

3. Thermodynamics Of Phase Transitions

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3.A. Introductory

3.B. Coexistence of Phases: Gibbs Phase Rule

Coexisting phases are in thermal & mechanical equilibrium.

They can also exchange matter.

Hence, they have the same T , Y , and μ .

YXT System of 1 Kind of Particles

The condition for the coexistence of 2 phases I and II is

$$\mu^I(Y, T) = \mu^{II}(Y, T) \quad (3.1)$$

where, according to the Gibbs-Duhem equation (2.62), μ is a function of intensive variables only.

Eq(3.1) can be solved to give the **coexistence curve** of the 2 phases

$$Y = Y(T) \quad (3.2)$$

in the Y - T plane.

The conditions for the coexistence of 3 phases I , II and III are

$$\mu^I(Y, T) = \mu^{II}(Y, T) = \mu^{III}(Y, T) \quad (3.3)$$

which can be solved to give the locations of **triple points** in the Y - T plane.

There cannot be a coexistence of more than 3 phases because the coexistence conditions will be over-determined.

YXT System of m Kinds of Particles

For a mixture of m different types of particles in a YXT system, the independent variables can be chosen as Y, T, n_i , where n_i is the number of moles of the i th type particles, and $i = 1, \dots, m$. For a closed system, the total number n of moles is a constant and we can write

$$\sum_{i=1}^m n_i = n \quad \sum_{i=1}^m x_i = 1$$

where $x_i = \frac{n_i}{n}$ is the **molar fraction** of particles of type i .

Thus, only $m - 1$ of the x_i 's are independent and the system itself has only $m + 1$

independent (intensive) variables Y, T, \mathbf{x} , where $\mathbf{x} = (x_1, \dots, x_{m-1})$.

The conditions for the coexistence of r phases are

$$\mu_1^I(Y, T, \mathbf{x}^I) = \mu_1^{II}(Y, T, \mathbf{x}^{II}) = \dots = \mu_1^r(Y, T, \mathbf{x}^r) \quad (3.4)$$

... ..

$$\mu_i^I(Y, T, \mathbf{x}^I) = \mu_i^{II}(Y, T, \mathbf{x}^{II}) = \dots = \mu_i^r(Y, T, \mathbf{x}^r) \quad (3.5)$$

... ..

$$\mu_m^I(Y, T, \mathbf{x}^I) = \mu_m^{II}(Y, T, \mathbf{x}^{II}) = \dots = \mu_m^r(Y, T, \mathbf{x}^r) \quad (3.6)$$

where μ_i^s is the chemical potential of the i -type particles in the s th phase whose composition is $\mathbf{x}^s = (x_1^s, \dots, x_{m-1}^s)$.

The number of independent equations in (3.4-6) is $m(r-1)$.

The number of unknowns is $2 + r(m-1)$.

The maximum number R of phases that can coexist simultaneously is therefore given by

$$m(R-1) = 2 + R(m-1)$$

i.e.,

$$R = m + 2$$

3.C. Classification of Phase Transitions

For a system of m kinds of particles,

$$G = \sum_{j=1}^m n_j \mu_j \quad (3.7)$$

Since

$$dG = \left(\frac{\partial G}{\partial T} \right)_{Y\{n_j\}} dT + \left(\frac{\partial G}{\partial Y} \right)_{T\{n_j\}} dY + \sum_{j=1}^m \left(\frac{\partial G}{\partial n_j} \right)_{TY\{n_i | i \neq j\}} dn_j$$

we have, for constant T and Y ,

$$(dG)_{YT} = \sum_{j=1}^m \left(\frac{\partial G}{\partial n_j} \right)_{TY\{n_{i \neq j}\}} dn_j = \sum_{j=1}^m \mu_j dn_j \quad (3.8)$$

At a transition point, 2 or more phases can coexist in equilibrium. The absence of matter exchange means that, for every kind of particles, the values of its chemical potential in the coexisting phases are equal, i.e.,

$$\mu_i^r = \mu_i^s \quad \text{for } i = 1, \dots, m \quad (a)$$

where r, s denotes the coexisting phases.

Without loss of generality, we shall restrict our discussion to cases where the entire system is always in a single homogeneous phase.

Eqs(a) and (3.7) mean that, at a transition point, G of all coexisting phases are equal.

In other words, the function $G(Y, T, \mathbf{x})$ is continuous at a transition point.

