Thermodynamic relations of Pippard's type for dielectric and magnetic properties of adsorbed layers near a λ-transition

1978 J. Phys. A: Math. Gen. 11 1645

(http://iopscience.iop.org/0305-4470/11/8/023)

J. Phys. A: Math. Gen. Vol. 11, No. 8, 1978. Printed in Great Britain

Thermodynamic relations of Pippard's type for dielectric and magnetic properties of adsorbed layers near a λ-transition

R A G Gibson† and P G Wright
Department of Chemistry, The University, Dundee, UK

Received 31 January 1977, in final form 22 March 1978

Abstract. A recent derivation of thermodynamic relations of Pippard's type for λ-transitions in adsorbed films is extended to include relations concerning dielectric and magnetic properties.

1. Introduction

For a considerable time, there has been a substantial body of work on dielectric and magnetic properties of adsorbed layers (see, for example, Young and Crowell 1962). Quite often, the adsorbed material may be one which exhibits a λ-transition associated with a drastic variation of dielectric or magnetic properties.

Thermodynamic discussions of Pippard's (1956) type have appeared in the literature for λ-transitions in materials in bulk whose dielectric and magnetic properties vary dramatically around a λ-temperature (Janovec 1966, Gambhir *et al* 1967, Viswanathan *et al* 1968, Wright 1972a,b, Gibson and Wright 1975a), and for λ-transitions in adsorbed layers without reference to dielectric or magnetic properties (Gibson and Wright 1975b). The present communication extends such discussions to cover dielectric and magnetic susceptibilities for adsorbed layers.

2. Notation

For the most part, the same symbols will be used as in the previous paper on λ-transitions in adsorbed layers (Gibson and Wright 1975b), but explicit definitions will be given for the dielectric and magnetic properties not considered there.

Consider, for definiteness, the magnetic behaviour exhibited when there is a powder of solid A, in the form of a long thin aggregate oriented parallel to a magnetic field, with gas B adsorbed on the solid. Let a quantity M^{a} (cf quantities Z^{a} in the previous paper) be defined as

$$\begin{pmatrix}\text{magnetic moment}\\ \text{of whole system}\end{pmatrix} - \begin{pmatrix}\text{magnetic moment}\\ \text{of unadsorbed gas}\\ \text{in the system}\end{pmatrix} - \begin{pmatrix}\text{magnetic moment which}\\ \text{the solid would have}\\ \text{had in the field if no}\\ \text{gas had been adsorbed}\end{pmatrix}.$$

† Present address: Physics Department, The University, Dundee, UK.

0305-4770/78/0008-1645$01.00

Similar definitions could readily be given if the adsorbed species B were not a gas but a solid or a liquid, or if it were an electric field that was involved.

Let quantities m^a and $\tilde{m}^a$ be defined by

$$m^a \equiv M^a / n_B^{ads}$$

(a 'moment' per unit amount of adsorbed B), and

$$\tilde{m}^a \equiv (\partial M^a / \partial n_B^{ads})_{T,H}$$

and then use a susceptibility χ^a (and a related $\tilde{\chi}^a$) defined by

$$\chi^a \equiv m^a / H, \qquad \tilde{\chi}^a \equiv \tilde{m}^a / H. \tag{1}$$

These definitions are formally applicable not only to the case of an adsorbed layer of a substance B which when in bulk exhibits a dielectric or magnetic λ-transition, but also to the case in which it is solid A that exhibits a λ-transition and the adsorbed species B on its own does not. In that second case, the formal 'susceptibility' χ^a may take negative values.

3. Relations implied by Tisza's argument

In the method used by Tisza (1961) and Garland (1964) for obtaining thermodynamic relations of Pippard's type, some suitable free energy is taken to be given approximately by an expression of the form

$$f(t) + tg(X_1) + h(X_1) + tm(X_2) + n(X_2) + \cdots$$

where $t \equiv T - T_\lambda(X_1, X_2, \ldots)$, and $X_1, X_2, \ldots$ are appropriate thermodynamic variables; and scrutiny of the algebraic forms implied for the various second derivatives of this free energy then leads to various approximate relations of linearity.

The free energy to be used here would be†

$$r \equiv u^a + pv^a - Ts^a - \mu_0 H m^a$$

(u^a, v^a, s^a being quantities as defined in the previous paper), whose differential dr is equal to

$$-s^a \, dT + v^a \, dp - \mu_0 m^a \, dH - \phi \, d[\Gamma^{-1}] \tag{2}$$

(the spreading pressure ϕ being $(\partial r / \partial [\Gamma^{-1}])_{T,p,H}$ in the present case involving a field); and the independent variables $X_1, X_2, \ldots$ would be the pressure, the square of the field (cf Wright 1972b), and some negative power Γ^{-D} of the amount adsorbed per unit area of surface (Gibson and Wright 1975b). Then (taking it that to a sufficient approximation the term $v^a dp$ may be omitted):

$$dr \approx -s^a \, dT - \frac{\mu_0}{2} \chi^a \, d[H^2] - \frac{\Gamma^{D-1} \phi}{D} \, d[\Gamma^{-D}] \tag{3}$$

and a set of six Pippard's relations follows from an application of Tisza's argument.

