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1969 J. Phys. A: Gen. Phys. 2 226

(http://iopscience.iop.org/0022-3689/2/2/012)

A simple alternative derivation of Pippard's thermodynamic relations for λ-transitions

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MS. received 28*th August* 1968, *in revised form* 20*th November* 1968

Abstract. Pippard's relations for λ-transitions are shown to be derivable by simple arguments relating to the slope of contours of constant C_p, or of contours of constant $(\partial V/\partial T)_p$.

1. Introduction

The thermodynamic relations obtained by Pippard (1956, 1957) have proved most valuable in the discussion of the effect of pressure on λ-transitions, and have been used, discussed and extended by various authors (Tisza 1961, Buckingham and Fairbank 1961, Hughes and Lawson 1962, Garland and Jones 1963, Garland 1964 a, b). In his original paper Pippard pointed out that these relations were closely connected with others already published in the literature. Among earlier publications (Lype 1946, Rice 1954, Kuper 1955), a paper by Rice contains some (seemingly neglected) thoughts which can be used to give a simple alternative derivation of Pippard's relations.

2. Basic approximation

The slope of the λ-line is approximately equal to the slope of contours of constant specific heat, constant coefficient of expansion, etc.

For *infinite* peaks in C_p (as distinct from higher-order transitions in Ehrenfest's sense) the λ-line (locus of points for which C_p, or C_p/T, is infinite) will lie very close to contours of constant C_p, or of constant C_p/T, if this constant value is high enough. The slope of the λ-line, then, will approximate to that of neighbouring contours of constant C_p, or of constant C_p/T. (The reasoning is very close to the treatment (Rice 1954, Buckingham and Fairbank 1961) of the slope of the λ-line as $\lim_{C_p\to\infty} (\partial p/\partial T)_{C_p}$, that is, of the λ-line for an infinite peak as a contour of constant $1/C_p$.) What has been said is applicable for any (reasonable) choice of independent variables, and in particular for the choice of p and T—those almost always used.

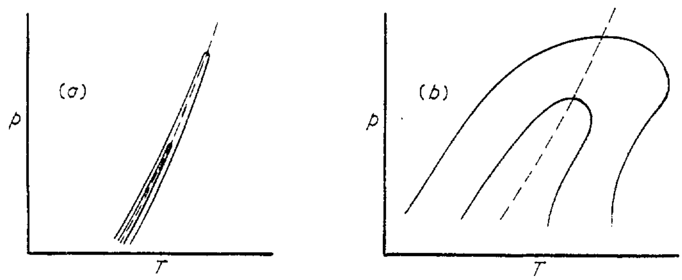

Figure 1. Behaviour of finite peaks in C_p: (a) thin high finite peaks; (b) broad peaks. The full lines denote contours of constant C_p. The broken line denotes the locus of maxima in C_p (maxima for given p).

For the experimentally almost indistinguishable case of *thin high finite* peaks the λ-line (now the locus of points for which C_p takes its greatest value for a given p) will again have a slope approximately equal to that of neighbouring contours of constant C_p (or approximately equal to that of neighbouring contours of constant C_p/T). Here, however, this constant value must not only be high enough but also must be not so high as to be too close to the value at the top of the peak (see figure 1(a)).

For a *broad* peak in C_p the analogue of a λ-line (in so far as there is one) may be taken to be the locus of points for which C_p takes its greatest value for a given p. This curve will ordinarily *not* approximate in slope to contours of constant C_p (nor of constant C_p/T) (see figure 1(*b*) and compare Rice's figure 10).

If the λ-transition may alternatively be treated as an 'anomaly' in $(\partial V/\partial T)_p$ (or in the coefficient of expansion), then the slope of the λ-line also approximates to that of neighbouring contours of constant $(\partial V/\partial T)_p$.

