

## Regarding molecular superfluid hydrogen

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 5071

(<http://iopscience.iop.org/0953-8984/12/24/301>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 05:12

Please note that [terms and conditions apply](#).

## Regarding molecular superfluid hydrogen

V S Vorob'ev and S P Malysenko

Institute for High Temperatures of the Russian Academy of Sciences, Moscow 127412,  
Izhorskaya 13/19, Russia

E-mail: vrbv@mail.ru (V S Vorob'ev) and litp@dataforce.net (S P Malysenko)

Received 28 January 2000

**Abstract.** We discuss different ways to produce liquid hydrogen at temperatures below its normal freezing temperature, where it can enter a superfluid state. Our consideration is based on the fact that solid and liquid phases may coexist in equilibrium at different pressures. To provide this pressure difference we take a look at the effect of a one-sided mechanical pressure on the solid phase and an external electrical field. We calculate thermodynamical functions for hydrogen both in stable and metastable domains, and its phase diagram, and find a domain of possible superfluidity, using a semiempirical thermodynamical model and recent data on critical temperatures of Bose liquids. We estimate both the value of the excess pressure on solid hydrogen and the electrical field strength necessary to stabilize the superfluid domain.

### 1. Introduction

Deeply supercooled hydrogen is a natural candidate for showing superfluidity since it is composed of two pairs of fermions in singlet bound states (in para-hydrogen) [1–5]. To produce superfluid  $H_2$  it is therefore necessary to find some way to supercool the liquid below its normal freezing temperature. Ginzburg and Sobyenin [1] proposed studying the properties of liquid hydrogen under negative pressures. The idea was that negative pressure would lower the solidification temperature. The limitation of this approach is the thermodynamical instability of the liquid against the formation of a gas phase. This type of instability has been considered by Aculichev and Bulanov [6]. They concluded tentatively that hydrogen cannot support a large enough static negative pressure to keep it liquid. In addition, some important issues have not been resolved to date. These issues include the relative positions of the line of thermodynamical loss of stability (spinodal) for a uniform liquid phase with respect to a gas phase, the liquid–solid phase equilibrium line in the domain of negative pressures and, finally, the position of a possible  $\lambda$ -transition line in the  $P$ – $T$  plane. There is also a question regarding the possibility of a  $\lambda$ -transition in supercooled liquid hydrogen under positive pressures. To give answers to these questions, we have at least to know the thermodynamical functions for solid and liquid hydrogen, allowing extrapolation into the domain of temperatures below the triple point both under positive and under negative pressures.

Here we shall discuss other possibilities for superfluid  $H_2$  production arising because a two-phase solid–liquid system may coexist in equilibrium at different pressures below its normal freezing temperature. If we somehow create one-sided excess pressure on the solid phase, then it may be possible for such a solid to coexist with a liquid at a smaller pressure.

On the other hand, as is known, strong external fields penetrating inside a body radically affect its thermodynamical properties and may change the phase equilibrium parameters [7]. Our interest is in attempting to find conditions in which liquid hydrogen will coexist

in equilibrium with solid at temperatures below its normal freezing temperature due to the presence of an electrical field. To this end, we will investigate general liquid–solid phase equilibrium conditions with a planar interface in the external electrical field. Our analysis will show basically that it is possible to realize the desirable shift of the phase equilibrium.

However, to calculate the necessary excess pressure of the solid phase, we must know the dependence of the chemical potentials for both the solid and the liquid supercooled phases on pressure, the position of the possible  $\lambda$ -transition line in the  $P$ – $T$  plane and the wide-range hydrogen thermodynamical functions.

Existing empirical and semiempirical methods of calculation of the thermodynamical functions of liquid hydrogen [8, 9] are constructed on the basis of experimental information about compressibility and curves of phase equilibrium; direct extrapolation into the domain of temperatures below the triple point is unreliable. Here we use a method (see the appendix) of constructing the equation of state proposed in previous publications [10, 11]. There the elastic oscillations of molecules about their equilibrium positions in both solid and liquid phases were described in terms of the Debye theory modified so as to obtain the ideal-gas equation of state in the limit of high temperature and low density. In contrast to the case for the approaches used previously [12–14], the elastic component of the liquid free energy (cold curve) is not equal to that of the solid phase. In addition, we introduce the configurational (common) entropy for the liquid phase, which is a measure of its disorder. The configurational entropy was also considered in earlier publications [15, 16]. The thermodynamical model described above contains functions to be defined: the volume dependence of the Debye temperature, the value of the configurational entropy and the elastic component of the free energy for both solid and liquid phases. These functions are determined from the condition that the thermodynamics constructed on the basis of our model must correspond to tabulated data for the thermodynamical functions along coexisting lines of different phases. In this paper we use the tables for thermodynamical properties of hydrogen [8], coordinated with the totality of experimental findings. This procedure allows us to find all the unknown functions and thus calculate any thermodynamic value—in particular, in the metastable domain at low temperature. As shown below, the difference between the elastic components of the solid and liquid phases and the presence of the configurational component of entropy for the liquid phase are the main contributions to the distinction between the solid and liquid states at temperatures below the triple point for hydrogen. We compare the calculated isotherms of pressure with experimental data and obtain a good agreement. The accuracy of our calculations is reasonable for finding the phase equilibrium lines in the  $P$ – $T$  plane and calculation of some thermodynamical functions at low temperatures.

