Statistical Thermodynamics of the λ Transition in Liquid Helium[1]

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Abstract: The statistical thermodynamics of the λ transition in liquid helium is treated by means of an isothermal-isobaric partition function, Z. It is assumed that we can write $Z = Z_l Z_s$, where Z_l is a lattice factor and Z_s an order–disorder factor. Z_s describes the anomalies at the λ transition and depends on an enthalpy or free enthalpy parameter J/kT. In turn J depends only on the pressure, P. Since $J^{-1}(dJ/dP) = T_\lambda^{-1}(dT_\lambda/dP)$, it is then shown that the behavior of the specific heat at constant volume C_v can be followed, and its value along the λ line predicted in terms of dT_λ/dP and the *lattice* contributions to various thermodynamic properties, especially the compressibility. The results compare very favorably with the purely thermodynamic calculation of C_v from properties of the λ line only.

As is well known, liquid helium undergoes a λ transition, which results from a cooperative order–disorder phenomenon involving the localized excitations called rotons. Pressure (P) and molal volume (V) are secondary variables so far as this transition is concerned. They are, however, variables which can be controlled by the experimenter, in contrast with the hidden order–disorder variables. Thus the specific heat may be measured at constant pressure (C_p) or constant volume (C_v). In liquid helium C_p appears to tend to infinity as any point on the locus of the λ transition is approached.[1] The thermodynamics of this situation has been discussed a number of times;[3-7] one conclusion is that no thermodynamic instability results, in contrast to the situation when C_v tends to become infinite. The behavior of C_v when C_p becomes infinite is a matter of some interest, and will be the principal subject of this paper.

The order–disorder phenomenon in liquid helium can be thought of as somewhat analogous to that of an Ising lattice. This is a very rough picture, but will be sufficient for the present purposes, in which not much detail is required. There will be an energy factor, J, analogous to the difference in energy of parallel and antiparallel neighbors in the Ising lattice; if it is C_p which becomes infinite, J will be assumed to be a function of P only and it should be an enthalpy rather than an energy, since it will refer to a process at constant pressure.[7]

We then set up an isobaric–isothermal partition function

$$Z = \sum_L \exp(-H_L/kT) \tag{1}$$

where H_L is the enthalpy of the Lth state of the assembly; and we make the assumption that Z can be factored

(1) This work was supported by the Army Research Office, Durham, and the Advanced Research Projects Agency.
(2) W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, Proceedings of the Fifth International Conference on Low Temperature Physics, Madison, Wis., 1957, p 50; C. F. Kellers, Ph.D. Thesis, Duke University, 1960.
(3) O. K. Rice, *J. Chem. Phys.*, **22**, 1535 (1954).
(4) A. B. Pippard, *Phil. Mag.*, **1**, 473 (1956); "Elements of Classical Thermodynamics," Cambridge University Press, Cambridge, 1957, Chapter 9.
(5) M. J. Buckingham and W. M. Fairbank in "Progress of Low Temperature Physics," Vol. III, C. J. Gorter, Ed., North Holland Publishing Co., Amsterdam, 1961, p 80 ff.
(6) C. W. Garland and R. Renard, *J. Chem. Phys.*, **44**, 1120 (1966), and following articles.
(7) O. K. Rice, *Phys. Rev.*, **153**, 275 (1967).

into two parts, $Z = Z_l Z_s$, where Z_l depends upon lattice functions (involving the phonons in liquid helium) and Z_s is the "spin" part (involving the rotons). Z_s is the factor which exhibits the anomaly which results in the λ transition and it depends only on $I = J/kT$. We shall show that this set of assumptions, which has been previously discussed,[7] is adequate to account for the behavior of C_v.

It has been shown[7] that these assumptions result in the following equations (in which the contributions to the thermodynamic functions are divided into lattice parts, subscript l, and spin parts, subscript s)

$$C_p = C_{p,l} + C_{p,s}$$
$$= C_{p,l} - (Z_s'/Z_s)^2 J^2/kT^2 + (Z_s''/Z_s)J^2/kT^2 \tag{2}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\partial V}{\partial P}\right)_{T,l} - \frac{T}{J^2}\left(\frac{dJ}{dP}\right)^2 C_{p,s} + \frac{H_s d^2J}{J\, dP^2} \tag{3}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_{P,l} + \frac{C_{p,s}}{J}\frac{dJ}{dP} \tag{4}$$

where H stands for molal enthalpy.