The manifest differences in the properties of the phases must then appear as discontinuities in some derivatives of G . If the 1st order derivatives are discontinuous, the transition is called **1st order**. Otherwise, it is called **continuous**.

In an older scheme introduced by Ehrenfest, the **order of the transition** is taken to be the lowest order of the derivatives that are discontinuous.

Typical behavior of G of a PVT system near a 1st order transition is shown in Fig.3.2.

Discontinuity in $\left(\frac{\partial G}{\partial P} \right)_{T\{n_j\}} = V$ means a finite difference of volumes of the 2 phases,

$$\Delta V = V^I - V^{II} = \left(\frac{\partial G}{\partial P} \right)_{T\{n_j\}}^I - \left(\frac{\partial G}{\partial P} \right)_{T\{n_j\}}^{II} \quad (3.9)$$

Discontinuity in $\left(\frac{\partial G}{\partial T} \right)_{P\{n_j\}} = -S$ means a finite difference of entropy of the 2 phases,

$$\Delta S = S^I - S^{II} = \left(\frac{\partial G}{\partial T} \right)_{P\{n_j\}}^{II} - \left(\frac{\partial G}{\partial T} \right)_{P\{n_j\}}^I \quad (3.10)$$

which means the heat capacities are not defined.

Since G is continuous, the difference in enthalpy (**latent heat**) is given by

$$\Delta H = \Delta(G + TS) = T\Delta S \quad (3.11)$$

The case for a continuous transition is shown in Fig.3.3.

The distinguishing feature is the peak in the heat capacity at the transition point.

3.D. Pure *PVT* Systems

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3.D.1. Phase Diagrams

The coexistence curves of a typical pure PVT system are shown in Fig.3.4.

In general, there are 3 possible phases, namely, vapor, liquid, and solid.

All transitions are 1st order with accompanying latent heat.

Coexisting phases	Name of curve	Symmetry change
vapor-liquid	vaporization	no
liquid-solid	fusion	yes
vapor-solid	sublimation	yes

Point A is the **triple point** at which all 3 phases coexist.

Point C is the **critical point** at the end of the vaporization curve.

The vaporization curve AC actually denotes a vapor-liquid coexistence region as shown in the P - v diagram in Fig.3.5. Note that the isotherms are also isobars in the coexistence region.

The 3-D P - v - T diagram is shown in Fig.3.6.

3.D.2. Coexistence Curves: Clausius-Clapeyron Equation

The molar Gibbs energies (chemical potentials), $g = \frac{G}{n} = \mu$, of 2 coexisting phases I and II , must be equal. Thus,

$$dg^I = dg^{II} \quad \text{along the coexistence curve}$$

For a PVT system, this means

$$v^I dP - s^I dT = v^{II} dP - s^{II} dT \quad (3.12)$$

i.e.,

$$\left(\frac{dP}{dT} \right)_{\text{coex}} = \frac{s^I - s^{II}}{v^I - v^{II}} = \frac{\Delta s}{\Delta v} \quad (3.13)$$

$$= \frac{\Delta h}{T \Delta v} \quad (3.14)$$

where $\Delta h = T \Delta s$ is the molar latent heat. Eq(3.14) is called the **Clausius-Clapeyron equation**.

Exercise 3.1

Prove that $\Delta h > 0$ in a transition from a low to a high T phase.

Answer

Let II be the low and I be the high T phase.

Since the stable state has the lowest G , we have

$$G^I > G^{II} \quad \text{for } T < T_c$$

$$G^I < G^{II} \quad \text{for } T > T_c$$

Coupled with the stability conditions of section 2.H.3, we obtain a situation as depicted in the Figure. Thus,

$$\left(\frac{\partial G^I}{\partial T} \right)_{P\{n_j\}} < \left(\frac{\partial G^{II}}{\partial T} \right)_{P\{n_j\}} \quad \text{for all } T$$

so that

$$S^I > S^{II} \quad \text{for all } T$$

and

$$\Delta H = T_c \Delta S = T_c (S^I - S^{II}) > 0$$

3.D.2.a. [Vaporization Curve](#)

3.D.2.b. [Fusion Curve](#)

3.D.2.c. [Sublimation Curve](#)

3.D.2.a. Vaporization Curve

Consider the coexistence curve between the liquid and gaseous phases of a pure substance. This is indicated as the vaporization curve between the triple A and critical point C in Figure 3.4.

If we neglect the volume changes of the liquid phase, we have

$$\Delta v_{lg} = v_g - v_l \approx v_g = \frac{RT}{P}$$

where the last equality assumes the vapor to be an ideal gas.

