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Elastic modulus, thermal expansion, and specific heat at a phase transition

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The interrelation of the elastic modulus, thermal-expansion coefficient, and specific heat of a transformed phase relative to the untransformed phase is calculated assuming a particular but useful form of the thermodynamic potential. For second-order phase transitions where this potential applies, measurements of modulus, expansion, and specific heat can yield the general (longitudinal as well as shear) first- and second-order stress (or strain) dependences of the transition temperature and of the order parameter at absolute zero. An exemplary application to one type of phase transition is given.

I. INTRODUCTION

A number of calculations are available which describe the behavior of the elastic modulus, and/or the thermal-expansion coefficient α relative to the specific heat C at a phase transition.[1–10] Generally, these results are restricted to a particular type of phase transition (e.g., λ or Ehrenfest second order), to a particular range in temperature (e.g., close to the transition temperature T_c), or to particular stress-type variables (e.g., volume expansion or compressibility). We derive below the interrelation of the elastic moduli, α, and C for a particular but useful form of the thermodynamic potential which will, in fact, include the results of previously calculated cases. The relationships are given for all $T < T_c$ and for general type stress (or strain) variables. We show how these formulas can, for certain cases of a second-order phase transition, yield the complete first- and second-order stress (or strain) dependences of T_c and of the order parameter at $T = 0$. A model application is shown.

II. THEORY

We assume that the difference in Gibbs free energy per mole, G, between the phases at $T < T_c$ can be written in the form

$$\Delta G = \sum_i \phi_i(\sigma) f_i[T/T_c(\sigma)], \tag{1}$$

where T_c and the ϕ_i are general functions of stress σ. The f_i's are general functions of T/T_c and normalized so that $f_i(0) = 1$ and $f_i(1) = 0$. In Eq. (1) and what follows we define for any property X

$$\Delta X(T) = X^H(T) - X^L(T) \tag{2}$$

as the difference between the (extrapolated) value of X for the high-temperature phase (X^H) and the observed value for the low temperature phase (X^L) at any $T < T_c$.

Equation (1) is a reasonably general form of ΔG and is the basis for useful approximations in many cases of common phase transformations (e.g., superconductivity, ferromagnetism, ferroelectricity, and some structural transformations). With $T_c = T_c(\sigma)$ we obtain the operation

$$\frac{df_i}{d\sigma} = \frac{\partial f_i}{\partial T_c}\frac{dT_c}{d\sigma} = -\frac{T}{T_c}\frac{\partial f_i}{\partial T}\frac{dT_c}{d\sigma}. \tag{3}$$

With Eqs. (1)–(3) and standard thermodynamic definitions one obtains the final result

$$\Delta\epsilon = -\left(\frac{d\ln T_c}{d\sigma}\right) T\Delta S - \sum_i \left(\frac{d\ln\phi_i}{d\sigma}\right)\Delta G_i, \tag{4}$$

$$\Delta\frac{d\epsilon}{dT} = \Delta\alpha = -\left(\frac{d\ln T_c}{d\sigma}\right)\Delta C_p + \left(\sum_i \frac{d\ln\phi_i}{d\sigma}\frac{\Delta S_i}{\Delta S} - \frac{d\ln T_c}{d\sigma}\right)\Delta S, \tag{5}$$

$$\Delta s_L = \left(\frac{d\ln T_c}{d\sigma}\right)^2 T\Delta C_p - AT\Delta S - \sum_i \left(\frac{1}{\phi_i}\frac{d^2\phi_i}{d\sigma^2}\right)\Delta G_i, \tag{6}$$

$$\Delta s_S = -\left(\frac{1}{T_c}\frac{d^2 T_c}{d\sigma^2}\right) T\Delta S - \sum_i \left(\frac{1}{\phi_i}\frac{d^2\phi_i}{d\sigma^2}\right)\Delta G_i, \tag{7}$$

