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PHYSICAL REVIEW A VOLUME 2, NUMBER 3 SEPTEMBER 1970

Desorption, Vapor Pressure, and Absolute Entropy of Adsorbed Films: Application to He^3 †

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The experimental heat capacities of physically adsorbed films are increased by contributions due to desorption to the vapor phase, and these contributions are usually treated as an experimental nuisance. If the desorption contributions can be isolated from the total heat capacity, the measurements can lead to a model-independent determination of the vapor pressure and heats of adsorption of the film. The theory is applied to recent results on He^3 monolayers. The vapor pressures and heats of adsorption deduced from desorption, together with the measured heat capacities, are used to estimate the absolute entropy of He^3 submonolayers at 0.5 °K.

I. INTRODUCTION

Measurements of the heat capacity of adsorbed films are sometimes complicated by unwanted desorption effects which cause the coverage to be temperature dependent and the total heat capacity to increase above the isosteric value. The equilibrium heat capacity can be corrected to the isosteric value if there are ancillary pressure measurements on the same system. For many experimental systems, the measurement of vapor pressure is relatively simple, but in some cases it is subject to considerable uncertainty arising from large and variable thermomolecular pressure differences. Vapor pressures in themselves yield important information on the thermodynamics of adsorption: If both vapor pressures and heat capacities are known, they can be used to deduce the absolute entropy of the film.

A recent study of the heat capacity of He^3 and He^4 monolayers[1] disclosed exponential increases in the heat capacities of He^3 films at relatively high coverage and temperature, and these increases appeared to have the magnitude and temperature dependence predicted on the basis of simple models of desorption. In this paper, we show that the desorption contribution can be related to the vapor pressure by purely thermodynamic considerations, i.e., without resorting to specific models. As a rough check on the technique, we carried out conventional pressure measurements on the same system.

There are certain obvious advantages to a single technique for obtaining heat capacities and vapor pressures on virtually identical specimens. The technique may be applicable to systems other than helium. In this paper we present the theory relating the vapor pressure to the desorption heat capacity, and we apply it to some recent results on He^3 monolayers.

The calculated pressures, together with the measured heat capacities of the film, provide the basis for a calculation of the excess entropy of the monolayers at $T = 0.5$ °K.

II. THEORY

The condition for equilibrium between the gas and adsorbed film is[2]

$$\frac{\partial F_f}{\partial N_f} = \frac{\partial F_g}{\partial N_g}, \tag{1}$$

where F_f, F_g are the Helmholtz free energies of film and gas, respectively.[3] Partial derivatives are given without subscripts where the variables held constant are obvious, the free energies being the functions $F_g(N_g, V_g, T)$ and $F_f(N_f, A_f, T)$.

The entropies are

$$S_f = -\frac{\partial F_f}{\partial T}, \quad S_g = -\frac{\partial F_g}{\partial T}, \tag{2}$$

and hence $$\frac{\partial S_f}{\partial N_f} - \frac{\partial S_g}{\partial N_g} = -\left(\frac{\partial^2 F_f}{\partial N_f \partial T} - \frac{\partial^2 F_g}{\partial N_g \partial T}\right). \tag{3}$$

The right-hand side of (3) can be simplified by means of (1). We note that (1) is valid only in phase equilibrium, i.e., it remains correct if we change N_f, N_g, and T in such a manner that the equilibrium is maintained. This condition is expressed from (1) by

$$\frac{\partial^2 F_f}{\partial N_f \partial T}\,\delta T + \frac{\partial^2 F_f}{\partial N_f^2}\,\delta N_f - \frac{\partial^2 F_g}{\partial N_g^2 \partial T}\,\delta T - \frac{\partial^2 F_g}{\partial N_g^2}\,\delta N_g = 0.$$

Here two of the increments may be chosen arbitrarily, and the relation then determines the third. One simple choice is to make $\delta N_f = 0$. Then the change of N_g with T reflects the slope of the vapor-pressure curve for constant coverage:

$$\frac{\partial^2 F_f}{\partial N_f \partial T} - \frac{\partial^2 F_g}{\partial N_g \partial T} = \frac{\partial^2 F_g}{\partial N_g^2}\left(\frac{\partial N_g}{\partial T}\right)_{N_f}. \tag{4}$$