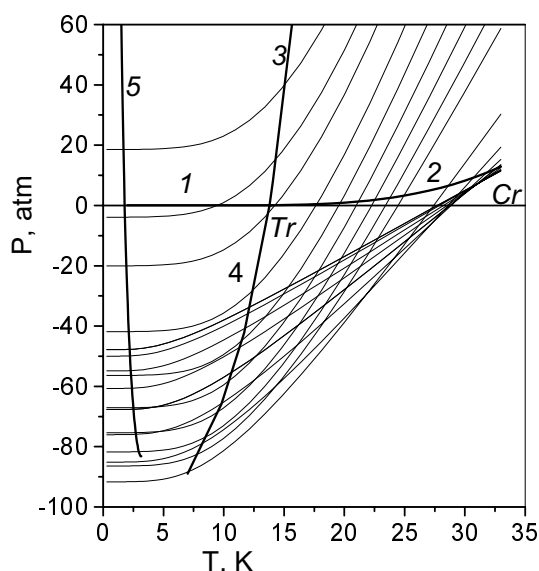
We present a domain of the pressure–temperature plane where the deeply supercooled hydrogen can be in a superfluid state. For that we use a recent calculation from Apenko [17] where the critical temperature of the  $\lambda$ -transition was determined for supercooled liquid hydrogen as a function of density.

The dependencies of the chemical potential upon pressure for the solid and supercooled liquid phases at the  $\lambda$ -transition temperature allow us to find the one-sided excess pressure of the solid phase, provided that the latter is stable. The value of this pressure is about 30 atm and it is of the same order as the pressure corresponding to the tensile strength of solid hydrogen at low temperatures.

We also estimate the electrical field strength under which liquid hydrogen can remain liquid at extremely low temperatures. This is of the order of  $5 \times 10^7$  V cm<sup>−1</sup> and it can exceed the breakdown strength.

## 2. The hydrogen $P$ - $T$ diagram and the domain of possible superfluidity

Using the method of calculation of the hydrogen thermodynamical functions given in the appendix, we calculate the phase diagram for  $H_2$ . Such a diagram is presented in figure 1. We can extend the melting curve into the domain of negative pressures and temperatures lying below the triple point. A set of isochores for the liquid state is also shown. It is known that the liquid–gas spinodal—the line of absolute loss of stability of the liquid state—envelops this set. This line is apparent in figure 1. One can see it restricting the possibility of extension of the melting line in the metastable domain to pressure values lower than  $-90$  atm. This practically excludes the possibility of obtaining stable superfluid hydrogen at negative pressures lower than the latter value. This possibility has been discussed in a number of works [1, 6].



**Figure 1.** The  $P$ - $T$  diagram for hydrogen. Thick lines: 1: the sublimation line; 2: the melting line; 3: the evaporation line; 4: the melting line extended into the metastable domain; 5: the boundary of the superfluid domain ( $d = 2.7$  Å);  $T_r$  is the triple point;  $Cr$  is the critical point. Thin lines: a set of isochores for values of  $v$  varying from  $v = 12.5$  (the upper isochore) to  $v = 31$   $\text{cm}^3 \text{g}^{-1}$  (the critical isochore). The envelope of this set of isochores forms the liquid spinodal.

The critical temperature of Bose–Einstein condensation of a 3D homogeneous system of hard-sphere non-ideal bosons has been determined recently [5]. In [17], a formula for the critical temperature of the superfluid transition in Bose liquid has been obtained. This formula can be written in the form

$$T_\lambda = 0.899 K \exp\left(-0.109 \frac{K}{T}\right) \quad (1)$$

where  $K$  is the kinetic energy. It can be calculated with the help of London's formula [18]

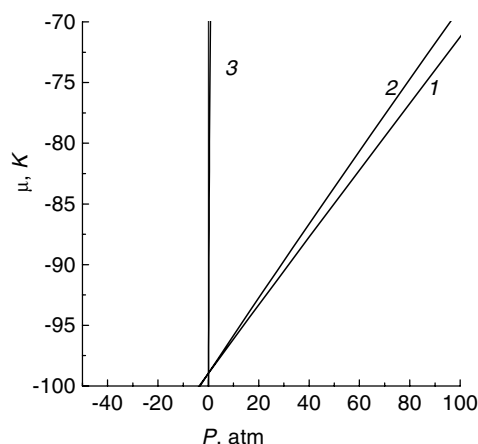
$$K = \frac{2\pi\hbar^2 d}{m(a - 0.891d)^2(a + 0.731d)} \quad (2)$$

where  $a = n^{-1/3}$ ,  $n = \rho/m$ . For hydrogen the value of the hard-core diameter  $d \simeq 2.7$  Å, as estimated in [19].

The accuracy of expression (1) was verified with experimental results for liquid helium. The calculated values for the critical temperature correlate well with experiment.

Using (1), we can find the value of the  $\lambda$ -line temperature for a given value of the density. Then, using our equation of state for supercooled hydrogen (see the appendix), we can calculate the corresponding values of the pressure and chemical potential. Thus we obtain a line dividing the plane of variables  $P$ – $T$  into domains of superfluid and normal liquid. The results of our calculation are depicted in figure 1 as line 5. We can see that the temperature of the superfluid transition is about 1–2 K. It should be noted that line 5 is similar to the  $\lambda$ -line of liquid helium. Besides this, for the isochores with  $v > 12.75 \text{ cm}^3 \text{ g}^{-1}$  there is a domain of positive pressures where deeply supercooled liquid hydrogen can become superfluid.