with

$$A = \left[\frac{2d\ln T_c}{d\sigma}\left(\sum \frac{d\ln\phi_i}{d\sigma}\frac{\Delta S_i}{\Delta S}\right) - 2\left(\frac{d\ln T_c}{d\sigma}\right)^2 + \frac{1}{T_c}\frac{d^2T_c}{d\sigma^2}\right], \tag{8}$$

$$\Delta S_i = -\frac{\phi_i \partial f_i}{\partial T}, \tag{9}$$

$$\Delta S = \int_{T_c}^{T} \frac{\Delta C_p}{T}\, dT, \tag{10}$$

$$\Delta G_i = \phi_i f_i = -\int_{T_c}^{T} \Delta S_i\, dT. \tag{11}$$

Here S (or S_i) is the total (or ith term) entropy, C_p is the specific heat at constant stress, ϵ is the strain, α is the linear thermal-expansion coefficient, and s_L (or s_S) is an isothermal longitudinal (or high-symmetry[11] shear) elastic compliance.

III. REMARKS

(i) If one assumes, in place of Eq. (1), that

$$\Delta H=\sum_i \phi_i(\epsilon) f_i[(T/T_c(\epsilon)], \qquad (12)$$

where H is the Helmholtz free energy and ϵ is the strain, one reobtains Eqs. (4)–(11) with the following replacements:

$$\begin{aligned} &\sigma \rightarrow M^H\epsilon \text{ in Eqs. (4) and (5),} \\ &\Delta s \rightarrow \Delta M \text{ and } \sigma \rightarrow \epsilon \text{ in Eqs. (6)–(8),} \qquad (13) \\ &\Delta C_p \rightarrow \Delta C_V \text{ in Eqs. (5)–(7), (10),} \end{aligned}$$

where M is the adiabatic stiffness modulus and C_V is the specific heat at constant strain. Generally, Eq. (12) yields results which are similar to those from Eq. (1) though not identical because the initial assumptions differ. The calculated differences in the modulus change, for example, are roughly of order $(1-s^H/s^L)$. For the relatively rare cases where this is large it will be necessary to determine from other arguments which thermodynamic potential (if either) is correct.[12]

(ii) Although tensor notation has not been used in the above formulas this may be introduced by the replacements $\epsilon \rightarrow \epsilon_\alpha$, $\Delta\alpha \rightarrow \Delta\alpha_\alpha$, and $d/d\sigma \rightarrow d/d\sigma_\alpha$ in Eqs. (4) and (5). For the moduli in Eqs. (6)–(8) replace Δs with $\Delta s_{\alpha\beta}$, $(dx/d\sigma)^2$ with $(dx/d\sigma_\alpha)\times(dx/d\sigma_\beta)$, $2(dx/d\sigma)\,(dy/d\sigma)$ with $(dx/d\sigma_\alpha)\,(dy/d\sigma_\beta)+(dx/d\sigma_\beta)\,(dy/d\sigma_\alpha)$, and $d^2x/d\sigma^2$ with $d^2x/d\sigma_\alpha d\sigma_\beta$. The subscripts α and β run from 1 to 6 and give the components of the usual 1×6 strain and stress matrices and the 6×6 compliance matrix. For hydrostatic pressure p, ϵ is replaced by the fractional volume change $(V-V_0)/V_0$, σ by $-p$, and Δs by ΔK, where K is the compressibility.

(iii) Generally ΔC_p is negative and ΔS [Eq. (10)] is positive (as defined) for T just below T_c. At lower T, however, ΔC_p may become positive (see Sec. V). When this occurs a "quick" analysis of α and s via Eqs. (4)–(11) can often be made by using only data at $T=T_c$, $T=0$, and T where $\Delta C_p=0$.

