_{nj} = \frac{1}{2} h \nu_n + j h \nu_n \quad (2-62)$$

The first summation in the numerator of Equation 2-60

is

$$\begin{aligned} \sum_{j=0}^{\infty} F_{nj} E_{nj} &= \frac{1}{2} h \nu_n \left(1 - e^{-h \nu_n / k T} \right) \sum_{j=0}^{\infty} e^{-j h \nu_n / k T} \\ &+ \left(1 - e^{-h \nu_n / k T} \right) h \nu_n \sum_{j=0}^{\infty} j e^{-j h \nu_n / k T} \\ &= \frac{1}{2} h \nu_n + h \nu_n \left(e^{h \nu_n / k T} - 1 \right) \end{aligned} \quad (2-63)$$

The second summation in the numerator of Equation 2-60 can

be written

$$\begin{aligned} \sum_{j=J}^{\infty} F_{nj} E_{nj} &= \left[\frac{1}{2} h \nu_n \left(1 - e^{-h \nu_n / k T} \right) \sum_{j=J}^{\infty} e^{-j h \nu_n / k T} \right. \\ &\left. + \left(1 - e^{-h \nu_n / k T} \right) h \nu_n \sum_{j=J}^{\infty} j e^{-j h \nu_n / k T} \right] \end{aligned} \quad (2-64)$$

The foregoing expression may be simplified by writing

$$\begin{aligned}
\sum_{j=J}^{\infty} e^{-j h \nu_n / k T} &= e^{-J h \nu_n / k T} \sum_{j=J}^{\infty} e^{-(j-J) h \nu_n / k T} \\
&= e^{-J h \nu_n / k T} \sum_{j'=0}^{\infty} e^{-j' h \nu_n / k T} \\
&= e^{-J h \nu_n / k T} \left(\frac{1}{1 - e^{-h \nu_n / k T}} \right)^{-1}
\end{aligned} \tag{2-65}$$

and

$$\begin{aligned}
\sum_{j=J}^{\infty} j e^{-j h \nu_n / k T} &= \sum_{j=J}^{\infty} (j-J) e^{-j h \nu_n / k T} + J \sum_{j=J}^{\infty} e^{-j h \nu_n / k T} \\
&= e^{-J h \nu_n / k T} \sum_{j'=0}^{\infty} j' e^{-j' h \nu_n / k T} \\
&\quad + J e^{-J h \nu_n / k T} \sum_{j'=0}^{\infty} e^{-j' h \nu_n / k T} \\
&= e^{-J h \nu_n / k T} \left[\frac{e^{-h \nu_n / k T}}{\left(1 - e^{-h \nu_n / k T}\right)^2} \right] \\
&\quad + J e^{-J h \nu_n / k T} \left(\frac{1}{1 - e^{-h \nu_n / k T}} \right)^{-1}
\end{aligned} \tag{2-66}$$

Combining Equation 2-64, Equation 2-65, and Equation 2-66 gives

$$\sum_{j=J}^{\infty} F_{nj} E_{nj} = \left\{ \frac{1}{2} h \nu_n e^{-J h \nu_n / k T} + h \nu_n e^{-J h \nu_n / k T} \left[\frac{e^{h \nu_n / k T}}{e^{-1} - 1} + J \right] \right\} \tag{2-67}$$

Combining Equation 2-63 and Equation 2-67 gives for the numerator of Equation 2-60

$$\begin{aligned}
 & \left\{ \sum_{j=0}^{\infty} F_{nj} E_{nj} - \sum_{j=J}^{\infty} F_{nj} E_{nj} \right\} \\
 = & \left[\frac{1}{2} h\nu_n \left(1 - e^{-Jh\nu_n/kT} \right) + h\nu_n \left(1 - e^{-Jh\nu_n/kT} \right) \left(e^{h\nu_n/kT} - 1 \right)^{-1} \right. \\
 & \left. - Jh\nu_n e^{-Jh\nu_n/kT} \right] \quad (2-68)
 \end{aligned}$$

