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Revised thermodynamic relations for λ transitions in adsorbed layers

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Abstract. Thermodynamic relations of the Pippard type have been obtained for λ transitions in adsorbed films on both liquid and solid surfaces. For gases adsorbed on solids, estimates based on these relations indicate that no marked change in the adsorption isotherm need necessarily accompany the λ peak in specific heat.

1. Introduction

Phenomena interpreted as freezing points lower in an adsorbed layer than in a film in bulk have been known for a long time (see, for example, Patrick and Kemper 1938). Similarly for the λ transition in liquid helium a lowering of the transition temperature for adsorbed as against bulk ^4He has been deduced from the data of Frederikse (1949) and Mastrangelo and Aston (1951) on the specific heat and from the data of Long and Meyer (1952) on superfluidity: the evidence has been reviewed by Long and Meyer (1953). The first attempt to treat the thermodynamics of this case was made by Meyer and Long (1952) who assumed the transition to be strictly second order and thereby obtained equations of the Ehrenfest type.

Likewise, phase transitions corresponding to observed changes of slope in the isotherms of adsorbed films on liquid surfaces (for example, long-chain acids and their derivatives adsorbed on water) have been identified as being of higher order and attempts made to fit them within Ehrenfest's classification of such transitions (Dervichian 1939, Harkins *et al* 1940, Harkins and Boyd 1941).

Equations of Ehrenfest's type should, however, normally be replaced by relations of Pippard's (1956) type, as has been done for mixtures (Wright 1972a). For these relations require only that various quantities exhibit sufficiently sharp peaks, and are not dependent on the existence of discontinuities in them. In the following sections such relations are first developed in general form and then applied to the specific cases of λ transitions in adsorbed layers on both liquid and solid surfaces.

2. Generalized relations for λ transitions

In this section thermodynamic relations for λ transitions in general will be obtained by suitably extending Tisza's (1961) derivation of Pippard's original relations.

The appropriate generalization is to assume that close to the λ peak we may express a suitable free energy as:

$$G(T, X_1, X_2, \dots) \simeq f(t) + tg(X_1) + h(X_1) + tm(X_2) + n(X_2) + \dots \quad (1)$$

where $t = T - T_\lambda(X_1, X_2, \dots)$, and X_1, X_2, \dots are appropriate thermodynamic variables. Such an approach has already been employed by Garland (1964) for the case of tensile stress. The required relations are now obtained in general form by noting that for constant $X \neq X_1$:

$$\begin{aligned} -(\partial G/\partial T)_{X_1, X_2, \dots} &= S = -f' - g - m \\ +(\partial G/\partial X_1)_{T, X \neq X_1} &= -f'\psi - g\psi + tg' + h' - m\psi \\ -(\partial^2 G/\partial T^2)_{X_1, X_2, \dots} &= C_X/T = -f'' \\ (\partial^2 G/\partial T \partial X_1)_{X \neq X_1} &= -f''\psi + g' \\ -(\partial^2 G/\partial X_1^2)_{T, X \neq X_1} &= -f''\psi^2 + 2g'\psi - tg'' - h'' \end{aligned} \quad (2)$$

where $\psi = (\partial T_\lambda/\partial X_1)_{X \neq X_1}$, leading to the results

$$\left(\frac{\partial^2 G}{\partial T \partial X_1}\right)_{X \neq X_1} = \frac{C_X}{T}\psi + g' \quad (3)$$

$$-\left(\frac{\partial^2 G}{\partial X_1^2}\right)_{T, X \neq X_1} = \left(\frac{\partial^2 G}{\partial T \partial X_1}\right)_{X \neq X_1} \psi + g'\psi - h'' - tg'' \quad (4)$$

Taking $T \simeq T_\lambda$ and assuming that $g'' \simeq 0$ leads to the approximate Pippard relations.

Before turning to the application of relations (3) and (4) to specific cases of adsorbed layers, it is important to consider the general principles which govern the selection of an appropriate variable X_1 for a given problem. These are two: firstly, that X_1 should be experimentally measurable rather than a derived quantity, and secondly to bear in mind that even if dG may be expressed in the form

$$dG = -S dT + \sum_j Y_j dy_j \quad (5)$$

the straightforward identification $X_j = y_j$ is not always valid. In fact it may be more appropriate to take $X_j = y_j^\alpha$, where α is a constant chosen so that

$$\lim_{y_j \rightarrow y_j^0} \frac{dT_\lambda}{d[y_j^\alpha]} = \text{constant} \neq 0$$

where y_j^0 is the constant value of y_j at which measurements are obtained. For example, for transitions in magnetic materials H^2 rather than H is an appropriate variable (Wright 1972b).