If we divide eq 3 by eq 4 we see, since $(\partial P/\partial T)_V$ approaches $dP_\lambda/dT = (dT_\lambda/dP)^{-1}$ along the λ line, that

$$J^{-1}(dJ/dP) = T_\lambda^{-1}(dT_\lambda/dP) \tag{5}$$

(Note that only the $C_{p,s}$ terms on the right-hand side need to be considered at the λ point.) This enables us to evaluate dJ/dP.

With a simple Ising-type model, eq 5 would imply that the roton part of the entropy would be constant along the λ line. Table I shows this not to be true; though the change is in the right direction to be accounted for by the phonon entropy (contrary to our earlier statement[7]), it seems much too large. This is based on the assumption that J is a true enthalpy; if it, itself, has some of the character of a free enthalpy, the situation would be more complicated.

The last term in eq 3 is always relatively small compared to $(\partial V/\partial P)_{T,l}$, and it varies more slowly than the term containing $C_{p,s}$. We shall write

$$(\partial V/\partial P)_{T,0} = (\partial V/\partial P)_{T,l} + (H_s/J)(d^2J/dP^2) \tag{6}$$

In order to study C_v we use the thermodynamic relationship

$$C_v = C_p + T(\partial V/\partial T)_P^2(\partial P/\partial V)_T \tag{7}$$

Table I. Calculation of $C_{V,\lambda}$ from Eq 10

T_λ, °K	ρ_λ,[a] g cm^{-3}	P_λ, atm	$-dP_\lambda/dT$, atm deg^{-1}	$-d\rho_\lambda/dT$, g cm^{-3} deg^{-1}	$T_\lambda(dS_\lambda/dT)$, cal[b] mole^{-1} deg^{-1}	$C_{V,\lambda}$, cal mole^{-1} deg^{-1}
2.172	0.1461	0.050	111.1	0.234	4.3	261
2.000	0.1670	14.69	73.0	0.0767	1.7	40.7
1.762	0.1804	29.81	55.0	0.0421	1.0	13.2

^{a} ρ is density. ^{b} 1 cm^3 atm = 0.02421 cal.

Table II. Calculation of $C_{V,\lambda}$ from Eq 9

		A. Calculation of a			
T_λ, °K	c,[a] msec^{-1}	$c^{-1}(dc/dP)$, atm^{-1}	κ_T,[b] atm^{-1}	$\partial(V/\partial T)_{P,1}$, cm^3 mole^{-1} deg^{-1}	$-a$, cal mole^{-1} deg^{-1}
2.172	238	0.0353	0.0118	0.304	3.5
2.000	323	0.0144	0.0060	0.035	0.2
1.762	384	0.0102	0.00425	0.008	0.0

			B. Calculation of b and $C_{V,\lambda}$			
T_λ, °K	$-(\partial V/\partial P)_{T,1}$, cal atm^{-2} mole^{-1}	H_s, cal mole^{-1}	$-T_\lambda^{-1}(d^2T_\lambda/dP^2)$, atm^{-2} ($\times 10^4$)	$-(\partial V/\partial P)_{T,0}$, cal atm^{-2} mole^{-1}	$-b$, cal mole^{-1} deg^{-1}	$C_{V,\lambda}$, cal mole^{-1} deg^{-1}
2.172	0.00782	2.68	2.85	0.00858	230	233
2.000	0.00348	2.10	1.21	0.00373	40	40
1.762	0.00228	1.58	2.55	0.00268	14.3	14.3

^{a} c is velocity of sound. ^{b} κ_T is isothermal compressibility.

and substitute from eq 3 and 4, using eq 5 and 6. It has been noted that the second term on the right-hand side of eq 4 is relatively large compared to the first, even several tenths of a degree from the λ line, so in squaring $(\partial V/\partial T)_p$ we shall neglect $(\partial V/\partial T)_{p,1}{}^2$. We thus get, for a given P

$$C_v = C_{p,1} + C_{p,s}\left[1 - \frac{1 + a/C_{p,s}}{1 - b/C_{p,s}}\right] \quad (8)$$

where

$$a = 2T_\lambda(\partial V/\partial T)_{P,1}(dP_\lambda/dT)$$

and

$$b = T_\lambda(\partial V/\partial P)_{T,0}(dP_\lambda/dT)^2$$

In the equations for a and b we have set $T = T_\lambda$.