(iv) This treatment does not require a critical choice of T_c. If the transition onset is broadened by some mechanism and occurs at T_0, and if Eq. (1) still applies, the results are still correct except that the "base line" for extrapolating X^H would be chosen so that $\Delta X=0$ at $T=T_0$. This will allow analyses of a transition which has been broadened by intrinsic effects (e.g., fluctuations) and, to some extent, even sample inhomogeneity,[13] provided always that Eq. (1) applies in that temperature interval.

(v) Equation (1) will apply to many second-order transformations. For Landau-type transformations ϕ is related to the order parameter at $T=0$ and f will give the temperature dependence of the order parameter. However, it must be determined from other theory to what extent (if any) it applies to all or any part of a first-order transformation.

(vi) If, in Eq. (1), one chooses the functional form $f_i(T_c-T)$ instead of $f_i(T/T_c)$ then Eqs. (3)–(11) are reobtained with the replacements given in Appendix A. These generally produce negligible changes at $T\sim T_c$ for a second-order phase transformation.

(vii) No attempt has been made to include explicit anharmonic effects since it will be difficult, in practice, to rely upon Eq. (1) to higher orders in σ. Furthermore, the complete anharmonic behavior necessary for these corrections is generally not known. However, these corrections should be estimated since they will determine the reliability of the analyses. A very rough estimate of volume anharmonic corrections for the modulus, as an example, can be established from

$$(\Delta s)_{\text{anh}} \sim s\,\frac{d\ln s}{d\ln V}\,\frac{\Delta V}{V},$$

where $\Delta V/V=3\Delta\epsilon$ and $d\ln s/d\ln V\sim$ twice the Gruneisen constant (typically ~ 1 to 3). When $(\Delta s)_{\text{anh}}$ is $\sim\Delta s$ in Eq. (6), a reliable analysis can no longer be made.

(viii) This analysis will be useful if, from a microscopic of phenomenological theory, a free energy in the form of Eq. (1) can be written. This will allow measurements of α and s to yield stress dependences of the parameters of the theory.

IV. ANALYSIS

Equations (4)–(7) show that for a second-order transformation at T_c the thermal-expansion coefficient undergoes a discontinuity $-(d\ln T_c/d\sigma)\Delta C_p(T_c)$ and the longitudinal compliance has a discontinuity $(d\ln T_c/d\sigma)^2 T_c\Delta C_p(T_c)$. [These results, of course, have been obtained previously and can be established through more general relations than Eq. (1).[14]] No discontinuity can occur for high-symmetry shear compliances since $d/d\sigma=0$ for all structure related properties. Close to the transition only the terms proportional to ΔC_p yield a significant contribution[15] unless $d\ln T_c/d\sigma$ is very small or A in Eq. (6) is very large. Thus, the thermal expansion and modulus anomalies at T_c should normally look like the specific-heat anomaly and with magnitudes relative to ΔC_p of $-d\ln T_c/d\sigma$ and $T_c(d\ln T_c/d\sigma)^2$, respectively.

In addition to the change in magnitudes of α and s at T_c there will also be changes in $d\alpha/dT$ and ds/dT which will be determined by the entropy[15] as well as the specific-heat terms in Eqs. (5) and (6). At lower temperatures the full Eqs. (4)–(8) will apply.

If ΔC_p has been measured [and ΔS calculated

TABLE I. Data analysis and base-line requirements. These results are for the simple potential given by Eq. (21). For the more general case [Eq. (1)] the substitutions in lines 2, 4, 5, 7, and 8 can be found by comparing Eqs. (5)–(8) with Eqs. (B1–B3).