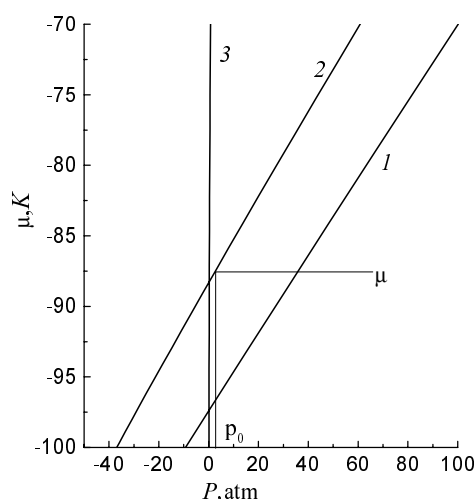
To investigate the possibility of existence of a deeply supercooled liquid state, let us construct isotherms of chemical potential for the solid and liquid states at different pressures. Isotherms at  $T = 13.8 \text{ K}$  are presented in figure 2. The value of 13.8 K corresponds to the triple-point temperature for hydrogen. Line 1 in figure 2 and in the following figures corresponds to the solid chemical potential. The values of the liquid-phase chemical potential are depicted in figure 2 (and the following figures) as line 2. One can see that these two lines have a point of intersection at a positive pressure close to zero. This pressure value correlates well with the experimental value of the melting pressure at the triple point—0.07 atm. Similar isotherms are drawn in figure 3 at  $T = 1 \text{ K}$ , approximately corresponding to the  $\lambda$ -transition temperature. In this case the values of the liquid chemical potential are larger than the solid ones and the point of intersection of the isotherms does not exist under positive pressures. Besides this, the liquid isotherm reaches the liquid spinodal point earlier than the expected intersection point with the solid isotherm under large values of negative pressures. Thus the solid phase is more advantageous thermodynamically for this temperature. Line 3 in the figure represents the ideal-gas chemical potential. At this temperature and this scale of pressure, the latter is presented as an almost vertical line.



**Figure 2.** The dependence of the solid (line 1) and liquid (line 2) chemical potentials on pressure for the triple-point temperature  $T = 13.8 \text{ K}$ . The point of intersection of the solid and liquid isotherms corresponds to the equilibrium melting pressure.

### 3. Coexistence of phases under different pressures

In general, solid and liquid phases may coexist in equilibrium at different pressures, provided that they are separated by a suitable wall. For example, some kind of porous wall, which the liquid will wet, may separate a high-pressure solid from a low-pressure liquid while the two



**Figure 3.** The dependence of the solid (line 1), liquid (line 2) and gas (line 3) chemical potentials on pressure for temperature  $T = 1$  K. The line  $\mu$  gives the value of the chemical potential in the presence of a field.

are in equilibrium through the wall. Since a transfer of mass is allowed in either direction, it is necessary for equilibrium that the values of the chemical potential of the pure substance should be the same on both sides of the wall. It is not necessary, however, that the pressures should be the same on both sides, because the nature of the wall is such that an increase of volume of the solid phase at the expense of that of the liquid phase is allowed.

A graphical interpretation of this kind of equilibrium is given in figure 3 for hydrogen at  $T \sim 1$  K. The line  $\mu$  gives the value of the full chemical potential if the phase pressures are not equal and the solid pressure is greater than the liquid one. Here we will not discuss the practical ways of creating the wall providing the existence of excess pressure acting only on the solid state. It is important for us to investigate in principle the possibilities of this method.

Now we can estimate the solid–liquid phase equilibrium parameters at different pressures. Assuming that the liquid pressure must be positive (in this case the gas phase cannot be formed), from figure 3 we obtain a value of the pressure difference of about 33 atm. So if we create a solid-phase pressure of about 33 atm and we simultaneously have the possibility of existence of a liquid phase at a pressure of the order of 0 atm, then phase equilibrium between these phases becomes possible. At such values of the phase pressures and a temperature of about 1 K, we can expect it to be possible for hydrogen to exist as a liquid and enter a superfluid state.

An obstacle to this may be the small mechanical strength of solid hydrogen. According to the data in [20], the static Young's modulus and relative expansion corresponding to the yield limit for hydrogen at temperatures of about 1–2 K are equal respectively to 3300 atm and 0.008. Therefore solid hydrogen can accept pressures of the order of 26 atm with no change of its form—of the same order as the excess pressure acting only on the solid state.

#### 4. Liquid–solid phase equilibrium in the presence of an electrical field

Let us investigate the possibility of creation of the different phase pressures with an external electrical field.

Consider a substance at a constant temperature in volume  $V$  in the presence of an electrical field. Let us assume that the substance breaks down into two phases. Phase 1 (solid) occupies the bottom of the volume  $V$  and phase 2 (liquid) the top. The phase boundary is a planar surface. As is known, the force per unit volume in a liquid dielectric can be written as

$$\mathbf{f} = \nabla \left[ \frac{E^2}{8\pi} \left( \rho \frac{\partial \varepsilon}{\partial \rho} \right)_T \right] - \frac{E^2}{8\pi} \nabla \varepsilon \quad (3)$$

where  $E$  is the strength of the electrical field,  $\varepsilon$  is the dielectric constant,  $\rho$  is the density and  $T$  is the temperature.

The volume force exerted on a solid dielectric by an electrostatic field can be accounted for by both the change in density (like in liquid) and deformation without any accompanying change of volume (shearing strains) [21]. Hereafter for simplicity we will neglect this kind of deformation. In this case, the force in the solid will also be described by (3) with the values of the density and dielectric constant corresponding to this solid.

Integrating (3) over a thin layer along the normal direction to the interface, just like in [22], we obtain

$$p_1 - p_2 = \Delta p - \frac{E_2^2}{8\pi} \left( \rho_2 \frac{\partial \varepsilon_2}{\partial \rho_2} \right)_T + \frac{E_1^2}{8\pi} \left( \rho_1 \frac{\partial \varepsilon_1}{\partial \rho_1} \right)_T \quad (4)$$

where  $p_2$  and  $p_1$  are the pressures of the liquid and the solid at the interface. In expression (4) the index 1 refers to the solid phase and 2 to the liquid one.  $\Delta p$  is the surface force at the phase boundary. This value is equal to

$$\Delta p = -\frac{\varepsilon_1 - \varepsilon_2}{8\pi} \left( E_t^2 + E_n^2 \frac{\varepsilon_1}{\varepsilon_2} \right) \quad (5)$$

where  $E_t$  and  $E_n$  are tangential and normal components of the electrical field strength;  $E_1^2 = E_t^2 + E_n^2$  and  $E_2^2 = E_t^2 + E_n^2 \varepsilon_1^2 / \varepsilon_2^2$  are the total electrical field strengths at the solid and liquid phase boundaries respectively.