In previously discussing the behavior of C_v we made approximations which were somewhat too drastic.[7] We shall therefore start afresh. We first note that along the λ line, where $C_{p,s}$ is infinitely large, eq 8 reduces to

$$C_{v,\lambda} = C_{p,1} - a - b \quad (9)$$

$C_{p,1}$, which would be the phonon specific heat, is entirely negligible at the λ point.

There is a thermodynamic equation for $C_{v,\lambda}$, derived by Buckingham and Fairbank,[5,8] shown by eq 10.

$$C_{v,\lambda} = T_\lambda(dS_\lambda/dT) - T_\lambda(dV_\lambda/dT)(dP_\lambda/dT) \quad (10)$$

Although dP_λ/dT is involved in both equations, it is seen that in general they depend on different quantities, and it will therefore be of interest to compare them. It is to be noted that eq 9 connects the value of C_v along the λ line with the "lattice" properties of the liquid helium. These properties will be evaluated in the same way used before.[7] The compressibility does not vary greatly with temperature away from the λ line, and we shall use values of $(\partial V/\partial P)_{T,1}$ at 1.30°K or below.[9]

(8) A derivation was suggested in section 3 of ref 7. In the second line following eq 29 of ref 7, the word "finite" should read "infinite."

(9) C. Baghosian and H. Meyer, *Phys. Rev.*, **152**, 200 (1966); D. L. Elwell and H. Meyer, *ibid.*, **164**, 245 (1967).

The value of H_s, which brings in a relatively small correction for the calculation of $(\partial V/\partial P)_{T,0}$, was obtained for the normal λ point from the roton part of the specific heat.[10] Elsewhere along the λ line it was calculated from the values of the entropy,[11] assuming H_s is proportional to $T_\lambda S_\lambda$. Since the specific heat peaks at the λ point we may write, roughly

$$S_\lambda = \int_0^{T_\lambda}(C_p/T)dT \approx T_\lambda^{-1}\int_0^{T_\lambda}C_p dT = T_\lambda^{-1}H_\lambda$$

$(\partial V/\partial T)_{P,1}$ was calculated from Atkins' formula[12] using data from Atkins and Stasior.[13] Finally dV_λ/dT and dP_λ/dT were obtained from the data of Kierstead.[14] For dS_λ/dT, which does not contribute greatly to the result, we used the values quoted by Buckingham and Fairbank[5] from Lounasmaa and Kojo.[11] The calculations are shown in Tables I and II.

The agreement between the two methods of calculating $C_{v,\lambda}$ is remarkably good, and may be taken as indicating that it is legitimate to separate the partition function into the "lattice" and "spin" factors.

The behavior of C_v as the λ point is approached may be inferred from eq 8. Since b is much greater in absolute value than a, the last fraction in eq 8 will be negligible until C_p begins to become comparable with b. Up to this point C_v will parallel C_p closely, and since b is rather large this will continue close to the λ point. Only near the upper end of the λ line may the difference be readily observed experimentally. When C_p becomes comparable to b, then C_v will gradually fall away from C_p, approaching its constant value on the λ line. From eq 8 it can be shown that if C_p approaches infinity logarithmically C_v has a cusp.

(10) H. C. Kramers, J. D. Wasscher, and C. J. Gorter, *Physica*, **18**, 329 (1952).

(11) O. V. Lounasmaa and E. Kojo, *Ann. Acad. Sci. Fennicae, Ser. A VI*, No. 36 (1959); O. V. Lounasmaa, *Cryogenics*, **1**, 212 (1961).

(12) K. R. Atkins, "Liquid Helium," Cambridge University Press, Cambridge, 1959, p 65.

(13) K. R. Atkins and R. A. Stasior, *Can. J. Phys.*, **31**, 1156 (1953); or see ref 12, p 130.

(14) H. Kierstead, *Phys. Rev.*, **162**, 153 (1967).

Finally, we should remark that Kierstead[15] has shown that $(\partial V/\partial P)_T$ shows a logarithmic rise near the λ line, and that $(\partial V/\partial P)_T$ appears to begin to depart from $(\partial V/\partial P)_{T,1}$ perhaps 0.1° below the λ line. As shown in ref 7, we should expect $(\partial V/\partial T)_P$ to begin to follow the

(15) H. Kierstead, Phys. Rev., 153, 258 (1967).

specific heat much sooner than $(\partial V/\partial P)_T$; some further analysis of the situation would be in order.