The summation in the denominator of Equation 2-60 is

$$\begin{aligned}
 \sum_{j=J}^{\infty} F_{nj} &= \sum_{j=J}^{\infty} \left(1 - e^{-h\nu_n/kT} \right) e^{-jh\nu_n/kT} \\
 &= \left(1 - e^{-h\nu_n/kT} \right) e^{-Jh\nu_n/kT} \sum_{j'=0}^{\infty} e^{-j'h\nu_n/kT} \\
 &= e^{-Jh\nu_n/kT} \quad (2-69)
 \end{aligned}$$

and the denominator is

$$\left[1 - \sum_{j=J}^{\infty} F_{nj} \right] = 1 - e^{-Jh\nu_n/kT} \quad (2-70)$$

From Equation 2-68 and Equation 2-70, it is found that

$$u_n = \frac{1}{2} h\nu_n + h\nu_n \left(e^{h\nu_n/kT} - 1 \right)^{-1} - Jh\nu_n \left(\frac{e^{-Jh\nu_n/kT}}{1 - e^{-Jh\nu_n/kT}} \right) \quad (2-71)$$

Since the J^{th} level corresponds to the absorption of an amount of energy $k\theta$ by a "consistent" mode of vibration,

$$Jh\nu_n = k\theta \quad (2-72)$$

and

$$J = k\theta/h\nu_n = n \quad (2-73)$$

where use has been made of Equation 2-58. Thus,

$$u_n = \frac{1}{2} h\nu_n + \frac{k\theta}{n} \left[\frac{1}{e^{\theta/n} - 1} - \frac{n}{e^{\theta} - 1} \right] \quad (2-74)$$

where

$$\theta = \theta/T$$

According to Assumption 8 the ground-state energy of the oscillators in normal coordinate space is to be identified collectively with the energy of the consistently vibrating molecules. Hence, the average energy belonging uniquely to an oscillator of frequency ν_n is

$$u'_n = \frac{k\theta}{n} \left[F_n - nF_1 \right] \quad (2-76)$$

where

$$F_n = \left(e^{\theta/n} - 1 \right)^{-1} \quad (2-77)$$

The total acoustical energy per mole, U_A , is obtained by summing over all wavelengths:

$$U_A = \sum_{n=1}^{\infty} N_n u'_n = \left[\frac{6R\theta}{1-f} \right] \sum_{n=1}^{\infty} H_n (F_n - nF_1) \quad (2-78)$$

where

$$H_n = \frac{(1-f)^{2n}}{(2n)^2} \quad (2-79)$$

A sort of configurational entropy is associated with each set of oscillators of frequency ν_n , owing to the one-dimensional regions over which waves are excluded due to the presence of vacancies. The number of intersections of intervals over which waves could extend in the absence of holes is $(1-f)^{2n} N^{1/3}/2n$. The average number of holes in such an array is $fn^{1/3}$. Since the total range excluded by holes may be between two wave-supporting regions, there is effectively no limit on the number of vacancies which separate adjacent waves. Hence the number of distinct combinations in a one-dimensional array of $N^{1/3}$ molecule is (in analogy to Equation 2-54)

$$W'_{A,n} = \left\{ \frac{N^{1/3}}{2n} (1-f)^{2n} + \frac{N^{1/3}}{2n} (2nf) \right\} / \left\{ \frac{N^{1/3}}{2n} (1-f)^{2n} \right\} \left\{ \frac{N^{1/3}}{2n} (2nf) \right\} \quad (2-80)$$

Considering that the assignment of a given vacancy distribution to each of $N^{2/3}$ columns completely determines the vacancy distribution in the system of N sites, the total number of distinct combinations is

$$W_{A,n} = N^{2/3} W'_{A,n}$$

and the associated configurational entropy per mole of oscillators of all permissible frequencies turns out to be

$$S_A = \left(\frac{f}{1-f} \right)^R \sum_{n=1}^{\infty} \left[(1+G_n) \ln(1+G_n) - G_n \ln G_n \right] \quad (2-81)$$

where

$$G_n = \frac{(1-f)^{2n}}{2nf} = \frac{2nE_n}{f} \quad (2-82)$$

Since, due to reflection from holes or boundaries, a given acoustical wave may propagate to any point in the liquid, various waves of the same frequency are indistinguishable from one another in the sense that there is no way of determining whether a wave corresponding to a given excited state of oscillation is the same wave which was excited in a previous condition or a different wave which has come to occupy the position of the former one. Hence it is not meaningful to speak of the distinguishable ways in which quanta of energy may be distributed among the abstract oscillators in normal

coordinate space that define a collection of waves of frequency ν_n . The thermal entropy associated with such distributions is therefore zero. However, the entropy given by Equation 2-31 could be regarded as a kind of thermal entropy, since it relates not just to the number of distinguishable hole distributions but to the permissible patterns of motion for acoustical disturbances in the liquid.