This surface force occurs only at the interface, depends on the local values of the parameters and must be compensated by strengths providing equilibrium of the substance as a whole—for example, due to the change of the hydrostatic pressure of the liquid at the interface [22].

Assuming that the Clausius–Mosotti law is valid, we can write the pressures in the liquid and the solid at the phase boundary in the form

$$p_2 = p_0 + \frac{E_2^2(\varepsilon_2 - 1)(\varepsilon_2 + 2)}{24\pi} \quad (6)$$

$$p_1 = p_0 + \frac{E_1^2(\varepsilon_1 - 1)(\varepsilon_1 + 2)}{24\pi} \quad (7)$$

where  $p_0$  is the pressure in the absence of the field.

As is known [7], the full chemical potentials of the phases, including the additional field component, at the phase boundary must be equal. Let us write this condition for our case:

$$\mu_1(p_1) - \frac{E_1^2}{8\pi} \left( \frac{\partial \varepsilon_1}{\partial \rho_1} \right)_T = \mu_2(p_2) - \frac{E_2^2}{8\pi} \left( \frac{\partial \varepsilon_2}{\partial \rho_2} \right)_T \quad (8)$$

where  $\mu_1(p_1)$  and  $\mu_2(p_2)$  are the chemical potentials of the phases under pressures  $p_1$  and  $p_2$  respectively. Using (6), (7), (8) and the fact that the chemical potential for condensed matter is practically proportional to pressure and expanding the chemical potential  $\mu_1$  in (8) into a Taylor series at the point  $p_1 = p_2$ , instead of (8) we obtain the following expression:

$$\mu_1(p_2) - \mu_2(p_2) = \frac{E_2^2(\varepsilon_2 - 1)(\varepsilon_2 + 2)}{24\pi} \left( \frac{1}{\rho_1} - \frac{1}{\rho_2} \right). \quad (9)$$

Let us take a look at figure 3. We would like to obtain the liquid phase in the presence of the field in the domain of pressure lying to the left of the gas chemical potential dependence (line 3). The gas chemical potential at this value of temperature is practically a vertical line under pressure  $p_g \simeq 0$ . So the liquid-phase pressure has to be at least positive. In this case, the gas phase cannot be formed.

Then from (9) we can find the electrical field strength, provided that we have at least positive values of  $p_2 \geq 0$ . Assuming that  $E_t = 0$ , we obtain

$$E_n = \frac{\varepsilon_2}{\varepsilon_1} \sqrt{\frac{24\pi \Delta\mu \rho_1 \rho_2}{(\varepsilon_2 - 1)(\varepsilon_2 + 2)(\rho_1 - \rho_2)}} \quad (10)$$

where  $\Delta\mu = \mu_2(p_2) - \mu_1(p_2)$  is the chemical potential difference.

For hydrogen, the values are  $\varepsilon_1 \simeq 1.3$ ,  $\varepsilon_2 \simeq 1.25$ ,  $\rho_1 = 0.087 \text{ g cm}^{-3}$  and  $\rho_2 = 0.078 \text{ g cm}^{-3}$ , taken from [8]; the value of the chemical potential difference at  $T \simeq 1 \text{ K}$  and pressure about zero taken from figure 3 is equal to  $\sim 10 \text{ K}$ . Substituting all of these values in (10), we obtain  $E_n \sim 5 \times 10^7 \text{ V cm}^{-1}$ . At such values of the electrical field strengths and temperatures, we can expect hydrogen to remain liquid and enter a superfluid state.

A serious obstacle to this is the possible breakdown of the dielectric. We do not know the breakdown strength for hydrogen under such conditions. So we can use only indirect data. According to [23], the breakdown strength may never exceed  $1 \times 10^6 \text{ V cm}^{-1}$  in liquid helium and  $1 \times 10^7 \text{ V cm}^{-1}$  in liquid nitrogen. These values are less than is necessary for our goals. However, if a pulse voltage is used, the breakdown strength can increase [24]. There are also other methods of improving the electrical strength.

## 5. Discussion

We have developed a thermodynamical model based on tabulated data for hydrogen thermodynamical functions along the lines of coexisting phases. This model makes it possible to calculate thermodynamical functions in the metastable domain. The predictions of this model in the stable domain are in good agreement with experimental data relating both to liquid and to solid hydrogen

The relative positions of the liquid–gas spinodal, the melting line and the  $\lambda$ -transition line exclude the possibility of superfluid hydrogen production through supercooling under negative pressures.

In the presence of an excess pressure acting only on the solid phase, coexistence of a two-phase solid–liquid equilibrium system is possible at temperatures corresponding to the expected  $\lambda$ -transition. Therefore the stable phase of deeply supercooled liquid  $\text{H}_2$  may be superfluid. However, the necessary values of this excess pressure are of the same order as the hydrogen failure limit.

To stabilize the two-phase solid–liquid hydrogen at  $T \sim 1 \text{ K}$ , an external electrical field can be used. The values of electrical field strength needed have to be of the order of  $\sim 5 \times 10^7 \text{ V cm}^{-1}$  and can exceed the breakdown strength, although direct measurements of the latter are unavailable.

Note further that, in the case of both mechanical and field compression of crystal, the intensity of the external effect on the liquid–solid two-phase system which is required to attain the parameters of the expected  $\lambda$ -transition in liquid hydrogen proves to be close to the limits of its mechanical or electric strength. However, the values of the excess pressure on the solid phase and the electrical field strength that are needed can be decreased if a combination of the suggested methods of compression (excess pressure on the solid phase together with an electrostatic field) is used.



To create a one-sided pressure on the solid phase, we can use, for example, a porous piston with a pore size of less than the critical wavelength of the liquid–solid interface instability, as discussed in [25]. Our estimations show that the pore has to be less than  $\sim 0.2 \mu\text{m}$ . For the liquid hydrogen, this pore piston will be permeable, but propagation of the solid–liquid interface inside the porous space makes permeability difficult to achieve if the pore size has this or a lower value.