The Interaction of Mercury 6(^{3}P$_1$) Atoms with Noble Gas Atoms

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Abstract: The interaction of Hg 6(^{3}P$_1$) atoms with noble gas atoms results in the formation of loosely bonded diatomic van der Waals molecules. Radiative decay of these excited molecules gives rise to an intense band emission. The kinetics of band emission obey the Stern–Volmer relation, indicating that molecule formation is a second-order process (in the 0–60 Torr pressure range) and making it possible to derive rate constants and cross sections for the quenching reactions of noble gas atoms. Lennard-Jones potential energy calculations show that crossings of excited- and ground-state potential energy curves of the van der Waals molecules occur at molecular compressions with prohibitively high repulsion energies. It is proposed that quenching of Hg 6(^{3}P$_1$) atoms by noble gas atoms occurs exclusively by radiative dissipation of excitation energy and not by the crossing mechanism proposed by Jablonski.

The quenching of Hg 6(^{3}P$_1$) atoms by noble gas atoms has been studied since the early days of mercury photosensitization.[1-3] The reaction is very inefficient, hardly measurable by the phosphorescence method, and hence reliable rate constants were difficult to determine. Olsen[4] succeeded in obtaining rate constants from measurements of the depolarization of the mercury resonance line. The quenching cross sections found for He and Kr were "negligible" while those of Ne and Ar were 0.325 and 0.222 Å^2, respectively.

These reactions have been considered to be examples of total "physical" quenching of excited mercury atoms.[5-7] According to Jablonski, the quenching occurs via the crossing of the repulsive potential curves representing the excited mercury atom–ground-state noble gas atom, and ground-state mercury–ground-state noble gas atom systems. The crossing would occur at potential energies slightly exceeding 112.7 kcal, the excitation energy of the mercury atom, and therefore quenching occurs only when the colliding atoms have sufficient translational energy to overcome the barrier. The crossover would be facilitated by heavy atom perturbations. After crossover the electronic excitation of the mercury atom would be converted into the translational energy of the departing atoms. This mechanism predicts a positive temperature coefficient for the quenching reactions and appears to be supported by

Oldenberg's observation that the quenching cross section of argon increases by a factor of ~4 in going from room temperature to 750°.

This interpretation of the quenching mechanism does not take account of the important observation made by Oldenberg[1] that resonance irradiation of mercury–noble gas mixtures gives rise to a number of intense fluorescence bands, appearing on both sides of the mercury resonance line. With the lighter gases only one maximum appeared on the short-wavelength side of the 2537-Å line, while the heavier gases, notably argon, krypton, and xenon, gave two broad, diffuse maxima. (More recently, a third band has been found for the Hg–Kr system.[8]) In addition to these continua, Oldenberg detected discrete band structures displaced toward the red when argon or krypton were used with mercury.

The origins of these spectra were interpreted in terms of loosely bonded van der Waals molecules formed between mercury and noble gas atoms. In a recent article, Fiutak and Frackowiak[9] discuss the electronic correlation and potential energy relations of the Hg–Ar van der Waals molecule. The closed shells of the separate atoms [Ar + Hg] are unperturbed by molecule formation and therefore only the outer two electrons of mercury need be considered. This leads to the following electronic configurations and term types of the molecule.

[closed shell] $(x\sigma)^2$ $^1\Sigma^+$ ground state

[closed shell] $(x\sigma)(y\sigma)$ $^1\Sigma^+$, $^3\Sigma^+$ ⎫
                                  ⎬ excited states
[closed shell] $(x\sigma)(v\pi)$ $^1\Pi$, $^3\Pi_r$ ⎭

The triplet excited states for large internuclear separations split into $\Omega = 0^-$, 0^+, and 1 states, the first of

(1) O. Oldenberg, Z. Physik, 47, 184 (1928); 49, 609 (1928); 50, 580 (1928); 51, 40, 605 (1928); 55, 1 (1929).
(2) H. Kuhn and O. Oldenberg, Phys. Rev., 41, 72 (1932).
(3) A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms," Macmillan and Co., Ltd., London, 1934, p 89.
(4) L. O. Olsen, Phys. Rev., 60, 739 (1941).
(5) A. Jablonski, Z. Physik, 70, 723 (1931).
(6) J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., p 78.
(7) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, New York, N. Y., 1949, p 123.

(8) A. Michels, H. De Kluvier, and D. Middlekoop, Physica, 25, 163 (1959).
(9) J. Fiutak and M. Frackowiak, Bull. Acad. Polon. Sci., Ser. Sci., Math., Astron. Phys., 11, 175 (1963).