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Abstract. By an argument akin to that which has been used by S V Subramanyam, R Ramachandra and E S R Gopal to obtain generalised Pippard's relations for the vicinity of a line of ordinary critical points of a fluid mixture, further generalisations are obtained for the vicinity of a line of tricritical or polycritical points in cases not involving special symmetries.

1. Introduction

Kohnstamm (1926) envisaged a possibility that *three* fluid phases might simultaneously cease to be distinguishable, instead of two as at an ordinary critical point. Such a phenomenon, and analogous behaviour in magnetic and other systems with special symmetries, has become a subject of increasing attention (relevant publications including those of Landau 1937, Zernike 1949, Radyshevskaya *et al* 1962, Krichevski *et al* 1963, Efremova and Shvarts 1966, Griffiths 1970, 1973, 1974, Straley and Fisher 1973, Chang *et al* 1973, Hankey *et al* 1973, Harbus *et al* 1973, Schulman 1973, Wegner and Riedel 1973, Lang and Widom 1975, Scott 1978).

The present communication is concerned with generalisations, to such tricritical points of fluid mixtures, and to corresponding points at which more than three phases simultaneously cease to be distinguishable, of the type of approximate thermodynamic relation originally obtained by Pippard (1956) for such cases as the λ transition of liquid helium. Among various discussions of behaviour near an ordinary critical point of a fluid mixture (Wheeler and Griffiths 1968, Saam 1970, Leung and Griffiths 1973, Chang 1973, Subramanyam *et al* 1974), the treatment by Subramanyam *et al* proves a particularly appropriate starting point for the present work. Their generalisations of Pippard's relations turn out to be very similar to those which are appropriate to the present more general cases.

2. Starting point of the argument to be used

Consider a mixture of components A, B, C . . . L. Possible states may be represented by points in a space in which the coordinates are T, p, and the mole fractions (x_B, x_C . . . x_L, say) of all but one of the components. The points of particular interest are any which represent a state for which two or more (k, say) phases simultaneously become

indistinguishable, as this state is approached from a region of heterogeneous states in which k phases are present. Alternatively, these points may be characterised as any which represent a state at which k phases simultaneously become just distinguishable, as this state is approached from a region of homogeneous states.

For there to be a one-dimensional continuum of such critical ($k = 2$), tricritical ($k = 3$) or polycritical ($k > 3$) points, there must (unless there are special symmetries) be $2k - 2$ components in all (Zernike 1949), and the space involved is $(2k - 1)$-dimensional. For example, for a line of ordinary critical points, there must be two components, and the space involved is three-dimensional with coordinates (T, p, x_B); and for a line of ordinary tricritical points, there must be four components, and the space is five-dimensional with coordinates (T, p, x_B, x_C, x_D).

To obtain generalisations of the relations inferred by Subramanyam *et al* (1974), an argument of the following type may be used. Take it that a critical, tricritical or polycritical point may be characterised by some quantity ϕ (such as C_p, or the thermal expansion) either becoming infinite or exhibiting singular behaviour of some other kind. When there is† a line $\mathscr{L}$ of such points at which ϕ exhibits a singularity as the point is approached from the region of points representing homogeneous states, it is to be expected (compare figure 1) that in this region there will be, near the line $\mathscr{L}$, a family of hypersurfaces $\mathscr{H}$ of constant ϕ which are nearly parallel to this line. (Compare an argument given by Rice (1954, 1967) for cases which involve only a two-dimensional space.) Then the value of (say) dT/dp along the line $\mathscr{L}$ will approximate to that of dT/dp for a curve $\mathscr{P}$ drawn roughly parallel to $\mathscr{L}$ in one of these hypersurfaces $\mathscr{H}$; and on this basis it is possible to infer approximate relations involving values of dT/dp, dx_B/dp, etc, along the line $\mathscr{L}$.

Figure 1. A partial analogue of the situation to be considered. A quantity ψ is infinite on line ab and surfaces acfb, adeb, agjb and ahib, and may be infinite or undefined within the wedge-like region from ab to cdef, and that from ab to ghij.

The surface η, close to ab, but not extending too close to acfb or ahib, is: (i) a surface on which ψ is large and constant; (ii) roughly parallel to ab.

† Not necessarily a straight line, but a line assumed to have only a well behaved mild curvature.