3. Derivation of Pippard's relations on this basis

(i) At a given point (T, p) the slope of a contour of constant $(\partial V/\partial T)_p$ is equal to the value thereat of

$$\frac{(\partial^2 V/\partial T^2)_p}{-\partial^2 V/\partial p\,\partial T}$$

which (if the crossed second derivative is continuous) is equal to

$$\frac{(\partial^2 V/\partial T^2)_p}{-\partial^2 V/\partial T\,\partial p}$$

a quantity which might be written (somewhat barbarously) as

$$\left\{\frac{\partial(\partial V/\partial T)_p}{\partial(-\partial V/\partial p)_T}\right\}_p.$$

That is, it is equal to the slope of a graph of $(\partial V/\partial T)_p$ against $(-\partial V/\partial p)_T$ (taking values, at a fixed pressure, for various temperatures close to that of the λ-transition).

Therefore this slope furnishes an approximation to the slope of the λ-line—as Pippard concluded (Pippard's second relation). In short, a graph of values of $(\partial V/\partial T)_p$, at a fixed pressure, for various temperatures close to that of the λ-transition, against corresponding values of $(-\partial V/\partial p)_T$, has a slope *approximately* equal to that of the λ-line and *exactly* equal at a given point to that of a contour of constant $(\partial V/\partial T)_p$.

(ii) The result (Pippard's first relation) that the slope of the λ-line approximates to that of a graph of C_p/T against $(\partial V/\partial T)_p$ (taking values, at a fixed pressure, for various temperatures close to that of the λ-transition) would be obtained by a corresponding argument in terms of the slope of a contour of constant C_p/T.

(iii) The slope of the λ-line might also be treated as approximating to that of a contour of constant $(-\partial V/\partial p)_T$ (or of constant values of the isothermal compressibility). Such a slope will be equal to that of a graph of values of $(\partial V/\partial T)_p$, for various pressures at a fixed temperature, against the corresponding values of $(-\partial V/\partial p)_T$ (or to the slope of a graph of values of the coefficient of expansion, for various pressures at a fixed temperature, against the corresponding values of the isothermal compressibility).

(iv) Pippard's (1956) 'cylindrical' approximation makes these various plots linear. This linearity may be inferred as follows. In the vicinity of a λ-line the several contours of constant C_p/T (or C_p, or $(\partial V/\partial T)_p$ or the coefficient of expansion) will often be almost parallel. Since the slope of each contour is the slope at a given point of the relevant plot, it follows that in such a case the slope of the plot will be almost constant.

It is thus deducible by the above arguments that in the vicinity of a λ-transition:

(i) For a fixed pressure

$$\left(\frac{\partial V}{\partial T}\right)_p \simeq \text{const.} + \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_\lambda \left(-\frac{\partial V}{\partial p}\right)_T.$$

(ii) For a fixed pressure

$$\frac{C_p}{T} \simeq \text{const.} + \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_\lambda \left(\frac{\partial V}{\partial T}\right)_p.$$

(iii) For a fixed temperature

$$\left(\frac{\partial V}{\partial T}\right)_p \simeq \text{const.} + \left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_\lambda \left(-\frac{\partial V}{\partial p}\right)_T$$

(relations due to Pippard).

The generalizations obtained by Garland (1964 a) can be inferred by similar arguments.

If there are no discontinuities either in C_p or in any of its derivatives, the observed peak qualifies as a 'phase transition of infinite order', as defined by Allen and Eagles (1960), and the 'λ-line' is the locus of points at which, for given p, C_p passes through a maximum, and so is a locus of points at which $(\partial C_p/\partial T)_p = 0$. As such, it is (exactly) a contour of constant $(\partial C_p/\partial T)_p$. Its slope is therefore *exactly* equal to

$$-\left(\frac{\partial^2 C_p}{\partial T^2}\right)_p \bigg/ \frac{\partial^2 C_p}{\partial p\, \partial T}.$$

This quantity, involving *second* derivatives of C_p, will not be readily obtainable from experimental observations. For example, the data (West 1959) for C_p for liquid sulphur, excellent as they are (Klement 1966), do not allow any quantitative estimate to be made of the curvature at the maximum in the graph of C_p against T. (It would in principle be possible instead to utilize a plot of $(\partial C_p/\partial T)_p$ against $(\partial C_p/\partial p)_T$.)

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