The Clausius-Clapeyron equation thus simplifies to

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta h_{lg}}{T\Delta v_{lg}} \approx \frac{P\Delta h_{lg}}{RT^2} \quad (3.15)$$

where Δh_{lg} is the molar latent heat of vaporization. Treating Δh_{lg} as a constant,

we get, along the vaporization curve,

$$\begin{aligned} \int \frac{dP}{P} &= \frac{\Delta h_{lg}}{R} \int \frac{dT}{T^2} \\ \ln P &= -\frac{\Delta h_{lg}}{RT} + const \\ P &= P_\infty \exp\left(-\frac{\Delta h_{lg}}{RT}\right) \end{aligned} \quad (3.16)$$

where P_∞ is the pressure for $T \rightarrow \infty$.

Exercise 3.2

Find the molar heat capacity c_{coex} along the vaporization curve.

Answer

$$c_{coex} = T \left(\frac{\partial s}{\partial T}\right)_{coex}$$

With T, P as independent variables, we have

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$$

On the vaporization curve, we have

$$dP = \left(\frac{dP}{dT}\right)_{coex} dT \approx \frac{P\Delta h_{lg}}{RT^2} dT$$

so that

$$\begin{aligned}
 (ds)_{coex} &= \left[\left(\frac{\partial s}{\partial T} \right)_P + \left(\frac{\partial s}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_{coex} \right] dT \\
 &\simeq \left[\left(\frac{\partial s}{\partial T} \right)_P + \left(\frac{\partial s}{\partial P} \right)_T \frac{P \Delta h_{lg}}{RT^2} \right] dT
 \end{aligned}$$

Thus

$$c_{coex} = c_P + \left(\frac{\partial s}{\partial P} \right)_T \frac{P \Delta h_{lg}}{RT}$$

Using

$$\left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P = - \frac{R}{P}$$

where the last equality is valid for an ideal gas, we have

$$c_{coex} = c_P - \frac{\Delta h_{lg}}{T} \quad (2)$$

which means for $T < \frac{\Delta h_{lg}}{c_P}$, we have $c_{coex} < 0$ so that the vapor gives off heat as T is

raised.

3.D.2.b. Fusion Curve

Consider now the coexistence curve between the solid and liquid phases.

This is depicted as the fusion curve AB in Fig.3.4.

Note that the fusion curve does not terminate.

It can have either positive or negative slope, as depicted with a solid and dotted line in Fig.3.4, respectively.

The relevant Clausius-Clapeyron equation is

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{\Delta h_{sl}}{T\Delta v_{sl}} \quad (3.17)$$

where $\Delta h_{sl} > 0$ is the molar latent heat of fusion. Hence, the sign of $\Delta v_{sl} = v_l - v_s$ determines that of the slope of the fusion curve. A well known example of a fusion curve that has a negative slope is that between ice and water.

3.D.2.c. Sublimation Curve

The coexistence curve between the solid and the gas phases is called the sublimation curve [see Fig.3.4]. The relevant Clausius-Clapeyron is

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{h_g - h_s}{T(v_g - v_s)} = \frac{\Delta h_{sg}}{T\Delta v_{sg}} \quad (3.18)$$

where Δh_{sg} is the molar latent heat of sublimation.

Neglecting v_s and using the ideal gas approximation for v_g , we have

$$\Delta v_{sg} \approx v_g = \frac{RT}{P}$$

so that

$$\left(\frac{dP}{dT}\right)_{coex} = \frac{P\Delta h_{sg}}{RT^2} \quad (3.19)$$

Thus, along the sublimation curve,

$$\Delta h_{sg} = R \frac{T^2}{dT} \cdot \frac{dP}{P} = -R \frac{d \ln P}{d\left(\frac{1}{T}\right)} \quad (3.20)$$

Exercise 3.3

Near triple point of NH_3 , we have

sublimation curve: $\ln P = 27.79 - \frac{3726}{T}$

vaporization curve: $\ln P = 24.10 - \frac{3005}{T}$

1. Find T and P of triple point.
2. Find latent heats of sublimation and vaporization.

Answer

1. The sublimation and vaporization curves meet at the triple point. Hence,

$$27.79 - \frac{3726}{T_t} = 24.10 - \frac{3005}{T_t} \quad \Rightarrow \quad T_t = 195.4K$$

$$\ln P_t = 27.79 - \frac{3726}{195.4} = 6.13kPa$$

2. For the sublimation curve,

$$\frac{dP}{PdT} = \frac{3726}{T^2} \Rightarrow \Delta h_{sg} \approx \frac{RT^2}{P} \left(\frac{dP}{dT} \right)_{coex} = \frac{3726}{R} \approx 31 \text{ kJ/mol}$$