The contributions to the total entropy denoted by Equation 2-51, Equation 2-55, and Equation 2-31 are the only ones to be considered in a consistent application of the present model. An omission which should be noted explicitly is the part of the configurational entropy associated with long-range disordering in the distribution of quasi-lattice sites. It is to be hoped that, well away from the critical point at least, this contribution is small. In the vicinity of the critical point, any model based on the assumption of a crystalline structure can be expected to fail (Ref. 11).

2.5 Hole Concentration and the Approach to Equilibrium

According to Assumption 9, the hole concentration, f , is the only significant independent variable in the determination of the Helmholtz free energy. Therefore, at constant temperature and density, the liquid should approach equilibrium by tending toward a value of f for which the Helmholtz free energy

$$F = U - TS \quad (2-83)$$

is minimum, where U and S are, respectively, the total internal energy and entropy due to the various contributions. The equilibrium state of the liquid is thus determined by (1) regarding each of a set of trial values of f as an independent variable (along with ρ and T) and determining the corresponding consistent-vibration frequency defined by Equation 2-41; (2) evaluating the associated values of U and S by adding U_Q and U_A and S_t , and S_c , and S_A , respectively; and (3) locating the value of f for which F is minimum. All of these operations can best be performed numerically with the aid of a high-speed computer.

2.6 Summary of Expressions for the Equilibrium State

The equilibrium state of a liquid according to the present model is defined by an equilibrium vacancy fraction f_e and a consistent-vibration parameter $\alpha_c(f_e)$. For any trial value of f , $\alpha_c(f)$ is the value of α that satisfies

$$K_N - K_R = 0 \quad (2-41)$$

where

$$K_N = \hbar^2 \alpha^4 / M \quad (2-40A)$$

and

$$K_R = \sum_i z_i \left[a_i^{-8} k_a(\gamma_i) + a_i^{-14} k_r(\gamma_i) \right] \quad (2-33)$$

where

$$v_i = \left(\frac{1-e^{-\phi}}{1+e^{-\phi}} \right)^{1/2} a_i, \quad \left(\phi = \frac{q}{r} \right) \quad (2-34)$$

$$k_a(\gamma_i) = -5v_c \left(\frac{2}{\sqrt{\pi}} \right) \gamma_i^7 \int_{L(\gamma_i)}^{\infty} u^{-7} e^{-(\gamma_i-u)^2} du \quad (2-35)$$

and

$$k_r(\gamma_i) = 22v_c \left(\frac{2}{\sqrt{\pi}} \right) \gamma_i^{13} \int_{L(\gamma_i)}^{\infty} u^{-13} e^{-(\gamma_i-u)^2} du \quad (2-36)$$

The molar well depth for the trial vacancy fraction f is given by substituting $a = a_c(f)$ into the relations

$$W = \sum_i z_i \left[a_i^{-6} u_a(\gamma_i) + a_i^{-12} u_r(\gamma_i) \right] \quad (2-37)$$

with

$$u_a(\gamma_i) = -N_A v_c \left(\frac{1}{\sqrt{\pi}} \right) \gamma_i^5 \int_{L(\gamma_i)}^{\infty} u^{-5} e^{-(\gamma_i-u)^2} du \quad (2-38)$$

and

$$u_r(\gamma_i) = -N_A v_c \left(\frac{1}{\sqrt{\pi}} \right) \gamma_i^{11} \int_{L(\gamma_i)}^{\infty} u^{-11} e^{-(\gamma_i-u)^2} du \quad (2-39)$$

The lower limit in the integrations is taken to be

$$L(\gamma_i) = \frac{1}{2} \left[\gamma_i - \sqrt{\gamma_i^2 - 26} \right] \quad (2-40)$$

The number of neighbors per shell, z_i , and the neighbor shell radius, a_i , for the i^{th} shell are proportional to $(1-f)$ and $(1-f)^{1/3}$, respectively, and are given for some specific types of quasi-lattice structure in Table 1.