If the vapor is a perfect gas, then we have

$$\frac{\partial^2 F_g}{\partial N_g^2} = \frac{kT}{N_g}, \qquad N_g = \frac{pV}{kT}.$$

Then from (3) and (4), we have

$$\frac{\partial S_f}{\partial N_f} - \frac{\partial S_g}{\partial N_g} = k\left[1 - \frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_{N_f}\right]. \tag{5}$$

For S_g, we may use the standard expression for a perfect monatomic gas (omitting, in the case of He^3, the nuclear-spin entropy, which remains constant throughout the temperature range studied):

$$\frac{\partial S_f}{\partial N_f} = k\left[\tfrac{3}{2}\, ln\left(\frac{2\pi mkT}{h^2}\right) + \tfrac{5}{2} - ln\left(\frac{p}{kT}\right) - \frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_{N_f}\right]. \tag{6}$$

This relation gives the partial entropy in terms of the vapor pressure.

The heat capacity of the whole system, film plus vapor, is

$$C = T\frac{\partial S}{\partial T} = C_f + C_d,$$

$$C_d = C_g + T\left(\frac{\partial S_g}{\partial N_g} - \frac{\partial S_f}{\partial N_f}\right)\left(\frac{\partial N_g}{\partial T}\right)_{N_f + N_g}, \tag{7}$$

where C_f is the isosteric heat capacity of the film, i. e., at constant N_f.

In the last term the temperature derivative has to be taken at constant $N_f + N_g$ because, in the experiments referred to, the total quantity of helium in the calorimeter does not change and the amount in the film diminishes as the vapor pressure rises. Now, we have

$$\left(\frac{\partial N_g}{\partial T}\right)_{N_f + N_g} = \left[1 + \left(\frac{\partial N_g}{\partial N_f}\right)_T\right]^{-1}\left(\frac{\partial N_g}{\partial T}\right)_{N_f}. \tag{8}$$

The correction term in the bracket, which depends on the variation of vapor pressure with coverage, is in the present experiments of the order of 1% and therefore negligible. (It could, if necessary, be allowed for by successive approximations.) With this approximation, the ideal gas law, and the substitution of (5) in (7), we obtain

$$C_d = (pV/T)\,\{\tfrac{3}{2} + [(T/p)(dp/dT) - 1]^2\}. \tag{9}$$

The proportionality with the gas volume V may help to distinguish the desorptive term C_d from the heat capacity of the film.

Equation (9) is, in principle, a differential equation for the vapor pressure if the desorptive heat capacity is known. The need for determining the constant of integration in its solution makes, however, the direct use of this relation for $p(T)$ inconvenient.

We can derive a more convenient expression by differentiating (6) with respect to the temperature:

$$T^{-1}\frac{\partial C_f}{\partial N_f} = \frac{\partial^2 S_f}{\partial N_f \partial T} = \frac{5}{2}\frac{k}{T} - \frac{k}{p}\left(\frac{dp}{dT}\right) - k\frac{d}{dT}\left(\frac{T}{p}\frac{dp}{dT}\right). \tag{10}$$

Here again p is understood to equal the vapor pressure at all temperatures.

Using (9) for expressing (T/p) (dp/dT) in terms of p and C_d, we finally obtain

$$\frac{\partial C_f}{\partial N_f} - \frac{3}{2}k = -k\left(\frac{\gamma T}{p} - \frac{3}{2}\right)^{1/2} + \frac{1}{2}\left(\frac{kT\gamma}{p}\right) - \frac{kT^2}{2p}\left(\frac{\gamma T}{p} - \frac{3}{2}\right)^{-1/2}\frac{d\gamma}{dT}, \tag{11}$$

where, for brevity, we have

$$\gamma = C_d/V. \tag{12}$$

Equation (11) is an exact relation between the pressure, the desorptive heat capacity, and the partial heat capacity of the film. In the present experiments the $\frac{3}{2}$ term in the square root is negligible, and, with the further abbreviation

$$x^2 = \gamma T/p, \tag{13}$$

the equation reduces to

$$x^2 - 2x\left(1 + \frac{T}{2\gamma}\,\frac{d\gamma}{dT}\right) - 2\left[k^{-1}\frac{\partial C_f}{\partial N_f} - \frac{3}{2}\right] = 0. \qquad (14)$$