For the vaporization curve,

$$\frac{dP}{PdT} = \frac{3005}{T^2} \Rightarrow \Delta h_{lg} \approx \frac{3005}{R} \approx 25 \text{ kJ/mol}$$

Low Temperature Case

Using

$$\begin{aligned} ds &= \left(\frac{\partial s}{\partial T} \right)_P dT + \left(\frac{\partial s}{\partial P} \right)_T dP \\ &= \frac{c_p}{T} dT - v\alpha_p dP \quad \text{where} \quad \left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P = -v\alpha_p \end{aligned}$$

the molar enthalpy can be written as

$$\begin{aligned} dh &= Tds + vdP \\ &= c_p dT + v(1 - T\alpha_p) dP \end{aligned} \quad (3.21)$$

Now, at low temperatures, the vapor pressure along the sublimation curve is very low.

Thus, we can neglect the pressure variation and write

$$dh \approx c_p dT \quad \text{on sublimation curve}$$

so that

$$h = h^0 + \int_{T_0}^T c_p dT$$

where $h = h^0$ at T_0 .

The latent heat of sublimation is therefore

$$\Delta h_{sg} = h_g - h_s \approx \Delta h_{sg}^0 + \int_{T_0}^T (c_p^g - c_p^s) dT \quad (3.22)$$

Eq(3.20) can thus be integrated to give

$$\begin{aligned} \ln \frac{P}{P_0} &= \frac{1}{R} \int_{T_0}^T \frac{\Delta h_{sg}}{T^2} dT \\ &= \frac{1}{R} \int_{T_0}^T \frac{1}{T'^2} \left[\Delta h_{sg}^0 + \int_{T_0}^{T'} (c_p^g - c_p^s) dT'' \right] dT' \\ &= \frac{\Delta h_{sg}^0}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) + \frac{1}{R} \int_{T_0}^T \frac{1}{T'^2} \left[\int_{T_0}^{T'} (c_p^g - c_p^s) dT'' \right] dT' \end{aligned} \quad (3.23)$$

which can be used to extrapolate experimental measurements.

3.D.3. Liquid-Vapor Coexistence Region

Consider the phase diagram in the P - v plane depicted in Fig.3.7. [cf. Fig3.4-6]. Along an isothermal $T_0 < T_C$, the straight line segment AB inside the vapor-liquid coexistence region indicates a mixture of the vapor and liquid phases. Here, both phases are at the same temperature T_0 and pressure P_0 as given by a point on the vaporization curve. The molar volumes of the pure vapor and liquid phases are given by $v_g = v_A$ and $v_l = v_B$, respectively. The state D of molar volume v_D thus represents a mixture of phases obeying the lever rule

$$v_D = x_g v_g + x_l v_l \quad (3.24)$$

where x indicates a molar fraction. With the help of the constraint $x_g + x_l = 1$, we can rewrite (3.24) as

$$\begin{aligned} (x_g + x_l)v_D &= x_g v_g + x_l v_l \\ \Rightarrow \frac{x_l}{x_g} &= \frac{v_g - v_D}{v_D - v_l} \end{aligned} \quad (3.25)$$

Metastable States

According to eq(2.179), mechanical stability requires

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T > 0 \quad \Rightarrow \quad \left(\frac{\partial v}{\partial P} \right)_T < 0 \quad (a)$$

Consider again the isotherm $T_0 < T_C$ in Fig.3.7. If we extend the gaseous state beyond point A into the coexistence region (see dashed line), mechanical stability can still be maintained as long as condition (a) is satisfied. However, since the free energy is not a minimum, the system is only metastable. These states are called supercooled (vapor) states. Similarly, metastable states resulting from the continuation of the liquid state past point B into the coexistence region are called superheated (liquid) state.

It is possible to extend the superheated liquid states into the negative pressure region. In which case, no wall is required to contain the system.

Note that at the critical point C , the molar volumes of both phases are equal. Since the relevant symmetries are also the same, these phases become indistinguishable.

Also, there are no metastable states.

Law of Corresponding States

The liquid-vapor coexistence curve in the T - ρ plane can be plotted in terms of reduced quantities $\frac{T}{T_C}$ and $\frac{\rho}{\rho_C}$, where the subscript C denotes a critical value.