To detect experimentally whether the liquid inside the porous space is superfluid we can use, for example, the sharp increase of the effective thermal conductivity of the porous body filled with liquid hydrogen at the transition point.

The possibility of practical realization of the methods suggested above depends on how surmountable the difficulties involved prove to be.

### Acknowledgments

We would like to thank Academician V L Ginzburg and participants of his seminar, especially A A Sobyenin and S M Apenko, who attracted our attention to this problem. This study was supported by the Russian Foundation for Basic Research, Projects No 99-02-16596 and No 99-02-16619.

### Appendix

#### A.1. The thermodynamic model of the solid phase

Following [10, 11] we will write the expression for the free energy per unit mass for the solid phase in the form

$$F_s = F_T(v, T) + U_s(v) \quad (\text{A.1})$$

where  $F_T$  is the thermal component of the energy and  $U_s(v)$  is the elastic (cold) component including the contribution of zero-point oscillations. We will write the former in the Debye approximation:

$$F_T = \frac{T}{m} \left[ 3 \ln(1 - e^{-\Theta_D/T}) - D\left(\frac{\Theta_D}{T}\right) \right] \quad (\text{A.2})$$

where  $m$  is the mass,  $T$  is the temperature,  $v$  is the specific volume,  $\Theta_D$  is the Debye temperature. The latter depends on the specific volume thus:

$$\Theta_D = \Theta_{0s} \exp\left(-\int_{v_0}^v \Gamma \, d \ln v\right). \quad (\text{A.3})$$

Here,  $\Theta_{0s}$  is the Debye temperature for  $T = 0$ , when  $v = v_0$ ,  $\Gamma$  is the Grüneisen coefficient and

$$D(x) = \frac{3}{x^3} \int_0^x \frac{y^3 \, dy}{e^y - 1} \quad (\text{A.4})$$

is the Debye function.

The expressions for the entropy and pressure following from (A.1) take the forms

$$S = \frac{k}{m} \left[ 4D\left(\frac{\Theta_D}{T}\right) - 3 \ln(1 - e^{-\Theta_D/T}) \right] \quad (\text{A.5})$$

$$p = \frac{3T\Gamma}{mv} D\left(\frac{\Theta_D}{T}\right) + \Pi_s(v) \quad (\text{A.6})$$

where

$$\Pi_s(v) = -dU_s(v)/dv \quad (\text{A.7})$$

is the elastic (cold) component of the pressure.

### A.2. The thermodynamical model of the liquid phase

We will write the expression for the free energy per unit mass for the liquid phase in the form [10, 11]

$$F_l = F_T(v, T) + U_l(v) + F_c. \quad (\text{A.8})$$

The thermal component  $F_T$ , describing the vibrations of molecules in the vicinity of the position of equilibrium, takes, as for solid phase (10), but with the effective Debye temperature, the form

$$\Theta = \Theta_D(1 + L) \quad (\text{A.9})$$

where

$$L = \frac{h\sqrt{T}}{(2\pi mk)^{1/2}(g_a m v)^{1/3}\Theta_D} \quad (\text{A.10})$$

is the generalized Lindeman parameter. In (A.10),  $g_a$  is the statistical sum for the gas atoms.

We also assume that solid and liquid phases are described by the unified volume dependence of the Debye temperature  $\Theta_D(v)$ . Its variation during the solid–liquid transition will correspond to the change of  $\Theta_D$  from the value  $\Theta_D(v_s)$  to  $\Theta_D(v_l)$ .

The quantity  $F_c$  in (A.8) is the configuration component of the free energy, which serves as a measure of the liquid disorder. In contrast to [10], here we use a somewhat different expression for this component:

$$F_c = -\frac{T_s}{m} \left[ 1 - D\left(\frac{\Theta}{T}\right) \right] \quad (\text{A.11})$$

where the dimensionless quantity  $s$  of the order of unity may be referred to as the residual entropy of liquid.

The value  $F_c \rightarrow -T_s/m$  when  $T \rightarrow 0$  and  $F_c \rightarrow 0$  when the density and temperature increase. The Debye function in expression (A.3) is appropriate here, because it is in the conventional Debye approximation.

Correspondingly, the expression for the configuration component of the entropy has the form

$$S_c = \frac{ks}{m} \left[ 1 + 2D - \frac{3\Theta}{T(e^{\Theta/T} - 1)} \right]. \quad (\text{A.12})$$

The elastic component of the free energy for liquid differs from that for solid. This difference is due to the different natures of liquid and solid states. In particular, the density and evaporation energy of liquid and solid both slightly differ. The expressions for the entropy and pressure following from (A.8) take the forms

$$S = \frac{k}{m} \left\{ 4D\left(\frac{\Theta}{T}\right) \left[ 1 - \frac{3L}{8(1+L)} \right] - 3 \ln(1 - e^{-\Theta/T}) + s \left[ 1 + 2D\left(\frac{\Theta}{T}\right) - \frac{3\Theta}{T(e^{\Theta/T} - 1)} \right] \right\} \quad (\text{A.13})$$

$$p = \frac{3T}{mv} \left[ D\left(\frac{\Theta}{T}\right) (1 - s) + s \frac{\Theta}{T(e^{\Theta/T} - 1)} \right] \frac{\Gamma + L/3}{1 + L} + \Pi_l(v) \quad (\text{A.14})$$

where

$$\Pi_l(v) = -dU_l(v)/dv. \quad (\text{A.15})$$

It may readily be shown that the free energy (A.8), entropy (A.13) and pressure (A.14) in the limit  $L \rightarrow \infty$  become the respective expressions for the ideal gas. On the other hand, the entropy of deeply supercooled liquid in the limit  $T \rightarrow 0$  remains finite, similarly to the entropy of amorphous solids. Its value is equal to  $ks/m$ . Nevertheless the derivative  $(\partial P/\partial T)_V = 0$  when  $T = 0$ —that is, the liquid entropy tends to a constant limit (not equal to zero) when  $T \rightarrow 0$ .