The last term causes, in the present case, a correction of only a few percent. If this is neglected, we find, to a good approximation,

$$\begin{aligned} p &= \gamma T[2 + (T/\gamma)(d\gamma/dT)]^{-2} \\ &= (T/V)C_d^3[2C_d + T(dC_d/dT)]^{-2}. \qquad (15) \end{aligned}$$

These results can now be used to evaluate the partial entropy of the layer according to (6). Here, it would not be convenient to redifferentiate the pressure as determined from (15). It is more convenient to substitute for $(T/p)(dp/dT)$ from (9):

$$\begin{aligned} \frac{\partial S_f}{\partial N_f} &= k\,\{\tfrac{3}{2}\,ln(2\pi mkT/h^2) + \tfrac{3}{2} - ln(p/kT) \\ &\quad - [(T/pV)C_d - \tfrac{3}{2}]^{1/2}\}. \qquad (16) \end{aligned}$$

III. APPLICATION TO HELIUM MONOLAYERS

The vapor pressures and heat capacities of monolayer and submonolayer He films have been studied in several laboratories in recent years.[4-12] Their heat capacities on various substrates, and over a wide range of coverage and temperature, show temperature dependences resembling two-dimensional solids. In recent experiments[1] on systems similar to those explored earlier by Goodstein *et al.*,[12] the heat capacities of He^3 adsorbed on Ar-plated copper were found to exhibit appreciable and rapid increases at relatively high temperature and coverage. We believe that the increases are due to desorption. The relevant data are shown in Fig. 1. An unequivocal separation between the isosteric heat capacity and desorption effects could be made by comparing films in two calorimeters having markedly different ratios of adsorbent area to vapor volume. Such a comparison has not yet been made, but it is possible at this time to effect an approximate separation by subtracting the extrapolated empirical curves fitted to the data at lower temperatures. The empirical curves, which are based on two-dimensional Debye functions,[1] are shown as solid lines in Fig. 1. The empirical curves are also good descriptions of the He^4 films of the same coverage even in the high-T region, the absence of strong desorption being presumably due to larger adsorption energies.

We find that the desorption heat capacities C_d have nearly exponential temperature dependences over a range of nearly two orders of magnitude in C_d. A slightly better fit is afforded by the function

$$C_d \propto T^{-3}e^{-q/kT}. \qquad (17)$$

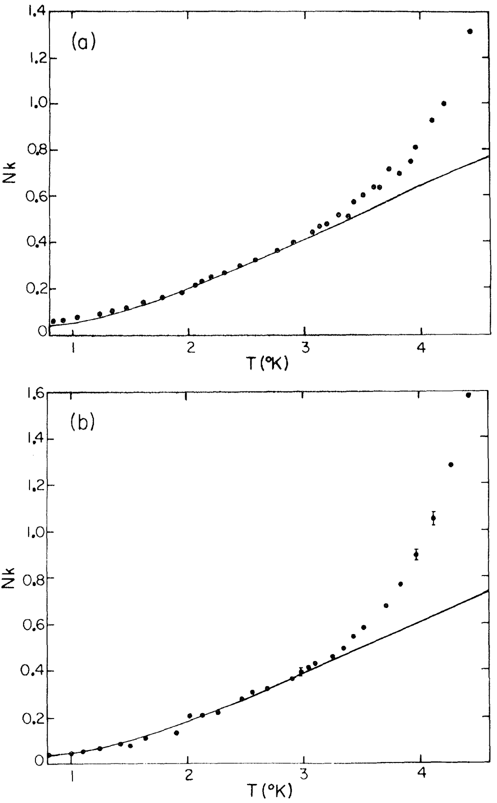

FIG. 1. Heat Capacities of He^2 films: (a) coverage $x = 0.72$, (b) coverage $x = 0.88$.