The internal energy for a trial value of f is

$$U = U_C + U_A \quad (2-84)$$

where

$$U_C = \frac{1}{2} \left[W + RV(\theta, T) \right] \quad (2-45)$$

with

$$V(\theta, T) = 3\theta \left[\frac{1}{2} + (e^\theta - 1)^{-1} \right] \quad (2-44)$$

and

$$\theta = \hbar^2 c^2 / Mk \quad (2-17)$$

and U_A is given by

$$U_A = \left[\frac{6R\theta}{(1-f)} \right] \sum_{n=1}^{\infty} H_n (F_n^{-n} F_1) \quad (2-78)$$

with

$$H_n = (1-f)^{2n} / (2n)^2 \quad (2-79)$$

and

$$F_n = \left(e^{\phi/n} - 1 \right)^{-1} \quad (2-77)$$

The absolute entropy for a trial value of f is

$$S = S_c + S_t + S_A \quad (2-85)$$

where

$$S_c = -R \left[\ln(1-f) + \frac{f}{1-f} \ln f \right] \quad (2-51)$$

$$S_t = 3R \left[(1+g) \ln(1+g) - g \ln g \right] \quad (2-55)$$

with

$$g = \left(e^{\phi} - 1 \right)^{-1} = F_1 \quad (2-53)$$

and where

$$S_A = \left(\frac{f}{1-f} \right) R \sum_{n=1}^{\infty} \left[(1+G_n) \ln(1+G_n) - G_n \ln G_n \right] \quad (2-81)$$

with

$$G_n = 2nH \sqrt{f} \quad (2-82)$$

The Helmholtz free energy for a trial value of f is

$$F = U - TS \quad (2-83)$$

The equilibrium state of the liquid is found by locating a value of f such that

$$\left(\frac{\partial F}{\partial f} \right)_{\rho, T} = 0 \quad (2-86)$$

If it is assumed that the present model provides accurate values of U and S , then, for a given density ρ and temperature T , the pressure is obtainable from the relation

$$P = - \left[\frac{\partial F}{\partial (1/\rho)} \right]_T \quad (2-87)$$

Therefore, insofar as it is valid, the model offers a complete solution to the problem of state with ρ and T as independent variables.

3. THE COMPUTER PROGRAM

3.1 Procedure

A computer program (designated T-74) has been written in the FORTRAN language for use on the IBM 7090 computer. The operations indicated in Section 2.6 are executed on the basis of given temperature, density, and assured quasi-lattice structure. Up to ten neighbor shells may be considered. For each of three trial values of f , provided as input, the procedure converges on a consistent-vibration parameter, $a_c(f)$, by an iterative process equivalent to Newton's method, which begins with the consideration of two trial values of a , also provided as input. Subsequently, the procedure converges on an equilibrium value of f by re-use of Newton's method to locate the intercept of $(\partial F/\partial f)_{T,\rho}$. A linear expression for the latter quantity at each value of f considered is obtained by using the derivative of the quadratic function defined by the values of F at that value of f and at the two values considered immediately prior to it. In order to obtain five-place accuracy in a_c , about six trial values of a must be considered for each trial value of f . In order to obtain four-place accuracy in f_e , about 10 trial values of f must be considered. (For some reason, the number of iterations required in each case is relatively insensitive to the estimates provided as input.) The

execution of all of the foregoing operations for a given state defined by T and ρ (in the cases considered thus far, at least) requires about 3 minutes of computer time.

3.2 Input and Output

The input data for a single problem (corresponding to a single state of the liquid) requires from 7 to 16 cards, depending on the number of neighbor shells considered. If n is the number of neighbor shells, then the information contained on the respective input cards is:

[1] Two abbreviations designating the type of liquid and assumed structure (used in the identification of input); the number of neighbor shells, n ; the temperature; the density (used only to specify what density is used in determination of the shell radii for the perfect lattice); the molecular mass in amu.

[2] The Lennard-Jones coefficients u_c and v_c (in units of \AA^6 ergs $\times 10^{-8}$ and \AA^{12} ergs $\times 10^{-8}$, respectively).