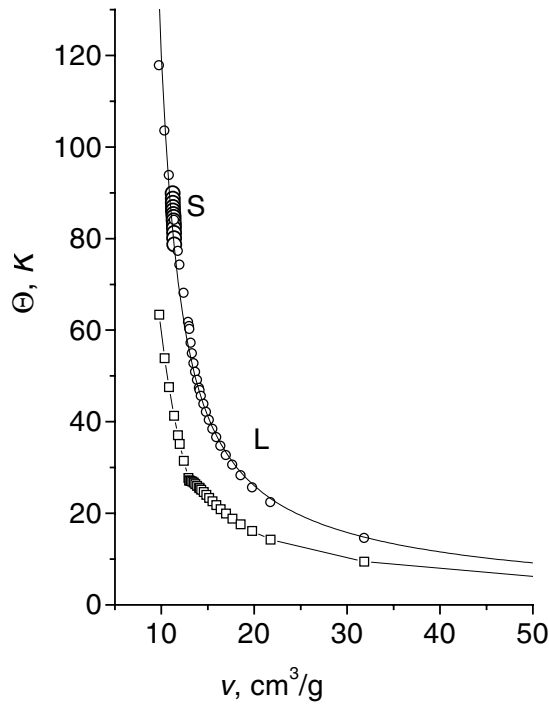
### A.3. Determination of the volume dependence of the Debye temperature and the residual entropy

The thermodynamical model described above fails to define the volume dependence of the Debye temperature, the parameter  $s$  in the configuration component of the free energy and the cold curves for the solid and liquid phases. As in [11], let us find these quantities from the condition of correspondence of the thermodynamics constructed using formulae (3)–(10) and (A.1)–(A.7) with tabulated data along coexisting lines of different phase states. We use thermodynamical functions for hydrogen tabulated in [8] and reconciled with the entire body of experimental data on the thermodynamical properties of hydrogen. We equate the entropy, calculated for the solid phase using (A.5) and for the liquid phase using (A.13), to the tabulated values. The value of  $\Theta_D(v)$  was found numerically from the equation thus obtained. This procedure was carried out for all five coexistence curves—namely, the sublimation, solidification, melting, evaporation and condensation curves. The results are presented in figure A1, which shows the dependence  $\Theta_D$  on  $v$ .

The open-square symbols show tabulated data for along coexisting lines for the liquid state, corresponding to the case of  $s = 0$ —that is, the absence of the configuration entropy. The large open circles show tabulated data for along the sublimation and solidification lines for the solid state. As one can see, without the configurational entropy, the solid–liquid transition is accompanied by a drastic jump of the Debye temperature. It is hard to explain this jump from the physical standpoint, because the loss of long-range order in the crystal cannot affect the vibration frequency of atoms in the neighbourhood of the position of equilibrium so radically (this circumstance is pointed out in Frenkel's monograph [26]). These positions depend, first and foremost, on the immediate environment of the atom, also changing during the transition to the liquid state, but not so strongly.

If we now consider non-zero configuration entropy, the situation will change. The results of the calculation for  $s = 0.72$  are plotted with small open circles. In this case, the Debye temperature varies continuously in all states of matter. The value found,  $s \cong \ln 2$ , does not run counter to the grid model [27], whereby the value of  $s$  for crystal is equal to 0 and for ideal gas to 1. Some intermediate value should be realized for the liquid, which is difficult to calculate exactly and, as noted in [27], 'the question of collective entropy of the liquid state remains unclear'. The fact that the excess entropy of liquids in comparison with solid is approximately equal to  $\ln 2$  for the same values of the specific volumes has been noted in [28]. In recent work [16], Wallace notes that the entropy of melting contains a universal disordering contribution of  $\sim 0.8$ . He suggests that liquid consists of a universal number of random structural valleys. It is of interest that the value that he proposed is close to the value that we found here.

One can see that, in such a wide region of volume variation, the Debye temperature is a monotonically decreasing function of volume, which may be approximated by a simple



**Figure A1.** The universal dependence of the Debye temperature on the specific volume. Large open circles correspond to values of the Debye temperature found from the tabulated data for the solid state. Open squares correspond to values for the liquid state with the value of  $s = 0$ . Small open circles correspond to the Debye temperature values found from the tabulated data for the liquid state with the value of  $s = 0.72$ . The continuous lines show the approximation (A.16).

formula. Such an approximation can be written as

$$\Theta(v) = 120 \times \frac{10}{v} \exp \left\{ 2.75 \left[ \left( \frac{10}{v} \right)^{2.83} - 1 \right] / 2.83 \right\} \text{ K.} \quad (\text{A.16})$$

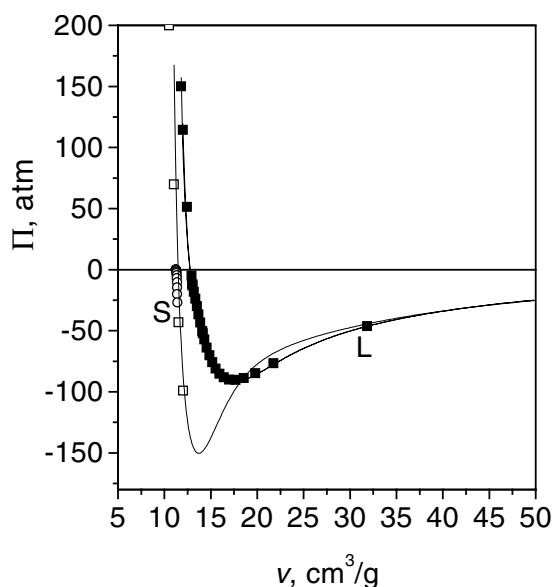
The Grüneisen coefficient is found as a logarithmic derivative from the Debye temperature dependence. From (A.16) it follows that

$$\Gamma(v) = 1 + 2.75 \left( \frac{10}{v} \right)^{2.83}. \quad (\text{A.17})$$

The expressions (A.16), (A.17) are valid while  $v \geq 11 \text{ cm}^3 \text{ g}^{-1}$ . The approximation curves for the Debye temperature calculated using (A.16) are plotted in figure A1 as a continuous curve without points. As is clear from figure A1, the approximation curves are fairly similar to those obtained from the tabular data.