			Base-line requirements		
Mode	Temperature interval	Quantity obtained	Thermal-expansion coefficient	Modulus	Specific heat
Thermal-expansion coefficient	$\sim T_c$	$d\ln T_c/d\sigma$	Not stringent		Not stringent
Thermal-expansion coefficient	$\sim$0 K to T_c	$d\ln\phi/d\sigma$	Conditional[a]		Stringent[b]
Shear compliance	$\lesssim T_c$	$d^2T_c/d\sigma^2$		Not stringent	Not stringent
Shear compliance	$\sim$0 K	$d^2\phi/d\sigma^2$		Conditional[a]	Not required
Shear compliance	$\sim$0 K to T_c	f or ϕf		Conditional[a]	Stringent[b]
Longitudinal compliance	$\sim T_c$	$(d\ln T_c/d\sigma)^2$		Not stringent	Not stringent
Longitudinal compliance	$\sim$0 K	$d^2\phi/d\sigma^2$		Conditional[a]	Not required
Longitudinal compliance	$\sim$0 K to T_c	$\frac{2d\ln\phi}{d\sigma}\frac{d\ln T_c}{d\sigma}+\frac{1}{T_c}\frac{d^2T_c}{d\sigma^2}$[c]		Conditional[a]	Stringent[b]

[a] Depends on magnitude of anomaly.

[b] Less stringent if Debye behavior applies.

[c] Assumes f has been obtained from shear compliances (line 5). Also yields $d\ln\phi/d\sigma$, $d^2T_c/d\sigma^2$, and $dT_c/d\sigma$ alone if thermal expansion is known.

from Eq. (9)], then the measurement of $\Delta\alpha$ will yield

$$\frac{d\ln T_c}{d\sigma} \tag{14}$$

and

$$\sum_i \frac{d\ln\phi_i}{d\sigma}\frac{\Delta S_i}{\Delta S}\,. \tag{15}$$

If Δs and ΔC_p have been measured one obtains in a similar way

$$\left(\frac{d\ln T_c}{d\sigma}\right)^2 \quad \text{for longitudinal } \sigma, \tag{16}$$

$$\frac{1}{T_c}\frac{d^2T_c}{d\sigma^2} \quad \text{for shear } \sigma, \tag{17}$$

$$\sum_i\left(\frac{1}{\phi_i}\frac{d^2\phi_i}{d\sigma^2}\right)\phi_i f_i \quad \text{for any } \sigma, \tag{18}$$

$$2\frac{d\ln T_c}{d\sigma}\sum_i\frac{d\ln\phi_i}{d\sigma}\frac{\Delta S_i}{\Delta S}+\frac{1}{T_c}\frac{d^2T_c}{d\sigma^2} \quad \text{for longitudinal } \sigma. \tag{19}$$

A method of analysis for these results (in simplified form) is outlined in Table I. Note that the sign of $d\ln T_c/d\sigma$ is obtained from the expansion, but not the modulus measurements. However, the modulus measurements yield additional information about other strain dependences.

Equations (14), (16), and (17) provide useful information, Eq. (18) somewhat less, and Eqs. (15) and (19) yield least of all since the ΔS_i, which are functions of temperature, cannot be evaluated separately.

To proceed further one must establish, from other theory, an analytical relationship among the f_i. One such choice which has been used for some transformations is $f_i=(1-T/T_c)^i$, where some or all integers i are allowed. In this case it immediately follows that

$$\Delta S_i=+(i\phi_i/T_c)(1-T/T_c)^{i-1}, \tag{20}$$

with which Eq. (15) now yields $\sum_i d\phi_i/d\sigma$ and Eq. (19) is also simplified.

V. APPLICATION OF THE THEORY IN SIMPLIFIED FORM

The simplest case which is still useful in many descriptions is to assume (i) all $\phi_i=\phi$ or (ii) all first-order (and all second-order) fractional stress dependences of ϕ_i are equal. In either case, this is equivalent of the starting assumption

$$\Delta G=\phi(\sigma)f[T/T_c(\sigma)]. \tag{21}$$

The thermal-expansion coefficient and modulus for this case are given in Appendix B.

Equation (21) is a reasonably good description of the superconducting,[2,7,8] some magnetic,[10] and other transitions. One may be able to further simplify Eqs. (B1)–(B3) if a law of corresponding states ($n d\ln\phi = d\ln T_c$) holds. For example, $n \sim \frac{1}{2}$ for some superconductors).

