

Landau order-disorder and its implementation

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Introduction

This relates to the use of Landau in Holland & Powell (2011) and its implementation in THERMOCALC with the dataset, `tc-ds62.txt`. This is necessary because there was an unfortunate omission in Holland & Powell (2011) regarding the form of the Landau used (which differs from that in Holland & Powell, 1998). This note is only really relevant if you are implementing Landau in your own computer code that reads and calculates with the Holland & Powell datasets.

Theory

We start with an expression for the Gibbs energy of ordering, G_{ord} (Holland & Powell, 1998):

$$G_{\text{ord}} = \frac{1}{2} (a(T - T_c) + a_v P) Q^2 + \frac{1}{6} a T_c Q^6$$

with Q the order parameter, and T_c the critical temperature at $P = 0$. This can be represented in terms of a pressure-dependent critical temperature, $T_c^* = T_c - \frac{a_v}{a} P$

$$G_{\text{ord}} = \frac{1}{2} a (T - T_c^*) Q^2 + \frac{1}{6} a T_c Q^6$$

To get e.g. V_{ord} as the P derivative of G_{ord} , the differentiation is simplified by invoking the chain rule as Q is also a function of PT , so in principle its derivatives need to be included. Now, using the chain rule

$$V_{\text{ord}} = \left(\frac{\partial G_{\text{ord}}}{\partial P} \right)_T = \left(\frac{\partial G_{\text{ord}}}{\partial P} \right)_{TQ} + \left(\frac{\partial G_{\text{ord}}}{\partial Q} \right)_{PT} \left(\frac{\partial Q}{\partial P} \right)_T$$

which, with the equilibrium condition,

$$\left(\frac{\partial G_{\text{ord}}}{\partial Q} \right)_{PT} = 0$$

gives

$$V_{\text{ord}} = \left(\frac{\partial G_{\text{ord}}}{\partial P} \right)_T = \left(\frac{\partial G_{\text{ord}}}{\partial P} \right)_{TQ} = \frac{1}{2} a_v Q^2$$

Similarly

$$S_{\text{ord}} = - \left(\frac{\partial G_{\text{ord}}}{\partial T} \right)_P = - \left(\frac{\partial G_{\text{ord}}}{\partial T} \right)_{PQ} = -\frac{1}{2}aQ^2$$

with H_{ord} found by $H_{\text{ord}} = G_{\text{ord}} + TS_{\text{ord}}$ as G_{ord} is linear in PT , or via

$$H_{\text{ord}} = \left(\frac{\partial G_{\text{ord}}/T}{\partial 1/T} \right)_P = \left(\frac{\partial G_{\text{ord}}/T}{\partial 1/T} \right)_{PQ}$$

Note that the above expression is for G_{ord} . In the various datasets we have chosen to make the STP dataset properties (i.e. for $P_0 = 0.001$ kbar and $T_0 = 298.15$ K) be for the equilibrium state of order of the phase. So, for quartz, the STP properties quoted are for ordered α -quartz, rather than for the metastable disordered form, β -quartz. This means that these properties include G_{ord} for P_0 and T_0 (that we will call $G_{\text{ord},0}$). Thus to calculate the properties at PT , the component parts of $G_{\text{ord},0}$ must be removed from the STP properties, *then* G_{ord} added. This can be thought of in terms of

$$G_{\text{dis}} \equiv -G_{\text{ord},0} + G_{\text{ord}}$$

The expression for G_{ord} may be reparameterised in terms of

$$V_{\text{max}} \equiv V_{\text{ord}}|_{Q=1} = \frac{1}{2}a_v$$

Similarly

$$S_{\text{max}} \equiv S_{\text{ord}}|_{Q=1} = -\frac{1}{2}a$$

Landau in the dataset is in terms of T_c , S_{max} and V_{max} parameters.

Landau in Holland & Powell (1998) and in THERMOCALC for ds55

Landau in the dataset generation for `tc-ds55.txt` is implemented exactly as written out in Holland & Powell (1998). *However* in 2007 we discovered that the equation we used for G_{disord} and therefore also for Q in Holland & Powell (1998) (and in THERMOCALC) was incorrect... We decided not to correct THERMOCALC at that time, which would have required also making a new dataset (i.e. `tc-ds56`), instead waiting to incorporate the correction in ds6. The main reason for delaying was that the resulting change would have been minor, but would still have disrupted all work in progress with `tc-ds55.txt` at that time. We also thought ds6 would be published well before 2011.

As implemented in THERMOCALC for use with `tc-ds55.txt`, G_{dis} is

$$G_{\text{dis}}^{\text{ds55}} = T_c S_{\text{max}}(Q_0^2 - \frac{1}{3}Q_0^6) - T_c^* S_{\text{max}}(Q^2 - \frac{1}{3}Q^6) - T \{S_{\text{max}}(Q_0^2 - Q^2)\} + P \{V_{\text{max}}Q_0^2 V_f\}$$

using the notation as in Holland & Powell(1998), in addition in which V_f “shapes” the V_{max} contribution using the same $\alpha - \kappa$ expression as used for integrating volume up pressure (see Holland & Powell, 1998). Using the equilibrium condition

$$\left(\frac{\partial G_{\text{dis}}^{\text{ds55}}}{\partial Q} \right)_{PT} = 0$$

gives the equilibrium value of Q to be

$$Q^4 = \frac{T_c^* - T}{T_c^*}$$

This equation for $G_{\text{dis}}^{\text{ds55}}$ and therefore also the equation for Q^4 are what turned out to be incorrect. They are however correct at 1 bar, where $T_c^* = T_c$, with the discrepancy increasing with increasing P , and decreasing T from T_c^* . As the dataset was calculated with these equations, then calculations with the dataset which also use these equations will not be deleteriously affected.

Landau in Holland & Powell (2011) and in THERMOCALC for ds62

As implemented in THERMOCALC for use with `tc-ds61.txt`, G_{dis} is

$$G_{\text{dis}}^{\text{ds61}} = T_c S_{\text{max}}(Q_0^2 - \frac{1}{3}Q_0^6) - S_{\text{max}}(T_c^* Q^2 - \frac{1}{3}T_c^* Q^6) - T \{S_{\text{max}}(Q_0^2 - Q^2)\} + P \{V_{\text{max}}Q_0^2\}$$

with the “shaping” term, V_f , an unnecessary complication, now omitted. Using the equilibrium condition

$$\left(\frac{\partial G_{\text{dis}}^{\text{ds61}}}{\partial Q} \right)_{PT} = 0$$

gives the equilibrium value of Q to be

$$Q^4 = \frac{T_c^* - T}{T_c}$$

In these expressions, the parts in red are those that differ from the ds55 (incorrect) versions. Run `thermocalc` in mode 0, for, for example, quartz or calcite, is an appropriate implementation.