Guggenheim found that such curves more or less coincide for a large number of pure substances (see Fig.3.8). This is an example of the **law of corresponding states**, which postulates that all pure classical fluids obey the same equation of state involving reduced quantities.

The curve in Fig.3.8 is given by Guggenheim as the solutions to the following equations

$$\frac{\rho_l + \rho_g}{2\rho_C} = 1 + \frac{3}{4} \left(1 - \frac{T}{T_C} \right) \quad (3.26)$$

$$\frac{\rho_l - \rho_g}{\rho_C} = \frac{7}{2} \left(1 - \frac{T}{T_C} \right)^{1/3} \quad (3.27)$$

Heat capacities

In the coexistence region, the total internal energy of a mixture (point D in Fig.3.7) is

$$U_{tot} = n_g u_g(v_g, T_0) + n_l u_l(v_l, T_0) \quad (3.28)$$

where n_i is the number of moles of phase i substance present and $u_i(v, T)$ is the molar energy of the substance when it is in the pure phase i with molar volume v and temperature T . Dividing by the total number of moles, we obtain the molar total internal energy

$$u_{tot} = x_g u_g(v_g, T_0) + x_l u_l(v_l, T_0) \quad (3.29)$$

so that the molar heat capacity at constant volume is

$$\begin{aligned} c_v &= \left(\frac{\partial u_{tot}}{\partial T} \right)_{v_D} \\ &= x_g \left(\frac{\partial u_g}{\partial T} \right)_{coex} + x_l \left(\frac{\partial u_l}{\partial T} \right)_{coex} + (u_l - u_g)_{coex} \left(\frac{\partial x_l}{\partial T} \right)_{v_D} \end{aligned} \quad (3.30)$$

where we've used $dx_g + dx_l = 0$.

The following steps are required to related (3.30) with directly measurable quantities.

1. From $u_l = u_l(v_l, T_0)$, we have

$$\begin{aligned} \left(\frac{\partial u_l}{\partial T}\right)_{coex} &= \left(\frac{\partial u_l}{\partial T}\right)_{v_l} + \left(\frac{\partial u_l}{\partial v_l}\right)_T \left(\frac{\partial v_l}{\partial T}\right)_{coex} \\ &= c_{v_l} + \left(\frac{\partial u_l}{\partial v_l}\right)_T \left(\frac{\partial v_l}{\partial T}\right)_{coex} \end{aligned} \quad (3.31)$$

Similarly,

$$\left(\frac{\partial u_g}{\partial T}\right)_{coex} = c_{v_g} + \left(\frac{\partial u_g}{\partial v_g}\right)_T \left(\frac{\partial v_g}{\partial T}\right)_{coex} \quad (3.32)$$

2. $(u_l - u_g)_{coex} = h_l - P_0 v_l - (h_g - P_0 v_g)$
 $= -\Delta h_{lg} + P_0 \Delta v_{lg}$

$$= \left[-T_0 \left(\frac{dP}{dT}\right)_{coex} + P_0 \right] \Delta v_{lg} \quad (3.34)$$

3. Finally, to calculate $\left(\frac{\partial x_l}{\partial T}\right)_{v_D}$, we begin with

$$v_D = x_l v_l + (1 - x_l) v_g$$

so that

$$0 = \left(\frac{\partial x_l}{\partial T}\right)_{v_D} v_l + x_l \left(\frac{\partial v_l}{\partial T}\right)_{coex} - \left(\frac{\partial x_l}{\partial T}\right)_{v_D} v_g + (1 - x_l) \left(\frac{\partial v_g}{\partial T}\right)_{coex}$$

$$\begin{aligned} \text{i.e.,} \quad \left(\frac{\partial x_l}{\partial T}\right)_{v_D} &= \frac{1}{\Delta v_{lg}} \left[x_l \left(\frac{\partial v_l}{\partial T}\right)_{coex} + (1 - x_l) \left(\frac{\partial v_g}{\partial T}\right)_{coex} \right] \\ &= \frac{1}{\Delta v_{lg}} \left[x_l \left(\frac{\partial v_l}{\partial T}\right)_{coex} + x_g \left(\frac{\partial v_g}{\partial T}\right)_{coex} \right] \end{aligned} \quad (3.36)$$