3. Some general relations for smooth curves in a space of four or more dimensions†

Let $\mathscr{C}$ be any smooth curve whatsoever in one of the hypersurfaces $\mathscr{H}$. Then along curve $\mathscr{C}$ a relation

$$\frac{\partial\phi}{\partial T}\frac{dT}{dp}+\frac{\partial\phi}{\partial p}+\sum_{\substack{\text{all } i \\ \text{other than A}}}\left(\frac{\partial\phi}{\partial x_i}\frac{dx_i}{dp}\right)=\frac{d\phi}{dp}=0 \tag{1}$$

holds (where the omission of subscripts in partial derivatives is to be taken as indicating that the quantities held constant are all other members of the set of variables $\{T, p, x_B, x_C \ldots x_L\}$). It then follows that along any smooth curve $\mathscr{C}$ lying in a hypersurface $\mathscr{H}$:

$$\frac{dT}{dp}=-\frac{\partial\phi/\partial p}{\partial\phi/\partial T}-\sum_{\substack{\text{all } i \\ \text{other than A}}}\left(\frac{\partial\phi/\partial x_i}{\partial\phi/\partial T}\frac{dx_i}{dp}\right) \tag{2}$$

(provided that $\partial\phi/\partial T$ is neither zero nor infinite).

In particular, such an equation holds for any curve $\mathscr{P}$ lying in a hypersurface $\mathscr{H}$, since such a curve is a special case of a curve $\mathscr{C}$ lying in that hypersurface.

4. Resulting generalisations of Pippard's relations

Let the subscript k indicate a quantity relating to a critical, tricritical or polycritical state (whichever it is that is involved). Then, for example, T_k will denote a critical, tricritical or polycritical temperature; and dT_k/dp will be equal to dT/dp for the line $\mathscr{L}$; and thus

$$dT_k/dp \sim dT/dp \qquad \text{for a curve } \mathscr{P}. \tag{3}$$

Similarly, the effect of pressure on a critical, tricritical or polycritical composition is given by

$$dx_{ik}/dp \sim dx_i/dp \qquad \text{for a curve } \mathscr{P}. \tag{4}$$

But, provided that $\partial\phi/\partial T$ is neither zero nor infinite, these derivatives along a curve $\mathscr{P}$ are related by equation (2) above; and therefore it can be seen that

$$\frac{dT_k}{dp}\approx-\frac{\partial\phi/\partial p}{\partial\phi/\partial T}-\sum_{\substack{\text{all } i \\ \text{other than A}}}\left(\frac{\partial\phi/\partial x_i}{\partial\phi/\partial T}\frac{dx_{ik}}{dp}\right) \tag{5}$$

where the values of $\partial\phi/\partial T$, $\partial\phi/\partial p$, $\partial\phi/\partial x_i$ relate *not* to a critical, tricritical or polycritical point, but to a *neighbouring homogeneous state* of the fluid mixture.

Some particular cases of this equation are as follows:

(i) If ϕ be taken to be C_p ($=\partial H/\partial T$) then, noting that $\partial C_p/\partial p = -T\partial^2 V/\partial T^2$ and $\partial H/\partial x_i = \tilde{H}_i - \tilde{H}_A$ (where the tilde denotes a partial molar quantity), it can be seen that equation (5) becomes

$$\frac{dT_k}{dp}\approx Th_{12}-\sum_{\substack{\text{all } i \\ \text{other than A}}}\left(\frac{dx_{ik}}{dp}h_{1i}\right) \tag{6}$$

where h_{12} denotes the slope of a Pippard-like plot of $\partial V/\partial T$ against C_p, and h_{1i} that of a corresponding plot of $\tilde{H}_i - \tilde{H}_A$ against C_p: in both cases plotting values for homogeneous states over a range of temperature close to T_k.

If the plots are roughly linear, it can be seen to follow that (for homogeneous states over a range of temperature close to T_k)

$$\frac{dT_k}{dp} C_p \approx \text{const} + T\frac{\partial V}{\partial T} - \sum_{\substack{\text{all } i \\ \text{other than A}}} \left(\frac{dx_{ik}}{dp}(\tilde{H}_i - \tilde{H}_A)\right). \tag{7}$$

(i') If ϕ were instead taken to be C_p/T $(=\partial S/\partial T)$, a similar argument would indicate that (if the plots involved were roughly linear)

$$\frac{dT_k}{dp} \frac{C_p}{T} \approx \text{const} + \frac{\partial V}{\partial T} - \sum_{\substack{\text{all } i \\ \text{other than A}}} \left(\frac{dx_{ik}}{dp}(\tilde{S}_i - \tilde{S}_A)\right). \tag{8}$$