[3 through $3+(n-1)$] The radius and number of molecules per shell for each neighbor shell of a perfect lattice of the assumed type (from this information the corresponding values in a lattice with a hole concentration f are computed by multiplication by the factors $(1-f)^{1/3}$ and $(1-f)$, respectively; thus, ρ is implicit in the "perfect-lattice" input).

[$3+n$] Two trial values of a in $\left(\frac{1}{f}\right)^{1/3}$.

[$3+n+1$] Three trial values of f .

[$3+n+2$] The mesh spacing (Δu) to be used in the integrations and an optional lower limit of

integration which can be used in the case of distant neighbor shells to reduce the amount of machine time required. The upper limit of integration in all cases is automatically chosen to give equal ranges of integration on either side of the maximum of the integrand associated with $k_r(\gamma_i)$.

[3+n+3] An option number which permits the termination of the convergence process and which also permits the inclusion or exclusion of acoustical terms (the properties of the "quiescent" liquid are of some interest); two integers which specify an upper limit to the number of trial values of a and f to be considered in a given problem; two (fractional) numbers which define the convergence criteria and hence the accuracy of a_c and f_e .

The output data include all of the input data and, for each trial value of f , the following in the order considered:

1. The value of f considered
2. The "consistent" values of γ_i for each neighbor shell
3. The contribution to the "consistent" stiffness coefficient due to each neighbor shell
4. The contributions to the effective molar well depth (designated as $U_g = 1/2 W$) due to each neighbor shell
5. The total effective molar well depth and stiffness coefficient
6. The consistent values of a , which is a_c , and θ
7. The total internal energy, total entropy, and the Helmholtz free energy
8. The value of $\frac{1}{RT} \left(\frac{\partial F}{\partial f} \right)$ for the value of f considered.

Each value of f corresponds to a single page of output; in a normal execution the last page of output provides the above data for the equilibrium state of the liquid.

4. APPLICATION TO LIQUID HYDROGEN

4.1 Liquid Structure and Intermolecular Potential

At first glance, the application of the consistent-vibrations model to liquid hydrogen might seem inauspicious due to the fact that hydrogen is diatomic. However, infrared spectroscopy (Ref. 12) reveals that the rotation of the molecule in the liquid (and even in the solid) is practically unhindered, and analysis of virial-coefficient data on hydrogen gas show that, when both the para- and ortho-hydrogen modifications are taken into account, the interaction between H_2 molecules is approximately satisfied by a Lennard-Jones potential (Ref. 13). Furthermore, in either modification the first-accessible excited rotational level of the molecule lies approximately 0.03 ev above the ground state. Hence, even at temperatures as high as $30^\circ K$, the fraction of molecules which are in the first excited state of either modification is only of the order $\exp(-.03/kT) \sim 10^{-5}$. Thus, contributions to the internal energy due to excited rotational states may conscientiously be neglected.

The Lennard-Jones parameters which have been used in all calculations to date are those cited by Knapp and Beenakker (Ref. 13). These are (in the notation and units selected for the present application)

$$\mu_c = 0.001267 \text{ \AA}^6 \left(\text{ergs} \times 10^{-9} \right) \quad (4-1)$$

and

$$v_c = 0.8113 \text{ \AA}^3 (\text{ergs} \times 10^{-8}) \quad (4-2)$$

These parameters are obtained from the properties of hydrogen gas and are not sufficiently accurate to justify a distinction between the ortho- and para-hydrogen modifications (although the relative difference between the coefficients of the two modifications can be specified, as is done in Reference 13).

The structure of the quasi-lattice in liquid hydrogen is assumed to be cubic close-packed. In all applications made thus far, the first four neighbor shells have been considered. The possibility that the type of lattice structure corresponding to the lowest Helmholtz free energy may change from cubic close-packed to some other form at the higher temperatures has yet to be investigated.

4.2 Results and Comparison with Experimental Data

The procedure has been applied to the case of liquid para-hydrogen at points on the P-V-T surface ranging from 20°K to 28°K along the saturation-point line. Typical results are exemplified by the output for the state defined by $T = 20.260^\circ \text{K}$, $\rho = 0.07077 \text{ gm/cm}^3$, which is shown in Table 2. The data refer to the equilibrium state of the liquid. In the case shown, the contribution of acoustical terms was not considered.