VI. EXAMPLE

To illustrate the above we use Eq. (21) and take

$$f = \left(1 - \frac{T^2}{T_c^2}\right)^2 . \tag{22}$$

The results for ΔG, ΔS, and ΔC_p are given in Appendix C. Here we have rewritten ΔG $(= \phi f)$, ΔS, and ΔC_p in terms of $\Delta C_p(T_c)$, the specific-heat discontinuity at T_c which is a convenient way to scale the data.

A. Remarks

(i) The discontinuity in ΔC_p at T_c again leads to discontinuities in $\Delta\alpha$ and Δs_L proportional to $d\ln T_c/d\sigma$ and its square, respectively. Either sign may occur for $\Delta\alpha$ but for s the transformation must always lead to an increase on cooling.

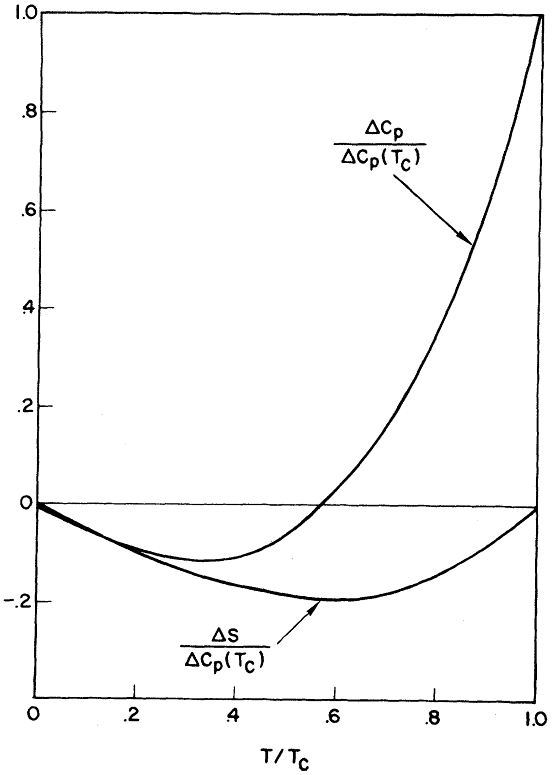

FIG. 1. Temperature dependence of ΔC_p and ΔS (normalized to the specific-heat discontinuity at T_c) obtained from Eqs. (22) and (C1–C3). These terms, modified by coefficient [see Eq. (B1)] yield the change in thermal-expansion coefficient resulting from a phase transformation.

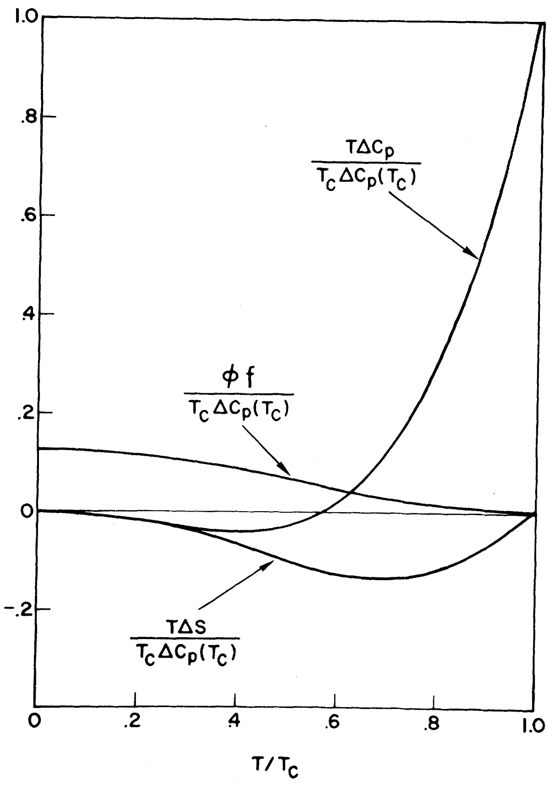

FIG. 2. Temperature dependence of $T\Delta C_p$, $T\Delta S$, and ϕf [normalized to $T_c \Delta C_p(T_c)$] obtained from Eq. (22). These terms, modified by coefficients [see Eqs. (B2) and (B3)], yield the change in elastic compliance resulting from a phase transformation.