Putting everything into (3.30) gives

$$c_v = x_g \left[c_{v_g} + \left(\frac{\partial u_g}{\partial v_g}\right)_T \left(\frac{\partial v_g}{\partial T}\right)_{coex} \right] + x_l \left[c_{v_l} + \left(\frac{\partial u_l}{\partial v_l}\right)_T \left(\frac{\partial v_l}{\partial T}\right)_{coex} \right]$$

$$\begin{aligned}
& + \left[-T_0 \left(\frac{dP}{dT} \right)_{coex} + P_0 \right] \left[x_l \left(\frac{\partial v_l}{\partial T} \right)_{coex} + x_g \left(\frac{\partial v_g}{\partial T} \right)_{coex} \right] \quad (3.37) \\
& = x_g \left\{ c_{v_g} + \left[\left(\frac{\partial u_g}{\partial v_g} \right)_T - T_0 \left(\frac{dP}{dT} \right)_{coex} + P_0 \right] \left(\frac{\partial v_g}{\partial T} \right)_{coex} \right\} \\
& \quad + x_l \left\{ c_{v_l} + \left[\left(\frac{\partial u_l}{\partial v_l} \right)_T - T_0 \left(\frac{dP}{dT} \right)_{coex} + P_0 \right] \left(\frac{\partial v_l}{\partial T} \right)_{coex} \right\} \quad (3.37a)
\end{aligned}$$

Now, from

$$du = Tds - Pdv$$

we have

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial s}{\partial v} \right)_T - P = T \left(\frac{\partial P}{\partial T} \right)_v - P \quad (3.38)$$

Also, using the Maxwell relation

$$\left(\frac{\partial x}{\partial y} \right)_z = \left(\frac{\partial x}{\partial y} \right)_w + \left(\frac{\partial x}{\partial w} \right)_y \left(\frac{\partial w}{\partial y} \right)_z \quad (2.8)$$

we can write

$$\left(\frac{\partial P}{\partial T} \right)_{coex} = \left(\frac{\partial P}{\partial T} \right)_v + \left(\frac{\partial P}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_{coex} \quad (3.39)$$

Putting (3.38-9) into the terms included in one of the square brackets in (3.37a), we get, in the coexistence region,

$$\begin{aligned}
\left(\frac{\partial u}{\partial v} \right)_T - T_0 \left(\frac{\partial P}{\partial T} \right)_{coex} + P_0 &= T_0 \left(\frac{\partial P}{\partial T} \right)_v - T_0 \left(\frac{\partial P}{\partial T} \right)_{coex} \\
&= -T_0 \left(\frac{\partial P}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_{coex}
\end{aligned}$$

Hence, (3.37) simplifies to

$$c_v = x_g \left\{ c_{v_g} - T_0 \left(\frac{\partial P}{\partial v_g} \right)_T \left(\frac{\partial v_g}{\partial T} \right)_{coex}^2 \right\} + x_l \left\{ c_{v_l} - T_0 \left(\frac{\partial P}{\partial v_l} \right)_T \left(\frac{\partial v_l}{\partial T} \right)_{coex}^2 \right\} \quad (3.40)$$

with all quantities on the right side measurable.

Since the isotherm is also an isobar in the coexistence region, c_p is infinite for a mixture in the coexistence region. Thus, adding heat at constant pressure to a mixture in the coexistence region only converts some liquid into vapor. The

temperature remains constant until the entire mixture is turned into vapor.

3.D.4. The van der Waals Equation

The (molar) van der Waals equation

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \quad (2.12)$$

can be written in various forms such as

$$P = -\frac{a}{v^2} + \frac{RT}{v - b} \quad (3.41a)$$

or

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0 \quad (3.41)$$

An isotherm with $T < T_C$ in the v - P plane is shown in Fig.3.9.

In order to simplify the notations, we shall replace all quantities x with their reduced values $\bar{x} = \frac{x}{x_C}$, where the subscript C denotes value at the critical point. Using the

fact that the isotherm $T = T_C$ has an inflection point at the critical point, we get

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_C} = \frac{2a}{v_C^3} - \frac{RT_C}{(v_C - b)^2} = 0 \quad (3.42)$$

$$\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_C} = -\frac{6a}{v_C^4} + \frac{2RT_C}{(v_C - b)^3} = 0 \quad (3.42a)$$