Table 2

T-74 OUTPUT FOR THE STATE OF LIQUID PARA-HYDROGEN

$$(T = 20.268^{\circ}\text{K}, \rho = 0.07077 \text{ gm/cm}^3)$$

i	γ_i	$KR(i) * (\text{ergs/cm}^2)$	$1/2W(i) * (\text{j/gm})$
1	6.6489	322.049	-453.401
2	9.4029	-7.914	-38.372
3	11.5163	-6.622	-45.108
4	13.2978	-1.042	-9.420

No. of a's considered = 6

(No. of f's considered) = 8

(Equilibrium) Hole Concentration $(f_e) = 0.08717$

Consistent $a (a_c) = 1.7392 \text{ \AA}^{-1}$

(Consistent) $\theta = 73.388^{\circ}\text{K}$

(Effective) Well Depth $(1/2W) = -546.301 \text{ j/gm}$

Internal Energy (U_Q) of Quiescent Liquid = -304.836 j/gm

Entropy $(S_c + S_t)$ of Quiescent Liquid = $2.9284 \text{ j/gm}^{\circ}\text{K}$

Helmholtz Free Energy of Quiescent Liquid = -364.189 j/gm

$$\frac{1}{RT} \left(\frac{\partial F}{\partial \rho} \right)_{\rho, T} = 0.00668$$

*Contributions to KR and 1/2 W from the i^{th} neighbor shell.

All of the problems referred to herein were run before the computer program had been modified to include the contribution of U_A to the internal energy or the contribution of S_A to the entropy. The subsequent evaluation of these quantities by hand has yielded values for the total energy and entropy which, in terms of the model, are valid for the equilibrium hole concentration found by the computer program but which do not necessarily correspond to the vacancy fraction that would have been determined had U_A and S_A been included in the minimization of F . Nevertheless, since the hand calculations show that U_A represent only about 20% of the absolute value of U and that S_A varies slowly with f , it is inferred that the value of the equilibrium vacancy fraction will not be greatly disturbed by the inclusion of such terms.

The most significant results of the computer calculations and the hand calculations of U_A and S_A are shown in Table 3. It is to be noted that f_e increases monotonically (and almost linearly) as one moves toward the critical point (33°K). This is just what would be expected, since all quasi-crystalline ordering is supposed to vanish in the neighborhood of the critical point. The quantities θ_i , which vary only slightly, are of immediate value, since they determine the liquid-lattice quantum levels that may be excited by cold-neutron scattering. The

Table 3

SUMMARY OF RESULTS FOR PARA-HYDROGEN

T (°K)	ρ (gm/cm ³)	f_e	$\frac{\alpha_c}{\lambda - 1}$	θ (°K)	$-U_c$ (j/gm)	$S_c + S_t$ (j/gm-°K)	U_A (j/gm)	S_A (j/gm-°K)
20.268	.07077	.0872	1.7392	73.388	304.836	2.928	59.400	4.779
22.855	.06756	.1152	1.7277	72.420	270.989	3.951	51.073	4.662
24.628	.06506	.1364	1.7180	71.607	244.408	4.715	45.471	4.651
26.00	.06300	.1541	1.7102	70.961	222.311	5.332	41.860	4.510
28.00	.05919	.1880	1.6947	69.677	183.266	6.368	33.797	4.387

internal energy and entropy of the quiescent liquid are seen to depend rather strongly on the state. As remarked previously, the acoustical contribution to the total entropy appears to be insensitive to the state, and hence to f_e .

The applicability of the proposed model can presumably be tested adequately by comparing the predicted values of the total internal energy and entropy with empirical results. Problems involving variations of the density at constant temperature and vice versa have not yet been run, so neither predictions of pressure nor of specific heat at constant volume are yet available.

Figure 2 shows the predicted value of the total internal energy $(U_2 + U_A)$ compared with values published by NBS (Ref. 14). Figure 3 shows the predicted entropy compared with the empirical results from the same reference.