(ii) At $T = T_c$ discontinuities in temperature derivatives of S, C_p, α, and s are obtained. These are given in Appendix D. The magnitude and temperature slope of these discontinuities are a convenient way to analyze data.

(iii) Analysis at $T = T_c/\sqrt{3}$ is convenient since $\Delta C_p = 0$. The remaining terms in $\Delta\alpha$ and Δs are proportional to ΔS which has its minimum value equal to $-\Delta C_p(T_c)/3\sqrt{3}$, $T\Delta S$ which equals $-\frac{1}{9} T_c \Delta C_p(T_c)$ and ϕf which equals $-\frac{1}{18} T_c \Delta C_p(T_c)$.

(iv) $T\Delta S$ has a minimum value of $-\frac{1}{8} T_c \Delta C_p(T_c)$ at $T = T_c/\sqrt{2}$.

A method of data analysis to obtain all quantities is outlined in Table I. Figures 1 and 2 show the temperature dependences of ϕf, ΔS, $T\Delta S$, ΔC_p, and $T\Delta C_p$ (all normalized) obtained from Eq. (22) which determine the separate contributions to $\Delta\alpha$ and Δs. Figure 3 shows the resulting behavior of $\Delta\alpha$ and Δs assuming, for illustrative purposes only,

$$\frac{d\ln T_c}{d\sigma} = \frac{1}{2}\frac{d\ln\phi}{d\sigma} \text{ and } \frac{1}{T_c}\frac{d^2 T_c}{d\sigma^2} = \frac{1}{2\phi}\frac{d^2\phi}{d\sigma^2} = \left(\frac{d\ln T_c}{d\sigma}\right)^2$$

for longitudinal compliances. For shear compli-

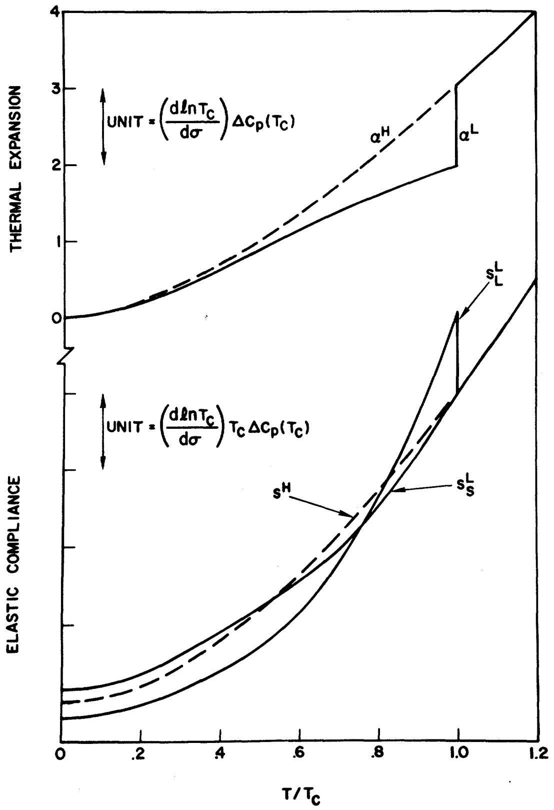

FIG. 3. Illustration of thermal expansion and compliance behavior predicted from Eqs. (B1)–(B3) and (C1)–(C3). The parameters assumed for these plots are given at the end of Sec. V. For convenience we have put $s^H_S = s^H_L = s^H$.

ances we also take $(1/T_c)(d^2T_c/d\sigma^2) = (1/2\phi)(d^2\phi/d\sigma^2)$ which we further set equal to $-(s_S^2/s_L)(d\ln T_c/d\sigma_L)$ for the longitudinal case.[16]