(ii) If ϕ were taken to be $\partial V/\partial T$, the first relation obtained in this way would be

$$\frac{dT_k}{dp} \approx v_{12} - \sum_{\substack{\text{all } i \\ \text{other than A}}} \left(\frac{dx_{ik}}{dp}v_{1i}\right) \tag{9}$$

where v_{12} denotes the slope of a Pippard-like plot of $-\partial V/\partial p$ against $\partial V/\partial T$, and v_{1i} that of a corresponding plot of $\tilde{V}_i - \tilde{V}_A$ against $\partial V/\partial T$; plotting values for homogeneous states over a range of temperature close to T_k. Then, if the plots were roughly linear, it would follow that

$$\frac{dT_k}{dp} \frac{\partial V}{\partial T} \approx \text{const} + \left(-\frac{\partial V}{\partial p}\right) - \sum_{\substack{\text{all } i \\ \text{other than A}}} \left(\frac{dx_{ik}}{dp}(\tilde{V}_i - \tilde{V}_A)\right). \tag{10}$$

Relations (6) to (10) would suggest that, for homogeneous states near a line of ordinary critical, tricritical or polycritical points, there would be correlated sharp maxima or minima in $\partial V/\partial T$, $-\partial V/\partial p$, $\tilde{H}_i - \tilde{H}_A$, and so forth, associated with the maximum in C_p. Relations (6) and (9), however, involving the slopes of Pippard-like plots and the dependence of T_k and x_{ik} on pressure, do not correspond to any connection so simple as the

$$dT_\lambda/dp \sim v_{12}$$

derived by Pippard for such cases as the λ transition of liquid helium. For an ordinary critical point, this difference was pointed out by Subramanyam *et al* (1974).

A further point which may be noted is that a peak in $\tilde{H}_i - \tilde{H}_A$ or $\tilde{V}_i - \tilde{V}_A$ is likely to be much less marked than one in C_p. Such a conclusion may be reached in various ways (compare Griffiths and Wheeler 1970), and in particular by considering the behaviour of $\partial^2 H/\partial x_B^2$ or $\partial^2 V/\partial x_B^2$ at an ordinary critical point. An argument that both would vanish (Rowlinson 1965) soon received experimental support (Dunlap and Furrow 1966, Myers *et al* 1966). Now the value of $\tilde{H}_B - \tilde{H}_A$ $(=\partial H/\partial x_B)$ for a binary mixture at its critical composition (for a given pressure) is

$$\left[\lim_{x_B \to 0} (\tilde{H}_B - \tilde{H}_A)\right] + \int_0^{x_{B \text{ crit}}} \frac{\partial^2 H}{\partial x_B^2} dx_B$$

(the integral being taken along a path of constant T and p), which is equal to

$$\tilde{H}_{\mathrm{B}}^{\ominus} - H_{\mathrm{A}}^{\circ} + \int_{0}^{x_{\mathrm{B \, crit}}} \frac{\partial^2 H}{\partial x_{\mathrm{B}}^2} \, \mathrm{d}x_{\mathrm{B}} \tag{11}$$

(where the superscript $^{\ominus}$ denotes a standard value for a solute species, and the superscript $^{\circ}$ a value for a pure substance). If the second derivative vanishes at the critical point, then expression (11) is necessarily finite, even at $T = T_{\mathrm{crit}}$. Any peak in $\tilde{H}_{\mathrm{B}} - \tilde{H}_{\mathrm{A}}$, as the critical point is approached by varying the temperature, is then a not very dramatic one. This detailed argument relates to an ordinary critical point, but its conclusion may be expected to apply to tricritical and polycritical points also.

4.1. Relations applying if there is one additional component

If there were one additional component, there would be not a one-dimensional but a two-dimensional continuum of critical, tricritical or polycritical points. In that case $(2k - 1$ components), it would be possible to direct attention to a line of critical, tricritical or polycritical points in a $(2k - 1)$-dimensional section, taken at constant p, of the $2k$-dimensional space that would be involved. Reasoning similar to that used above then gives relations

$$C_p + \sum_{\substack{\text{all } i \\ \text{other than A}}} \left(\left(\frac{\partial x_{ik}}{\partial T} \right)_p (\tilde{H}_i - \tilde{H}_{\mathrm{A}}) \right) \approx \text{const} \tag{12}$$

somewhat analogous to (7);

$$\frac{C_p}{T} + \sum_{\substack{\text{all } i \\ \text{other than A}}} \left(\left(\frac{\partial x_{ik}}{\partial T} \right)_p (\tilde{S}_i - \tilde{S}_{\mathrm{A}}) \right) \approx \text{const} \tag{13}$$

somewhat analogous to (8); and

$$\frac{\partial V}{\partial T} + \sum_{\substack{\text{all } i \\ \text{other than A}}} \left(\left(\frac{\partial x_{ik}}{\partial T} \right)_p (\tilde{V}_i - \tilde{V}_{\mathrm{A}}) \right) \approx \text{const} \tag{14}$$

somewhat analogous to (10).