Eliminating T_C gives

$$\frac{4a}{v_C^3(v_C - b)} = \frac{6a}{v_C^4} \quad \Rightarrow \quad v_C = 3b$$

so that (3.42) becomes

$$T_C = \frac{2a}{Rv_C^3}(v_C - b)^2 = \frac{8a}{27bR}$$

which turns (3.41a) into

$$P_C = -\frac{a}{9b^2} + \frac{4a}{27b^2} = \frac{a}{27b^2}$$

Eq(2.12) thus becomes

$$\begin{aligned} & \left(\frac{a\bar{P}}{27b^2} + \frac{a}{9b^2\bar{v}^2}\right)(3b\bar{v} - b) = \frac{8a}{27b}\bar{T} \\ \Rightarrow & \left(\bar{P} + \frac{3}{\bar{v}^2}\right)(3\bar{v} - 1) = 8\bar{T} \end{aligned} \quad (3.44)$$

$$\bar{P} = -\frac{3}{\bar{v}^2} + \frac{8\bar{T}}{3\bar{v}-1} \quad (3.44a)$$

$$\bar{v}^3 - \frac{1}{3} \left(1 + \frac{8\bar{T}}{\bar{P}} \right) \bar{v}^2 + \frac{3}{\bar{P}} \bar{v} - \frac{1}{\bar{P}} = 0 \quad (3.44b)$$

Note that the independence of these equations on a and b is another example of the law of corresponding states.

Maxwell Construction

An isotherm with $T < T_C$ in the v - P plane is shown in Fig.3.9.

Now, for equilibrium states, an isotherm $v(P)$ must be single-valued except at transition points. Thus, if one tries to bring the system quasi-statically and isothermally from A to I, the actual path followed must be one similar to ABCEGHI. The task is to determine the position of the vertical line segment CEG, which indicates a coexistence of phases [cf. Fig.3.7].

Note that one implication of the above discussion is that the states on the segment DEF are not in equilibrium. This is indeed the case since the slope of the curve there is positive so that

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T < 0 \quad \Rightarrow \quad \text{mechanical instability}$$

Consider now the molar Gibbs free energy $g(T, P)$ along the isotherm in Fig.3.9.

Since $T = \text{const}$, we have $dg = v dP$ or

$$\begin{aligned} g_X &= g_A + \int_{P_A}^{P_X} v(P) dP \quad (3.46) \\ &= g_A + I(X, A) \end{aligned}$$

where $I(X, A) = \int_{P_A}^{P_X} v(P) dP$. The values of g as X moves from A to I are shown in

Fig.3.10. The salient features are as follows:

1. From A to D: $g_X = g_A + I(X, A)$ increases monotonically from g_A to

$$g_D = g_A + I(D, A).$$

2. From D to F: $g_X = g_D + I(X, D) = g_D - I(D, X)$ decreases monotonically

from g_D to $g_F = g_D - I(D, F)$.

3. From F to I: $g_X = g_F + I(X, F)$ increases monotonically from g_F to

$g_I = g_F + I(I, F)$.

As shown in Fig.3.10, the segments AD and FI intersect in the g - P plane. Since the equilibrium state has the lowest energy, the quasi-static isothermal path in the g - P plane runs as $A \rightarrow \text{intersect} \rightarrow I$. Referring back to the v - P plane, we see that C and G must be the position of this intersect on the segments AD and FI, respectively.

Now, the condition $g_C = g_G$ means

$$\begin{aligned} g_A + I(C, A) &= g_F + I(G, F) \\ &= g_D - I(D, F) + I(G, F) \\ &= g_A + I(D, A) - I(D, F) + I(G, F) \end{aligned}$$

$$\Rightarrow I(C, A) - I(D, A) = -I(D, F) + I(G, F) \quad (\text{a})$$

Using

$$I(C, A) - I(D, A) = -I(D, C)$$

and

$$I(D, F) = I(D, E) + I(E, F)$$

eq(a) becomes

$$I(D, C) - I(D, E) = I(E, F) - I(G, F) \quad (3.48)$$

i.e., $Area\ 2 = Area\ 1$ [see shaded areas in Fig.3.9]

This is called the **Maxwell construction**.