VII. SOME LIMITATIONS

(i) Successful analysis requires that the proper base lines for C_p, α, and s of the high-temperature phase be extrapolated to 0 K. If T_c is low, Debye (for C_p) and Grüneisen (for α) behavior may be used to approximate the behavior. The compliance can be extrapolated using similar models. At high T the extrapolations are more difficult. For C_p above T_c one may calculate the Debye contribution (C_V) and assume the remaining portion (electronic, and volume and shear anharmonic contributions) to be proportional to T. This will allow a reasonable though not accurate extrapolation to low T. Similar methods, including the use of the Grüneisen relation, can be used for α and s. Uncertainty in this extrapolation may restrict the amount of data obtained from the analysis. Table I indicates how critically the various parameters depend upon the base-line accuracy.

(ii) In all relations above the static isothermal values of C, α, and s are implied. If the modulus is measured by ac techniques then dispersion from various relaxation phenomena may contribute error. In addition to those discussed elsewhere[8] the experimenter must determine if there are relaxations resulting from critical behavior (when $\omega\tau \sim 1$) close to T_c. Fortunately, it is often possible to bypass this small temperature region and still obtain useful data.

(iii) If the transformation involves a change in microscopic (x-ray structure) or macroscopic (domain formation) symmetry some effect on α or s measurements may occur. For the latter, domain wall motion, especially at low frequencies, may contribute in a manner similar to the "ΔE" effect in ferromagnetism. If the effect is large it may be best to remove the domains with an appropriate force (magnetic, electric, or stress) field whose direct effect on the modulus is small or can be determined separately.

We have attempted to outline some of the experimental problems in applying the thermodynamic derivation given above without giving detailed solutions to them. The most effective methods will depend upon the experimental conditions and the material being studied.

An application of these results to a ferromagnetic transition will be given in a forthcoming paper.[17]

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APPENDIX A

For f_i in Eq. (1) of the form $f_i(T_c - T)$ instead of $f_i(T/T_c)$, Eqs. (3)–(11) are reobtained with the replacements

$T/T_c \rightarrow 1$ in Eq. (3), $T \rightarrow T_c$ in Eq. (4),

$\Delta C_p \rightarrow \frac{T_c}{T}\Delta C_p$ in Eq. (5), $\frac{d\ln T_c}{d\sigma}\Delta S \rightarrow 0$ in Eq. (5),

$T\Delta C_p \rightarrow (T_c^2/T)\Delta C_p$ in Eq. (6), $T\Delta S \rightarrow T_c\Delta S$

in Eqs. (6) and (7),

$-2\left(\frac{d\ln T_c}{d\sigma}\right)^2 \rightarrow 0$ in Eq. (8).

APPENDIX B

The thermal expansion and modulus obtained from Eq. (21) are

$$\Delta\alpha = -\left(\frac{d\ln T_c}{d\sigma}\right)\Delta C_p + \left(\frac{d\ln\phi}{d\sigma} - \frac{d\ln T_c}{d\sigma}\right)\Delta S, \qquad \text{(B1)}$$

$$\Delta s_L = \left(\frac{d\ln T_c}{d\sigma}\right)^2 T\Delta C_p - \left[2\frac{d\ln\phi}{d\sigma}\,\frac{d\ln T_c}{d\sigma} - 2\left(\frac{d\ln T_c}{d\sigma}\right)^2 + \frac{1}{T_c}\frac{d^2T_c}{d\sigma^2}\right] T\Delta S - \left(\frac{1}{\phi}\frac{d^2\phi}{d\sigma^2}\right)\phi f, \tag{B2}$$

$$\Delta s_S = -\frac{1}{T_c}\frac{d^2T_c}{d\sigma^2}\, T\Delta S - \left(\frac{1}{\phi}\frac{d^2\phi}{df^2}\right)\phi f, \tag{B3}$$