5. An alternative form of the relations

The relations just inferred have been presented in terms of the effect of pressure on the critical, tricritical or polycritical temperature and composition, in the case of a system of $2k - 2$ components: and in terms of the effect of temperature on the critical, tricritical or polycritical composition at a given pressure, in the case of a system of $2k - 1$ components. A slight modification of the argument gives equivalent results expressed in terms of the effect of adding the component L. That is, the results can be presented, for a system of $2k - 2$ components, in terms of the effect of adding L on a critical, tricritical or polycritical temperature, pressure, and composition-so-far-as-the-other-components-are-concerned: and in a corresponding way for a system of $2k - 1$ components at a given pressure.

Let y_i, for any i other than L, denote the quantity

$$x_i \bigg/ \bigg(\sum_{\substack{\text{all } i \\ \text{other than L}}} x_i \bigg) = \frac{x_i}{1 - x_L}. \tag{15}$$

(It is, in a sense, 'what the mole fraction of i would be if L were not there'.) Use the set of variables

$$\{T, p, y_B, y_C \dots y_K, x_L\}$$

and let omission of subscripts in a partial derivative now denote the constancy of all but one of the members of *this* set.

The relevant analogue of equation (5) above for the case of $2k - 2$ components is then

$$\frac{dT_k}{dx_L} \approx -\frac{\partial\phi/\partial x_L}{\partial\phi/\partial T} - \frac{\partial\phi/\partial p}{\partial\phi/\partial T}\frac{dp_k}{dx_L} - \sum_{\substack{\text{all } i \\ \text{other than} \\ \text{A and L}}} \bigg(\frac{\partial\phi/\partial y_i}{\partial\phi/\partial T}\frac{dy_{ik}}{dx_L}\bigg) \tag{16}$$

and it follows, taking ϕ to be C_p, C_p/T, or $\partial V/\partial T$, that analogues of (7), (8) and (10):

$$\frac{dT_k}{dx_L}C_p \approx \text{const} + T\frac{dp_k}{dx_L}\frac{\partial V}{\partial T} - (1 - x_L)\sum_{\substack{\text{all } i \\ \text{other than} \\ \text{A and L}}} \bigg(\frac{dy_{ik}}{dx_L}(\tilde{H}_i - \tilde{H}_A)\bigg)$$

$$-\bigg(\tilde{H}_L - \sum_{\substack{\text{all } i \\ \text{other than L}}} (y_i\tilde{H}_i)\bigg) \tag{17}$$

$$\frac{dT_k}{dx_L}\frac{C_p}{T} \approx \text{const} + \frac{dp_k}{dx_L}\frac{\partial V}{\partial T} - (1 - x_L)\sum_{\substack{\text{all } i \\ \text{other than} \\ \text{A and L}}} \bigg(\frac{dy_{ik}}{dx_L}(\tilde{S}_i - \tilde{S}_A)\bigg)$$

$$-\bigg(\tilde{S}_L - \sum_{\substack{\text{all } i \\ \text{other than L}}} (y_i\tilde{S}_i)\bigg) \tag{18}$$

and

$$\frac{dT_k}{dx_L}\frac{\partial V}{\partial T} \approx \text{const} + \frac{dp_k}{dx_L}\bigg(-\frac{\partial V}{\partial p}\bigg) - (1 - x_L)\sum_{\substack{\text{all } i \\ \text{other than} \\ \text{A and L}}} \bigg(\frac{dy_{ik}}{dx_L}(\tilde{V}_i - \tilde{V}_A)\bigg)$$

$$-\bigg(\tilde{V}_L - \sum_{\substack{\text{all } i \\ \text{other than L}}} (y_i\tilde{V}_i)\bigg) \tag{19}$$

result† for a case in which the Pippard-like plots are roughly linear.