For a system of small vapor volume Eq. (17) has a functional form corresponding to a relatively large ($\gg kT$) and temperature-independent heat of adsorption q, where q is the isoteric heat of adsorption. This condition is satisfied in the present experiments. The excess heat capacities as T^3C_d are plotted semilogarithmically versus T^{-1} in Fig. 2.

Vapor pressures and heats of adsorption were determined from the slopes and values of the desorption heat capacities, according to Eqs. (15) and (17). (The vapor volume V, which is required for the calculation, was measured by He-gas isotherms at room temperature and 77 °K: $V = 6.09 \pm 0.01$ cm^3.) Results are given in Table I. Calculated errors correspond to estimated experimental uncertainties in C_d of $\pm$ 0.02 k per atom.

The calculated vapor pressures are considerably greater than those previously obtained by McCormick *et al.*[12] on a similar substrate at comparable ratios $N(He^3):N(Ar)$. Hence, as a check on the desorption technique, conventional pressure measurements were made on the same cell as used in the current heat-capacity study, under nearly identical conditions of Ar and He^3 coverage.[13]

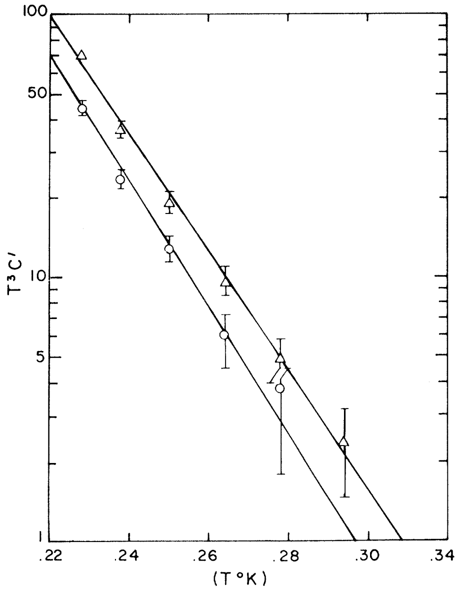

FIG. 2. Temperature dependence of the excess heat capacity attributed to desorption. Circles, $x = 0.72$; triangles, $x = 0.88$.

For these measurements the cell was directly immersed in a He^4 bath, and pressures were measured by a sensitive capacitance manometer communicating with the cell through a thin-walled 0.109-in.-i.d. stainless-steel capillary. The measured pressures required substantial thermomolecular corrections, and for these we used the empirical factors recently given by McConville[14] for He^3 in stainless-steel tubes. It is noteworthy that McConville found that the thermomolecular pressure differences depend upon the composition and surface finish of the capillary tubing, variations which had not been noted in the older study of Weber and Schmidt.[15]

IV. RESIDUAL ENTROPY OF HE^3 MONOLAYERS

The partial entropy of the films can be calculated from the vapor pressures and desorption heat capacity according to Eq. (16). This is interesting because some possible models of the adsorbed layer imply the existence of very-low excitation energy, which would remain uniformly occupied even at the lowest temperatures in the experiment. By comparing the thermal and absolute entropy one can therefore check whether there should be a further contribution to the heat capacity at still lower temperatures. For models[1] where the heat capacity is first-order homogeneous in N_f, a comparison of the partial entropies is equivalent to a mean entropy comparison. We obtain, for 4.2 °K,

$$9.45\ \mathrm{cm}^3:\ \frac{\partial S_f}{\partial N_f} = (0.41 \pm 0.83)k;$$

$$11.56\ \mathrm{cm}^3:\ \frac{\partial S_f}{\partial N_f} = (0.31 \pm 0.48)k.$$

The partial thermal entropies $(\partial S_f/\partial N_f)_{\mathrm{th}}$ were determined by integration of the differential heat capacities[1] from 0.5 to 3.0 °K, and the extrapolated isosteric heat capacities from 3.0 to 4.2 °K. Smooth extrapolation of the heat capacities from $T = 0$ to 0.5 yields contributions of less than 0.01 k for both films. Calculated values for the 9.45- and 11.56-cm^3 samples at 4.2°K are found to be the same:

$$\left(\frac{\partial S_f}{\partial N_f}\right)_{\mathrm{th}} = \int_0^T \frac{1}{T}\left(\frac{\partial C_f}{\partial N_f}\right) dT = (0.26 \pm 0.02)\ k.$$

Comparing $(\partial S_f/\partial N_f)_{\mathrm{th}}$, and the values obtained by comparison with the vapor, we find that there are no substantial ($\sim k$) contributions at 0.5 °K other than those due to nuclear spin.