3. Adsorbed films on liquid surfaces

Here the appropriate variable X_1 is readily identified as π , the conventional surface pressure, on several grounds. It is suggested by the form of the equation for the free energy of the surface phase:

$$dz^a = -s^a dT + o d\pi \quad (6)$$

where o is the area of surface per unit amount adsorbed, by analogy with the bulk case, and because only π , and not o , is measurable for both soluble and insoluble adsorbed films.

Thus, substituting appropriately into (3) and (4) leads to the results:

$$\left(\frac{\partial o}{\partial T}\right)_\pi \simeq \text{constant} + \frac{dT_\lambda}{d\pi} \frac{c_\pi}{T} \quad (7)$$

$$-\left(\frac{\partial o}{\partial \pi}\right)_T \simeq \text{constant} + \frac{dT_\lambda}{d\pi} \left(\frac{\partial o}{\partial T}\right)_\pi \quad (8)$$

where c_π is:

$$T \left(\frac{\partial}{\partial T}\right)_\pi \left[\left(\text{Gibbs surface excess entropy} \right)_{\text{for surface covered by film}} - \left(\text{Gibbs surface excess entropy} \right)_{\text{for surface of pure solvent}} \right].$$

For no system yet studied do sufficiently precise data seem to be available for the application of (7) and (8) to be illustrated by a suitable plot; one consequence of their applicability may however be outlined. For adsorption of a soluble substance of activity a in the bulk solution, the Gibbs adsorption isotherm requires that

$$o \left(\frac{\partial \pi}{\partial o}\right)_T = \left(\frac{\partial}{\partial o}\right)_T RT \ln a \quad (9)$$

and therefore

$$\frac{1}{o} \left(\frac{\partial o}{\partial \pi}\right)_T = \frac{a}{RT} \left(\frac{\partial o}{\partial a}\right)_T \quad (10)$$

A maximum in $-(\partial o/\partial \pi)_T$ therefore corresponds automatically to a minimum in $(\partial o/\partial a)_T$, and so to a maximum in $(\partial \Gamma/\partial a)_T$, where $\Gamma = 1/o$ is the amount adsorbed per unit area. Thus the occurrence of a λ transition in an adsorbed layer on a liquid surface should be accompanied by a steepening of the adsorption isotherm over a short range of values of a . However, this steepening might be inappreciable in some cases where the dependence of T_λ on π is not very marked: rough numerical estimates given at the end of § 4 show that for adsorbed films on *solid* surfaces such a steepening of the isotherm might be small and easily overlooked.

4. Adsorbed films on solid surfaces

In dealing with the specific case of adsorption from the vapour phase onto a solid surface, the appropriate choice of variable for X_1 is not so readily made. Let $R \equiv U^a + pV^a - TS^a$, where each Z^a is defined by:

$$Z^a = \left(Z \text{ for whole system} \right) - \left(Z \text{ for unadsorbed gas in the system} \right) - \left(Z \text{ for the solid if no gas were adsorbed on it} \right).$$

Then

$$dR = -S^a dT + V^a dp - \phi dO + \mu_B dn_B^{\text{ads}} \quad (11)$$

where ϕ is the spreading pressure, O the total area of adsorbent and B the adsorbed species. Let small letters denote 'molar' quantities defined as:

$$r \equiv R/n_B^{\text{ads}}, \quad s^a \equiv S^a/n_B^{\text{ads}}, \dots$$

then transforming to dr :

$$dr = -s^a dT + v^a dp - \phi d(\Gamma^{-1}) \tag{12}$$

since $o = 1/\Gamma$. Moreover if $v^a dp$ may be omitted (to a sufficient approximation) then

$$dr = -s^a dT - \phi d(\Gamma^{-1}). \tag{13}$$

This equation should be contrasted with (6), and the different independent variable noted. In this the thermodynamics reflects the experimental situation where the amount adsorbed is indeed the accessible variable for adsorption onto a solid. (The origin of the different forms for the two classes of adsorption may be found in any suitable text on the subject, for example, Young and Crowell (1962).)