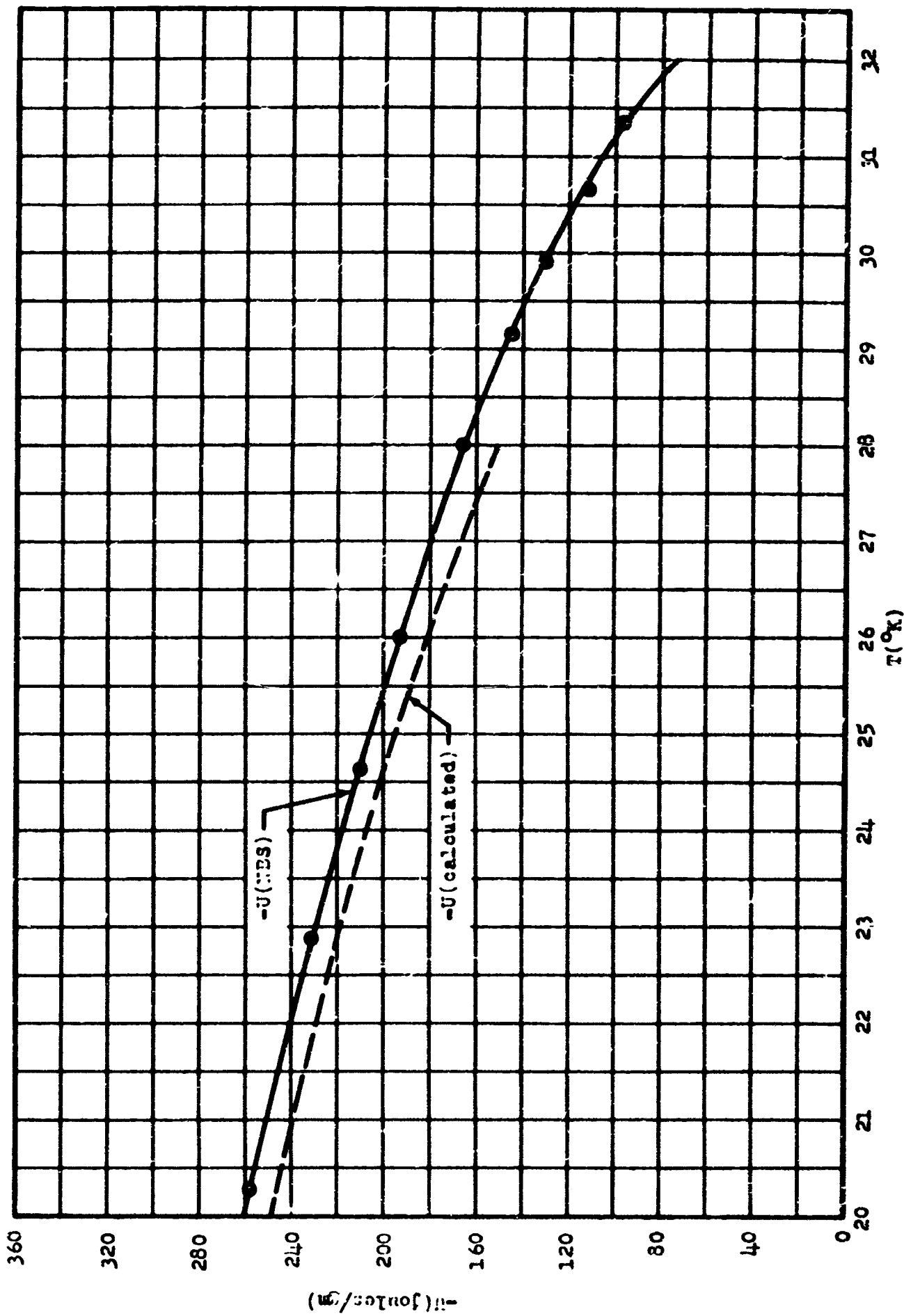


Figure 2 Calculated and Empirical Internal Energy of Liquid Hydrogen Along the Saturation Line