† The μ_0 is required if the expression is to be in SI form instead of Gaussian.

Two of these six relations are the two which were obtained in the previous discussion of λ-transitions in adsorbed layers (Gibson and Wright 1975b). Two more:

$$\left(\frac{\partial \chi^{\mathrm{a}}}{\partial T}\right)_{H,\Gamma} \approx \mathrm{const} - \frac{2}{\mu_0}\left(\frac{\partial T_\lambda}{\partial [H^2]}\right)_\Gamma \frac{C_{pH\Gamma}}{T} \tag{4}$$

and

$$\left(\frac{\partial \chi^{\mathrm{a}}}{\partial [H^2]}\right)_{T,\Gamma} \approx \mathrm{const} - \left(\frac{\partial T_\lambda}{\partial [H^2]}\right)_\Gamma \left(\frac{\partial \chi^{\mathrm{a}}}{\partial T}\right)_{H,\Gamma} \tag{5}$$

are analogues for adsorbed layers of two of the Pippard's relations (Wright 1972b) for the magnetic or dielectric properties of a bulk specimen. The remaining two:

$$\left(\frac{\partial \chi^{\mathrm{a}}}{\partial [\Gamma^{-D}]}\right)_{T,H} \approx \mathrm{const} - \left(\frac{\partial T_\lambda}{\partial [\Gamma^{-D}]}\right)_H \left(\frac{\partial \chi^{\mathrm{a}}}{\partial T}\right)_{H,\Gamma} \tag{6}$$

and

$$\left(\frac{\partial \chi^{\mathrm{a}}}{\partial [\Gamma^{-D}]}\right)_{T,H} \approx \mathrm{const} - \frac{2}{\mu_0}\left(\frac{\partial T_\lambda}{\partial [H^2]}\right)_\Gamma \left(\frac{\partial s^{\mathrm{a}}}{\partial [\Gamma^{-D}]}\right)_{T,H} = \mathrm{const} - \frac{2}{\mu_0}\left(\frac{\partial T_\lambda}{\partial [H^2]}\right)_\Gamma \frac{\Gamma^D}{D} \frac{q_{st} - Q}{T} \tag{7}$$

(or $\chi^{\mathrm{a}} - \tilde{\chi}^{\mathrm{a}} \approx \mathrm{const} - 2\mu_0^{-1}(\partial T_\lambda/\partial[H^2])_\Gamma(s^{\mathrm{a}} - \tilde{s}^{\mathrm{a}})$) are more definitely new. Both involve the dependence of the susceptibility χ^{a} on the extent of adsorption, with an implication that this dependence might be expected to vary relatively drastically around T_λ. (Compare the behaviour of a susceptibility of a homogeneous bulk specimen of a solid solution (Wright 1972a, Gibson and Wright 1975a).) Of the last two relations, one would correlate any drastic variation in the dependence of χ^{a} on Γ with the dependence of T_λ on field. The other would correlate it with the dependence of T_λ on the extent of adsorption.

If (which unfortunately appears not to be the case) sufficiently complete measurements were available on the dependence of a dielectric or magnetic χ^{a} on T and Γ in the vicinity of T_λ, then it could be ascertained how nearly linear a plot corresponding to (6) would be, and it would be possible to check on whether (say) an estimate of $(\partial T_\lambda/\partial[\Gamma^{-D}])_H$ found in this way was in close agreement with one inferred as suggested in the previous discussion (Gibson and Wright 1975b). Similarly, if sufficient complete measurements giving the heats of adsorption q_{st} and Q were available, use could be made of a plot corresponding to (7) to form an estimate of how drastically T_λ for an adsorbed layer would be affected by an applied field.

Acknowledgment

One of us (RAGG) wishes to thank the Carnegie Trust for the Universities of Scotland for a research scholarship.

References

Gambhir R D, Vaidya S N and Gopal E S R 1967 *J. Ind. Inst. Sci.* **49** 48–60
Garland C W 1964 *J. Chem. Phys.* **41** 1005–8
Gibson R A G and Wright P G 1975a *J. Phys. Chem. Solids* **36** 321–4
——1975b *J. Phys. A: Math. Gen.* **8** 1586–92

Janovec V 1966 *J. Chem. Phys.* **45** 1874–80
Pippard A B 1956 *Phil. Mag.* **1** 473–6
Tisza L 1961 *Ann Phys., NY* **13** 1–92
Viswanathan B, Vaidya S N and Gopal E S R 1968 *J. Ind. Inst. Sci.* **50** 83–99
Wright P G 1972a *J. Phys. A: Gen. Phys.* **5** 1015–7
—— 1972b *J. Phys. A: Gen Phys.* **5** 1206–19
Young D M and Crowell A D 1962 *Physical Adsorption of Gases* (London: Butterworths) chap. 10