† Use is made, in the course of the argument, of relations of the type

$$\partial Z/\partial x_L = \tilde{Z}_L - \sum_{\substack{\text{all } i \\ \text{other than L}}} (y_i\tilde{Z}_i)$$

and

$$\partial Z/\partial y_i = (1 - x_L)(\tilde{Z}_i - \tilde{Z}_A)$$

which are readily inferred, for any extensive quantity Z, from the Gibbs–Duhem equation for Z.

If, instead, there are $2k - 1$ components, the corresponding relations are:

$$\left(\frac{\partial T_k}{\partial x_L}\right)_p C_p \approx \text{const} - (1 - x_L) \sum_{\substack{\text{all } i \\ \text{other than} \\ \text{A and L}}} \left(\left(\frac{\partial y_{ik}}{\partial x_L}\right)_p (\tilde{H}_i - \tilde{H}_A)\right)$$

$$- \left(\tilde{H}_L - \sum_{\substack{\text{all } i \\ \text{other than L}}} (y_i \tilde{H}_i)\right) \tag{20}$$

and two others which resemble equations (18) and (19) in much the same way that this resembles (17) (absence of any derivative of p_k, and the fact that the derivatives that are present are partial). It may be noted that, if addition of L did not affect the various y_{ik}, then these three relations would be virtually the same as the approximate relations which have been deduced (Wright 1972a) for the effect of composition on the λ temperature of such binary mixtures as $^4\text{He}/^3\text{He}$.

Appendix by R A G Gibson and P G Wright

A direct clarification should perhaps be given of the distinction between cases which give relations of Pippard's original type and cases which give relations of the less simple type obtained by Subramanyam *et al* (1974). To this end, consider, for three or more variables, the application of (say) the approach used by Zemansky (1968) for a deduction of the ordinary case of Pippard's relations for the two variables (T, p).

For definiteness, take an instance in which there are three variables (T, p, H^2)†. Let Q denote the continuum of points analogous to those of a λ curve as considered by Zemansky. Then

$$d(U + pV - TS - \mu_0 HM) = -S \, dT + V \, dp - \tfrac{1}{2}\mu_0 \chi \, d[H^2]$$

and any attempt to obtain a set of Pippard's relations would proceed by taking it that $(dS/dT)_Q$, $(dV/dT)_Q$ and $(d\chi/dT)_Q$ do not vary to any drastic extent.

Now

$$\left(\frac{dS}{dT}\right)_Q = \left(\frac{\partial S}{\partial T}\right)_{p,H} + \left(\frac{\partial S}{\partial p}\right)_{T,H}\left(\frac{dp}{dT}\right)_Q + \left(\frac{\partial S}{\partial [H^2]}\right)_{T,p}\left(\frac{d[H^2]}{dT}\right)_Q \tag{A1}$$

and it could appear at first sight that taking this quantity to be roughly constant gives only a relation

$$\left(\frac{\partial S}{\partial T}\right)_{p,H} + \frac{1}{dT_Q/dp}\left(\frac{\partial S}{\partial p}\right)_{T,H} + \frac{1}{dT_Q/d[H^2]}\left(\frac{\partial S}{\partial [H^2]}\right)_{T,p} \approx \text{const} \tag{A2}$$

while similar companion relations would be obtained by taking $(dV/dT)_\lambda$ and $(d\chi/dT)_\lambda$ to be roughly constant. These are not of Pippard's original simple type, yet relations of that type have been published for various situations involving three or more variables (table 1).

The resolution of any difficulty lies in noticing that there are two distinct cases to be considered, according to whether (in the three-dimensional space with coordinates T, p and H^2) Q constitutes a one-dimensional or a two-dimensional continuum. The former

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† It is to be noted that here, in contrast to the main text, H denotes a magnetic field.

Table 1. Two distinct cases.