Thus, it might be expected that Γ^{-1} would be a suitable choice for X_1 , if we assume that Tisya's G may be replaced by r , a partial analogue of a Gibbs free energy. Relations (3) and (4) would then predict that over a range of temperatures close to the value of T_λ for a bulk specimen, $dT_\lambda/d(\Gamma^{-1})$ would be constant, ie that T_λ varies linearly as Γ^{-1} . Such seems not to be the case. Log-log plots of depression of T_λ against thickness of adsorbed film, using available data for helium (Frederikse 1949), nitrogen (Morrison *et al* 1952) and argon (Morrison and Drain 1951), though crude, reveal unambiguously a dependence of T_λ on something like Γ^{-2} (moving toward Γ^{-1} for thinner films).

Therefore considering the second principle governing the choice of X_1 , outlined in § 2, the safest course appears to be to take the independent variable to be Γ^{-D} with D an unspecified index, not necessarily an integer and not necessarily the same for one system as for another.

4.1. Relations resulting

Recasting (13) in the form

$$dr = -s^a dT - \frac{\Gamma^{D-1}\phi}{D} d(\Gamma^{-D}), \tag{14}$$

relations (3) and (4) become

$$\left(\frac{\partial s^a}{\partial[\Gamma^{-D}]}\right)_T \simeq \text{constant} - \psi \left(\frac{\partial s^a}{\partial T}\right)_T \tag{15}$$

$$\frac{1}{D} \left(\frac{\partial}{\partial[\Gamma^{-D}]}\right)_T (\Gamma^{D-1}\phi) \simeq \text{constant} - \psi \left(\frac{\partial s^a}{\partial[\Gamma^{-D}]}\right)_T \simeq \text{constant} + \psi^2 \left(\frac{\partial s^a}{\partial T}\right)_T$$

where

$$\psi \equiv dT_\lambda/d[\Gamma^{-D}]$$

(T_λ varying roughly linearly not with Γ^{-1} but with Γ^{-D})

$$(\partial s^a/\partial T)_T = c_{p\Gamma}/T$$

$$\begin{aligned} \left(\frac{\partial s^a}{\partial[\Gamma^{-D}]}\right)_T &= \frac{\Gamma^D}{D} (s^a - \tilde{s}^a) & \left(\tilde{s}^a \equiv \left(\frac{\partial S^a}{\partial n_B^{\text{ads}}}\right)_T, \Gamma = \frac{n_B^{\text{ads}}}{O}\right) \\ &= \frac{\Gamma^D}{D} \frac{q_{\text{st}} - Q}{T} \end{aligned} \tag{17}$$

$$\frac{1}{D} \left(\frac{\partial}{\partial [\Gamma^{-D}]} \right)_T (\Gamma^{D-1} \phi) = -\frac{D-1}{D^2} \Gamma^{2D-1} \phi + \frac{RT}{D} \Gamma^D \left(\frac{\partial \ln p}{\partial [\Gamma^{-D}]} \right)_T \quad (18)$$

(Results (17) and (18) were obtained using the standard relations

$$Q = q_{st} + T(\bar{s}^a - s^a)$$

where q_{st} is the isosteric, and Q the equilibrium, heat of adsorption; and

$$\left(\frac{\partial \phi}{\partial \ln p} \right)_T \simeq \Gamma RT$$

given, for example, by Young and Crowell (1962).

It is to be expected that the results obtained will be more informative in terms of $q_{st} - Q$, on $(\partial \ln p / \partial [\Gamma^{-D}])_T$ than in the original forms (15) and (16).

Thus, taking $\psi \equiv dT_\lambda / d[\Gamma^{-D}]$ to be negative, a maximum is to be expected in $q_{st} - Q$ near the maximum in $c_{p\Gamma}$; and, whatever the sign of ψ , a maximum is to be expected in the right-hand side of (18), probably in the $(\partial \ln p / \partial [\Gamma^{-D}])_T$ part of it. This would amount to a minimum in $(\partial[\Gamma^{-D}] / \partial p)_T$ and so to a maximum in $(\partial \Gamma / \partial p)_T$ (figure 1).

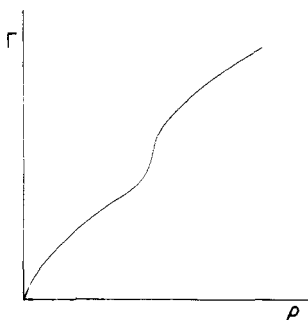


Figure 1. Hypothetical form of isotherm for a substance adsorbed on a solid, and undergoing a λ transition.