$$\phi f = \Delta G\,. \tag{B4}$$

APPENDIX C

From Eq. (22) one obtains

$$\Delta G = -\tfrac{1}{8}\, T_c \Delta C_p(T_c)\,(1 - T^2/T_c^2)^2, \tag{C1}$$

$$\Delta S = -(T/2T_c)\,\Delta C_p(T_c)\,(1 - T^2/T_c^2), \tag{C2}$$

$$\Delta C_p = -(T/2T_c)\Delta C_p(T_c)\,(1 - 3T^2/T_c^2), \tag{C3}$$

$$\Delta C_p(T_c) = -8\phi/T_c. \tag{C4}$$

APPENDIX D

From Eqs. (22) and (C1)–(C3) one obtains at $T = T_c$

$$\frac{d\Delta S}{dT} = \frac{\Delta C_p(T_c)}{T_c}\,, \tag{D1}$$

$$\frac{dT\Delta S}{dT} = \Delta C_p(T_c), \tag{D2}$$

$$\frac{d\Delta C_p}{dT} = \frac{4\Delta C_p(T_c)}{T_c}\,, \tag{D3}$$

$$\frac{dT\Delta C_p}{dT} = 5\Delta C_p(T_c). \tag{D4}$$

From these and Eqs. (B1)-(B3) one obtains, at T_c, the discontinuities in temperature derivative

$$\frac{d\Delta\alpha}{dT} = \left(\frac{d\ln\phi}{d\sigma} - \frac{5d\ln T_c}{d\sigma}\right)\frac{\Delta C_p(T_c)}{T_c}\,, \tag{D5}$$

$$\frac{d\Delta s_L}{dT} = \left[7\left(\frac{d\ln T_c}{d\sigma}\right)^2 - 2\frac{d\ln\phi}{d\sigma}\,\frac{d\ln T_c}{d\sigma} - \frac{1}{T_c}\frac{d^2T_c}{d\sigma^2}\right]\Delta C_p(T_c), \tag{D6}$$

$$\frac{d\Delta s_S}{dT} = -\left(\frac{1}{T_c}\frac{d^2T_c}{d\sigma^2}\right)\Delta C_p(T_c). \tag{D7}$$

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[11] High-symmetry shear stresses are those for which positive and negative stress produce identical structures by symmetry. A sufficient condition is that the particle displacement direction be perpendicular to a mirror plane.

[12] Scaling-law theories for behavior very close to T_c generally use the Gibbs rather than the Helmholtz potential.

[13] The application of Eq. (1) to transitions broadened by sample inhomogeneity would assume that ϵ, s, and C average the inhomogeneity in the same way. This is a reasonable first approximation, but by no means precise.

[14] If one applies the Clausius-Clapeyron equation $dT/d\sigma = -\Delta\epsilon/\Delta S$ to a transition with no entropy or strain change at T_c ($dT_c/d\sigma = 0/0$) then, by L'Hospital's rule, temperature and stress derivatives of the indeterminate fraction will yield the results obtained above.

[15] The ΔS terms, which, for a second-order transition, are the first to contribute in addition to the ΔC_p terms below T_c will generally increase linearly with $T_c - T$ at the transition. The terms containing ΔG will increase more slowly at T_c than those containing ΔS.

[16] The basis for the last equality is that since second-order shear strains lead to first-order volume changes one expects a (volume) contribution to $d/d\sigma_S^2$ which is $\sim -d/d\sigma_L$. [See H. B. Huntington, Solid State Phys. 7, 237 (1958).] To this must be added, of course, the (volume independent) pure shear contributions. Figure 3 shows that the contribution of just the volume effect to the shear modulus is small near T_c compared to that for the longitudinal modulus. In practice, the shear modulus changes are often large indicating the importance of the pure symmetry-breaking effects.

[17] G. Hausch and L. R. Testardi (unpublished).