V. DISCUSSION

The directly measured pressures and those deduced from the desorption heat capacity disagree by more than the estimated uncertainties due to statistical errors and the differences between thermomolecular corrections in stainless-steel

TABLE I. Vapor pressures and heats of adsorption for He^3 films adsorbed on Ar-plated copper at 4.2 °K.

Sample	Desorption measurements		Direct-pressure measurements $p(10^{-3}$ Torr)	
cm^3 STP: coverage x[a]	$p(10^{-3}$ Torr)	$k^{-1}q$ (°K)	Present work	McCormick *et al.*[b]
9.45 cm^3; $x = 0.72$	38.7 ± 3.4	55.7 ± 3.4	23.4 ± 3.9	0.6
11.56 cm^3; $x = 0.88$	80.3 ± 4.2	53.4 ± 2.1	141.5 ± 4.5	1.0

[a] Coverage x corresponds to the ratio N(He) to the number of Ar atoms in a BET monolayer at 77°.
[b] Data of Ref. 12 scaled to same coverage as present work.

and Pyrex capillaries. We believe that the differences between thermomolecular corrections for stainless steel and Pyrex are relevant to our data because they illustrate the sensitivity to the internal surface of the pressure tubing. Although in our measurements the capillary was stainless steel, we suspect that it was plated with Ar along an appreciable fraction of its length, and that the Ar surface can affect the measurements to a considerable degree. Additional sources of error can arise from slight differences between the coverages of samples studied by the two methods: The sensitivity of vapor pressure to coverage indicates that this can account for the major portions of the discrepancies.

The desorption and direct measurements both yield pressures considerably greater than those obtained by McCormick *et al.*[12] at equivalent monolayer coverage x (see Table I). We have no explanation for the disagreement, but suspect it to be due to systematic differences in the two substrates and in the measurement of surface areas by N_2 and Ar isotherms. Measurements now in progress are designed to explore these effects.[13]

A third-law comparison is particularly interesting when applied to adsorbed monolayers. According to classical theories of physical adsorption, the adsorbed atoms are localized on definite surface sites at liquid-helium temperatures; a partial monolayer of randomly distributed localized atoms would retain an appreciable configurational entropy at $T = 0$. This configuration entropy has an analog in the context of quantum-mechanical band theory,[16] if the lowest translational band is narrow and lies well below the thermally excited states. It has been shown that such a low-lying band will give rise to a peak in the heat capacity at a value of kT approximately equal to the bandwidth: The peak corresponds to the removal, at sufficiently low temperatures, of the configuration entropy of the localized model.

The present data allows the possibility of a small, coverage-dependent residual entropy. Resolution of this question and a detailed comparison with theoretical models can be made when more precise data are available.

ACKNOWLEDGMENTS

We wish to thank M. Bretz for his data on directly measured vapor pressures, which are part of a detailed study now in progress.

[†] Research supported by the National Science Foundation.

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[3] The relation (1) is sometimes expressed as $G_f/N_f = G_g/N_g$ where G is the Gibbs free energy, defined by

$$G_g = N_g \frac{\partial F_g}{\partial N_g} \equiv F_g + pV_g ,$$

$$G_f = N_f \frac{\partial F_f}{\partial N_f} \equiv F_f + \phi A_f ,$$

p being the vapor pressure and ϕ a two-dimensional "pressure" in the film; V_g, A_f are the volume available to the gas and the area available to the film. In the present case, the vapor is to good accuracy a perfect gas, and the conversion between the two expressions for the gas is immediate, but ϕ is not otherwise observable, and is best defined from these equations; hence the use of the Helmholtz free energy appears to be more direct.

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