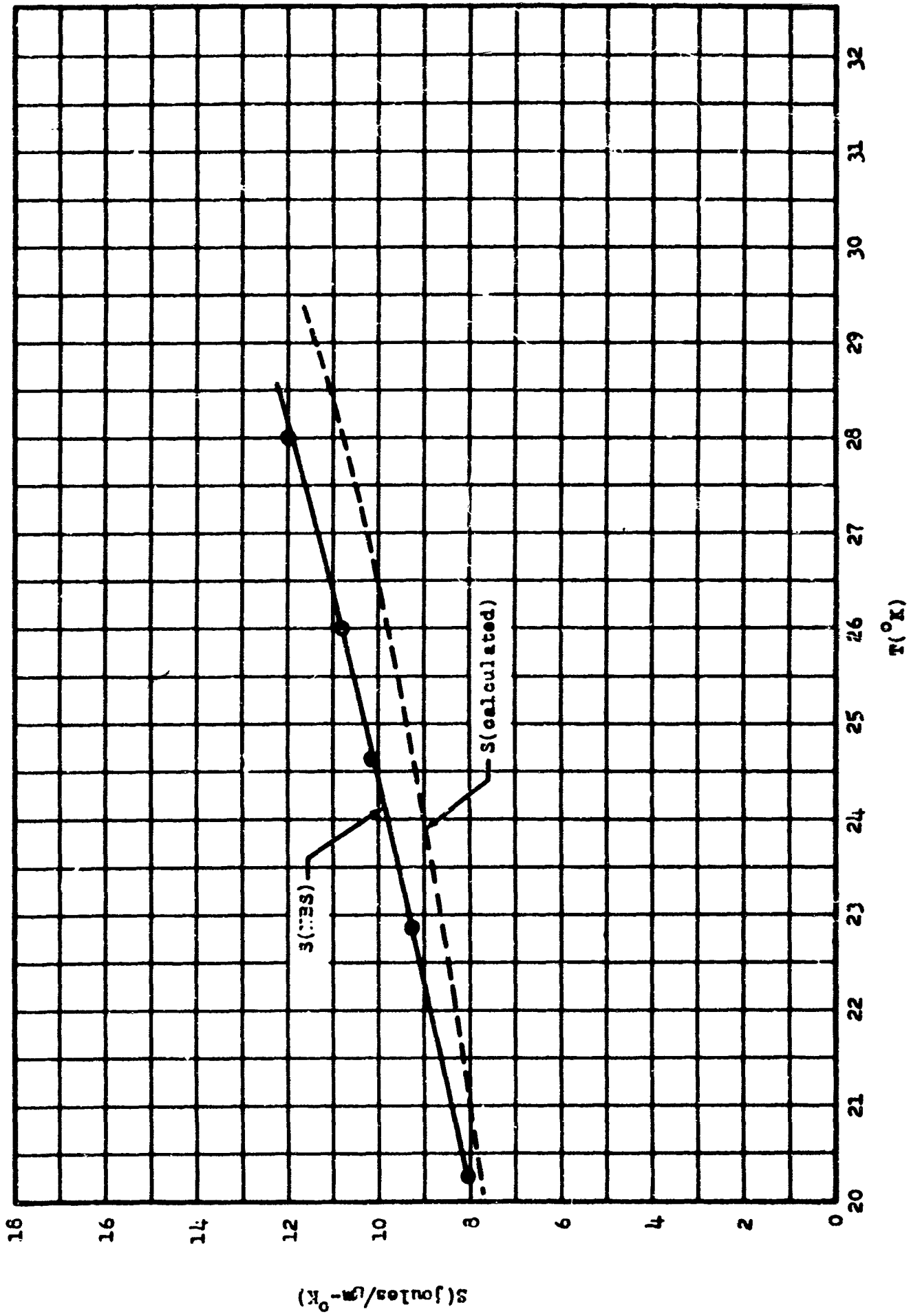


Figure 3 Calculated and Empirical Entropy of Liquid Hydrogen Along the Saturation Line

5. RESULTS AND CONCLUSIONS

The predicted internal energies and entropies lie within 6% of the empirical results at points on the saturation line below about 25° (Fig. 3). At points nearer the critical point, the predicted results, especially those for the entropy, give less satisfactory agreement. However, this is to be expected since the concept of a close-packed quasi-lattice tends to lose its meaning when the equilibrium vacancy fractions approaches 20%.

When it is considered that the agreement, in the case of the internal energy, at least, would almost certainly improve if more than four neighbor shells were considered (judging from the relative contributions to $1/2 W$ and K_R), the results obtained thus far constitute highly encouraging evidence for the validity of the proposed model. It is therefore tentatively concluded that the model anticipates the most significant general features of motion in the liquid and that the state-dependent microscopic data provided by the model, such as θ and the neighbor wave functions determined by α_c , may be implemented in calculations of quantities such as cross sections and recombination rates which are dependent on the details of the internal dynamics and microscopic structure.

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