#### A.4. Determination of the elastic components of the energy and pressure

The information on the volume dependencies of  $\Theta_D$  and  $\Gamma$  makes it possible to calculate the thermal components of the pressure, (A.6) and (A.14). In this case, the elastic component of the pressure may be determined as a difference between the tabular values of the pressure on the phase coexistence lines and the thermal components calculated. The results for cold pressure obtained thus are plotted in figure A2. The tabulated values correspond to open circles

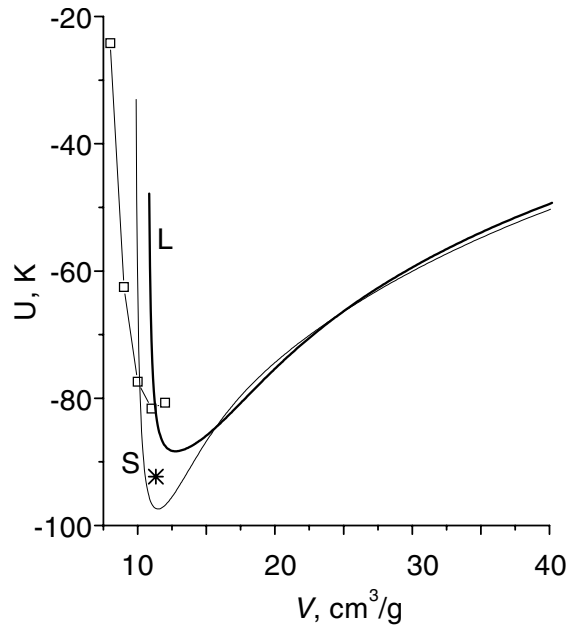


**Figure A2.** The dependence of the elastic (cold) pressure for the solid and liquid phases on the specific volume. The open circles represent the tabulated data for the solid phase. The solid squares represent the tabulated data for the liquid phase. The open squares correspond to experimental data [29]. The continuous lines are constructed on the basis of expression (A.18).

and solid squares for liquid. For the solid phase (S), this method enables one to obtain only a section of the cold pressure curve because the tabular data terminate at the triple point with the maximum possible volume for the solid phase. Using the method described in [11], we can restore the full cold curve for the solid phase, also shown in figure A2. This curve passes through the tabulated values for the solid phase. For the liquid (L), the data for the pressure on the lines of melting, saturation and condensation permit the cold curve to be fully restored. The liquid cold curve intersects the axis of volumes at the point  $v_{0l} = 12.76 \text{ cm}^3 \text{ g}^{-1}$ , which is somewhat greater than the value in the analogous case for a solid ( $v_{0s} = 11.48 \text{ cm}^3 \text{ g}^{-1}$ ). The open squares in figure A1 present experimental data for solid hydrogen [29]. The latter correlate well with our calculations.

A method for constructing curves for cold energy from the cold curves for pressure is described in [11]. The approximation curves for cold energies for  $T = 0$ , corresponding to those for cold pressure, are shown in figure A3. They have minima at the points  $v_{0l}$  and  $v_{0s}$ , equal to  $q_{0l}$  and  $q_{0s}$  respectively. The solid phase has a deeper minimum than the liquid one. This means that the solid state for  $T = 0$  is more advantageous thermodynamically than the liquid one. The line connecting open squares represents the variational calculations of [30]. The asterisk plots the experimental value of the hydrogen energy obtained in [31]. This value is in reasonable agreement with our calculations.

Quantum effects are known to reduce the internal energy very drastically. If quantum effects for hydrogen were absent, then the maximal depth of the energy would equal  $\sim 6D$ , where  $D$  is the depth of the pair molecular potential. This relation is valid for systems with a short-range potential when the law of corresponding states holds. For hydrogen,  $D = 37 \text{ K}$ , so the maximal depth of the energy must equal approximately  $-222 \text{ K}$ . Instead, we have only the value  $-92 \text{ K}$ . The difference of these two values emphasizes the role of quantum effects for molecular hydrogen.



**Figure A3.** The dependence of the elastic (cold) energy for the solid and liquid phases on the specific volume. Continuous lines show our calculations on the basis of approximation (A.18). The open squares correspond to the variational calculation of [30]. The asterisk is the experimental point from [31].

The cold curves for the pressure and energy that we found can be approximated by the expression

$$U = -q_0 \frac{1 + a_1 x + a_3 x^3}{1 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4} \quad (\text{A.18})$$

where

$$x = v/v_0 - 1. \quad (\text{A.19})$$

In table A1, we give the values of the constants contained in expression (A.18).

**Table A1.**

Phase	$q_0$ (J g <sup>-1</sup> )	$a_1$	$a_2$	$a_3$	$a_4$	$v_0$ (cm <sup>3</sup> g <sup>-1</sup> )
Solid	402.5	6.38	3.977	25.95	9.53	11.48
Liquid	365	5.74	1.704	25.55	9.53	12.76

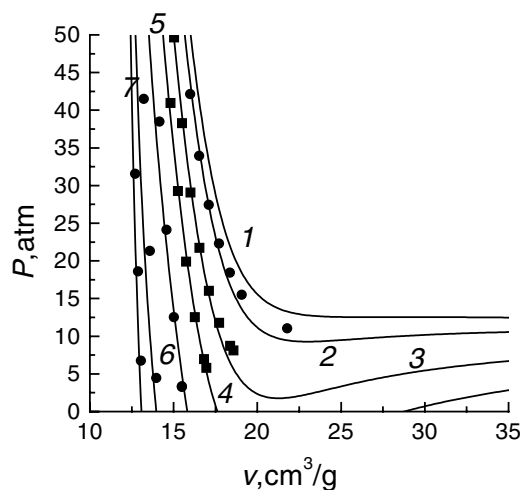
The cold pressure curve may be found from (A.18) by simple differentiation.