The kink in an observed isotherm might be too small to be detected experimentally, but certainly corresponds to what is expected for smeared out 'melting' of the type observed by Morrison *et al* (1952) for nitrogen adsorbed on rutile. Bartis (1969) has emphasized the applicability of Pippard's approach to such cases.

Although, as for liquid surfaces, there appear to be no data sufficiently precise for plotting, it seems worthwhile to make a rough estimate of the magnitude of the effect likely to be observed.

If ϕ varies sufficiently smoothly then relation (16) can be reduced, rather crudely, to

$$\frac{RT}{D} \Gamma^D \left(\frac{\partial \ln p}{\partial [\Gamma^{-D}]} \right)_T \simeq \text{constant} + \left(\frac{dT_\lambda}{d[\Gamma^{-D}]} \right)^2 \frac{c_{p\Gamma}}{T} \quad (19)$$

As an example, for the system helium adsorbed on jeweller's rouge, take it that $D = 2$, say. The data of Frederikse (1949) on the specific heat of this system show that for $\Gamma = 5$, with Γ measured in number of layers, $dT_\lambda / d[\Gamma^{-2}]$ is -4.0 K (layer)^2 . For this value of Γ , the rise in $c_{p\Gamma}$ is approximately $5.0 \text{ J mol}^{-1} \text{ K}^{-1}$: equation (19) then

implies a rise of $(\partial \ln p / \partial [\Gamma^{-2}])_T$ by roughly 0.20 layer^2 ; but

$$(\partial \ln p / \partial [\Gamma^{-2}])_T = -(\Gamma^2/2)(\partial \ln p / \partial \ln \Gamma)_T$$

and so we may expect a rise in $(\partial \ln p / \partial \ln \Gamma)_T$ of roughly -0.015 .

Now the Freundlich empirical isotherm is $\Gamma = Ap^n$ where A is a constant and n is approximately 0.5 for many systems. That is, $(\partial \ln p / \partial \ln \Gamma)_T$ is normally about 2 and its reciprocal, the slope of a log-log plot such as might be used for testing the Freundlich isotherm, would be expected to change by only about 0.01 in the region of the phase transition, a change which might well remain unnoticed.

Similarly for the data of Morrison *et al* (1952), $dT_\lambda/d[\Gamma^{-2}]$ is approximately -75 K layer^2 for $\Gamma = 4.8$ layers, which corresponds to an observed rise in $c_{p\Gamma}$ of about $50 \text{ J mol}^{-1} \text{ K}^{-1}$ in the region of the transition temperature of 61 K . This leads to an expected rise of roughly 0.6 layer^2 in $(\partial \ln p / \partial [\Gamma^{-2}])_T$ which again translates into a change in the Freundlich exponent of about 0.01 . It thus appears that phase changes corresponding to marked rises in the specific heat of a film adsorbed on a solid surface produce no very great effect on the observed isotherm, in contrast to the marked change in isotherm slope observed in some (but not necessarily all) similar transitions on liquid surfaces: and equally, the observation of a smoothly varying isotherm does not necessarily preclude the existence of a peak in the specific heat.

5. Higher-order Pippard plots

These may be obtained by the following argument. If the peak in specific heat is such that there are no discontinuities in $c_{p\Gamma}$ or any of its derivatives (and such appears to be the case, as is evidenced by the data of Frederikse (1949), then the phase transition is one of 'infinite order' according to the definition of Allen and Eagles (1960). The ' λ line' in the (Γ^{-D}, T) plane is then a locus of points for which $(\partial c_{p\Gamma} / \partial T)_\Gamma = 0$. It is thus exactly a contour of constant $(\partial c_{p\Gamma} / \partial T)_\Gamma$, and its slope $dT_\lambda/d[\Gamma^{-D}]$ is therefore exactly equal to

$$-\frac{\partial^2 c_{p\Gamma} / \partial [\Gamma^{-D}] \partial T}{(\partial^2 c_{p\Gamma} / \partial T^2)_\Gamma}.$$

Although it is extremely unlikely that this quantity involving second derivatives of $c_{p\Gamma}$ will be directly obtainable from experiment, it is in principle obtainable from a plot of $(\partial c_{p\Gamma} / \partial [\Gamma^{-D}])_T$ against $(\partial c_{p\Gamma} / \partial T)_\Gamma$.

By a similar argument, for adsorption on a liquid surface, $dT_\lambda/d\pi$ will be given by the slope of a plot of $(\partial c_\pi / \partial \pi)_T$ against $(\partial c_\pi / \partial T)_\pi$.

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