Coordinates in an n-dimensional space	Critical points forming an $(n-1)$-dimensional continuum: 'normal' set of Pippard's relations is applicable.	Critical points forming an $(n-2)$-dimensional continuum: 'normal' set of Pippard's relations is not applicable, but generalisations are (provided that $n \geqslant 3$)
$n=2$ $\begin{cases} T, p \\ \\ T, \Gamma^{-D} \end{cases}$	λ transitions of He, NH_4Cl, etc (Pippard 1956, Rice 1967, Tisza 1961, Buckingham and Fairbank 1961) λ transitions in adsorbed films (Gibson and Wright 1975)	(Ordinary liquid–vapour critical point: an isolated point only)
$n=3$ $\begin{cases} T, p, H^2 \text{ or } E^2 \\ \\ T, p, x_B \\ \\ T, p, m^{-1/3} \\ \\ T, \Gamma^{-D}, H^2 \text{ or } E^2 \end{cases}$	Typical antiferromagnetic and antiferroelectric transitions (Sawatzky and Bloom 1964; Skalyo *et al* 1967, Griffiths and Wheeler 1970, Wright 1972c) λ transitions for such mixtures as $^4He/^3He$ (Wright 1972a, Subramanyam *et al* 1974) Simple λ transitions in small particles (Wright and Gibson 1975) Antiferromagnetic and antiferroelectric transitions in adsorbed films (Gibson and Wright 1978)	Ordinary liquid–vapout critical points as affected by a magnetic or electric field Ordinary critical mixing for two components (Subramanyam *et al* 1974)
$n=4$ $\quad T, p, x_B, H^2$ or E^2	Antiferromagnetic and antiferroelectric transitions in mixtures (Wright 1972b)	Ordinary critical mixing for two components, as affected by magnetic or electric field
$n=7$ $\quad T, X_1,$ $X_2 \dots X_6$	λ transitions in strained elastic solids (Viswanathan 1963, Garland 1964, Janovec 1966)	

case, of a *curve* Q in a three-dimensional space, may be exemplified by the ordinary liquid–vapour critical phenomenon as affected by a field; the latter, of a *surface* Q in a three-dimensional space, may be exemplified by a typical antiferromagnetic transition.

(i) In the case of a *curve* Q in a three-dimensional space, there is indeed only a relation of the type (A2) to be obtained from the condition $(dS/dT)_Q = 0$, another of the type from the condition $(dV/dT)_Q = 0$, and a third of that type from the condition $(d\chi/dT)_Q = 0$. It is a set of *three* relations of *this* type that is predicted to apply, not a set of six Pippard's relations of the original simpler type.

(ii) In the case of a *surface* Q in a three-dimensional space, Zemansky's argument based on equating a $(dS/dT)_Q$ to zero can be applied *twice*: first to a section of this surface at constant H, and then to a section at constant p. This gives rise to *two separate* relations

$$\left(\frac{\partial S}{\partial T}\right)_{p,H} + \frac{1}{(\partial T_Q/\partial p)_H}\left(\frac{\partial S}{\partial p}\right)_{T,H} \approx \text{const} \tag{A3a}$$

and

$$\left(\frac{\partial S}{\partial T}\right)_{p,H} + \frac{1}{(\partial T_Q/\partial[H^2])_p}\left(\frac{\partial S}{\partial[H^2]}\right)_{T,p} \approx \text{const.} \tag{A3b}$$

Two more result from equating a $(dV/dT)_Q$ to zero: first for a section of the surface Q at constant H, and then for a section at constant p. Two more result from similar reasoning for a $(d\chi/dT)_Q$. These are the six relations constituting the 'normal' set of simple Pippard's relations (Wright 1972c) for (say) an antiferromagnetic transition. Moreover, with this set of six, it is predicted unambiguously that the slope of a graph of (say) $-(\partial S/\partial p)_{T,H}$ against $(\partial S/\partial T)_{p,H}$ is approximately equal to $(\partial T_Q/\partial p)_H$; but with the set of three, arising in (i), it is not evident that the slope of such a graph, even if roughly linear, could be so interpreted.

The demonstrable possibility of obtaining the 'normal' set for the case of a λ surface in such a way (or, as is equally demonstrable, of obtaining it by Rice's approach) seems sufficient to validate the 'normal' set of Pippard's relations for any instance in which the λ points form an $(n-1)$-dimensional continuum in an n-dimensional space $(n \geq 2)$. Such instances include typical antiferromagnetic and antiferroelectric transitions in pure substances or mixtures in bulk, or in adsorbed layers.

When, however, it is only an $(n-2)$-dimensional continuum that is involved, the 'normal' set has to be replaced by relations of the type found by Subramanyam *et al* (1974). For the specific case of the ordinary liquid–vapour critical phenomenon in a field, these are

$$\frac{dT_c}{d[H^2]}\left(\frac{\partial S}{\partial T}\right)_{p,H} + \frac{dp_c}{d[H^2]}\left(\frac{\partial S}{\partial p}\right)_{T,H} + \left(\frac{\partial S}{\partial[H^2]}\right)_{T,p} \approx \text{const} \tag{A4}$$

together with two similar equations in which S is replaced by V and by χ.

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