So we find the dependence of the Debye temperature and potential parts of the energy and the pressure on the volume using tabulated values of the entropy and pressure for along coexisting lines of different phases. We have a full equation of state for hydrogen and we may calculate any thermodynamical function in both stable and metastable domains.

#### A.5. Thermodynamical properties

A test of the accuracy of our calculations can be performed by comparing the calculated isotherms of pressure for the liquid state with experimental data. Such isotherms of pressure

for the liquid state are shown in figure A4. Here you can see the critical isotherm and isotherms for  $T = 33$  K. Experimental data from the works [32–34] with values of the temperature of  $T = 15, 20, 25, 27, 30, 32$  K are also shown in this figure as symbols. Our calculations are presented as continuous lines for the same values of the temperature. The agreement between experimental and calculated values is good.



**Figure A4.** The isotherms of the pressure for different temperatures. 1 is the critical isotherm; 2:  $T = 32$  K; 3:  $T = 30$  K; 4:  $T = 27$  K; 5:  $T = 25$  K; 6:  $T = 20$  K; 7:  $T = 15$  K. The experimental points are obtained from the works [32–34], for the corresponding values of the temperature.

It is significant that the low-temperature-domain thermodynamical properties for both the solid and the liquid phases are determined mainly by the elastic component of the pressure which we found on the basis of experimental data. In this connection, using our model for the calculation of thermodynamical functions at low temperatures is quite justified.

## References

- [1] Ginzburg V L and Sobyenin A A 1972 *JETP Lett.* **15** 242
- [2] Maris H J, Seidel G M, and Huber T E 1983 *J. Low Temp. Phys.* **51** 471
- [3] Gordillo M C and Ceperley D M 1997 *Phys. Rev. Lett.* **79** 3010
- [4] Ceperley D M and Gordillo M C 1997 *Proc. Int. Workshop on Condensed Matter Theory* vol 12, ed J W Clark and P Y Plant (New York: Nova Science)
- [5] Gruter P, Ceperley D M and Laloe F 1997 *Phys. Rev. Lett.* **79** 3549
- [6] Aculichev V A and Bulanov V A 1974 *Sov. Phys.–JETP* **38** 329  
Aculichev V A and Bulanov V A 1974 *Sov. Phys.–Acoust.* **20** 107  
Aculichev V A and Bulanov V A 1975 *Sov. Phys.–Acoust.* **20** 501
- [7] Vorob'ev V S and Malysenko S P 1997 *Phys. Rev. E* **56** 3959
- [8] McCarty 1975 *Hydrogen Technological Survey—Thermophysical properties* (Washington, DC: NASA)
- [9] Malysenko S P 1975 *Proc. 5th Symp. on Thermophysical Properties* (Warrendale, PA: ASME)
- [10] Vorob'ev V S 1995 *JETP Lett.* **62** 574  
Vorob'ev V S 1996 *Sov. Phys.–JETP* **82** 85
- [11] Vorob'ev V S 1996 *High Temp.* **34** 391
- [12] Urlin V D 1962 *Sov. Phys.–JETP* **15** 477
- [13] Grover R 1971 *J. Chem. Phys.* **55** 3435
- [14] Djissiere C and Fiorese G 1977 *Revue Phys. Appl.* **12** 857
- [15] Corti D S, Debenedetti P G, Sastry S and Stillinger F H 1997 *Phys. Rev. E* **55** 5522

- [16] Wallace D C 1997 *Phys. Rev. E* **56**
- [17] Apenko S M 1999 *Phys. Rev. B* **60** 3052
- [18] London F 1954 *Superfluids* vol 2 (New York: Dover) chs 4, 5 (reprinted 1964)
- [19] Wilks J 1967 *The Properties of Liquid and Solid Helium* (Oxford: Clarendon)
- [20] Verkin B I (ed) 1984 *Properties of Condensed Phases of Hydrogen and Oxygen* (Kiev: Naukova Dumka) (in Russian)
- [21] Landau L D and Lifshitz E M 1984 *Electrodynamics of Continuous Media* (Oxford: Pergamon)
- [22] Abraham, Becker and Dougall 1932 *The Classical Theory of Electricity and Magnetism* (Oxford: Blackie)
- [23] Gerhold J 1999 *Proc. ICDL'99: 13th Int. Conf. on Dielectric Liquids (Nara, Japan, 20–26 July)* p 365
- [24] Gerhold J, Hubman M and Tesler E 1999 *Proc. ICDL'99: 13th Int. Conf. on Dielectric Liquids (Nara, Japan, 20–26 July)* p 445
- [25] Grinfel'd M A 1986 *Sov. Phys.–Dokl.* **31** 831
- [26] Frenkel Ya I 1955 *Kinetic Theory of Liquid* (New York: Dover) ch 7
- [27] Hill T D 1956 *Statistical Mechanics. Principles and Selected Applications* (New York: McGraw-Hill)
- [28] Stishov C M 1975 *Sov. Phys.–Usp.* **17** 625
- [29] Stewart J W 1955 *Phys. Rev.* **97** 578  
Stewart J W 1956 *J. Phys. Chem. Solids* **1** 146
- [30] Ostgaard E 1972 *J. Low Temp. Phys.* **8** 479
- [31] Simon F 1955 *Z. Phys.* **15** 307
- [32] Goodwin R D 1961 *J. Res. NBS* **65c** 231  
Goodwin R D 1966 *J. Res. NBS* **70a** 541
- [33] Roder H *et al* 1964 *NBS Monograph* No 94 (Washington, DC: US Government Printing Office)
- [34] Goodwin R D, Diller D E, Roder H M and Weber Z A 1962 *J. Res. NBS* **67a** 173