3.D.4.a. Cubic Equation

The cubic equation

$$x^3 + ax^2 + bx + c = 0$$

has 3 roots given by

$$x_1 = S + T - \frac{1}{3}a$$

$$x_2 = -\frac{1}{2}(S + T) - \frac{1}{3}a + i\frac{\sqrt{3}}{2}(S - T)$$

$$x_3 = -\frac{1}{2}(S + T) - \frac{1}{3}a - i\frac{\sqrt{3}}{2}(S - T)$$

where

$$S = \sqrt[3]{R + \sqrt{Q^3 + R^2}} \quad T = \sqrt[3]{R - \sqrt{Q^3 + R^2}}$$

$$Q = \frac{b}{3} - \left(\frac{a}{3}\right)^2 \quad R = \frac{a}{3} \cdot \frac{b}{2} - \frac{c}{2} - \left(\frac{a}{3}\right)^3$$

The character of the roots is determined by the discriminant

$$D = Q^3 + R^2$$

so that

$$D > 0 \quad \Rightarrow \quad 1 \text{ real \& 2 complete conjugates}$$

$$D = 0 \quad \Rightarrow \quad \text{all real with at least 2 equal}$$

$$D < 0 \quad \Rightarrow \quad \text{all real \& all equal}$$

3.E. Superconductors

For some metals, the resistance drops to zero when the temperature falls below a critical value T_C . The metal is then said to be in the superconducting state.

Naively, one may be tempted to associate zero resistance with an infinite conductivity. However, the superconducting state cannot be so described, as will be shown below.

Substituting the Ohm's law for a metal,

$$\mathbf{J} = \sigma \mathbf{E} \quad (3.50)$$

into the Faraday's law

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t} \quad [\text{Gaussian units}] \quad (3.51)$$

we get

$$\frac{\partial \mathbf{B}}{\partial t} = -\frac{c}{\sigma} \nabla \times \mathbf{J}$$

Hence,

$$\frac{\partial \mathbf{B}}{\partial t} = 0 \quad \text{for } \sigma \rightarrow \infty$$

i.e., \mathbf{B} is time independent inside a metal of infinite conductivity, which leads to hysteresis (\mathbf{B} depends on sample history) as shown in Fig.3.12.

However, the superconducting state was found experimentally to be a thermodynamic state with perfect diamagnetism ($\mathbf{B} = 0$ regardless of sample history). This is called the **Meissner effect**.

According to the BCS theory, transition to the superconducting phase is a Bose-Einstein condensation, in momentum space, of Cooper pairs. Here, a Cooper pair is a boson representing a bounded state of 2 electrons of opposite spins interacting under an attractive effective potential caused by electron- phonon interactions.

Thus, the superconducting state is a macroscopic quantum state. The onset of superconductivity is an order- disorder phase transition with an effective wave

function as order parameter. Here, $n_s = |\Psi|^2$ gives the density of

superconducting electrons. The vanishing of electrical resistance is due to the ineffectiveness of the scattering offered by individual impurities against the entire electron condensate.

Superconductivity can be destroyed by an applied field $H > H_c(T)$ (see Fig.3.13).

Thus, $H_c(T)$ defines the coexistence curve in the H - T plane (see Fig.3.14). It was found empirically that,

$$H_c(T) \approx H_0 \left(1 - \frac{T^2}{T_C^2}\right) \quad (3.53)$$

where $H_0 = H(0)$. Note that

$$\frac{dH_c}{dT} = -\frac{2H_0T}{T_C^2} \quad \Rightarrow \quad \frac{dH_c}{dT} \leq 0$$

with $\left. \frac{dH_c}{dT} \right|_{T=0} = 0$.

Using

$$dg = -sdT - \frac{1}{4\pi} B dH \quad (3.57)$$

we have, along the coexistence curve,

$$-s_n dT - \frac{1}{4\pi} B_n dH = -s_s dT - \frac{1}{4\pi} B_s dH \quad (3.54)$$

$$\Rightarrow \left(\frac{dH}{dT} \right)_{coex} = 4\pi \left(\frac{s_n - s_s}{B_s - B_n} \right)_{coex} = -4\pi \frac{(s_n - s_s)_{coex}}{H_c(T)} \quad (3.55)$$

where we've used $B_s = 0$ and $B_n = H_c(T)$ on the coexistence curve.

Eq(3.55) is the Clausius- Clapeyron equation for superconductivity.

Using (3.53), eq(3.55) becomes

$$-\frac{2H_0T}{T_C^2} = -4\pi \frac{(s_n - s_s)_{coex}}{H_c(T)}$$

$$\Rightarrow (s_n - s_s)_{coex} = \frac{H_0T}{2\pi T_C^2} H_c(T) = \frac{H_0^2}{2\pi T_C^2} \left(1 - \frac{T^2}{T_C^2}\right) T$$

so that

$$\begin{aligned}
(c_n - c_s)_{coex} &= \left[T \frac{\partial (s_n - s_s)}{\partial T} \right]_{coex} = \frac{H_0^2}{2\pi T_C^2} T \left[1 - \frac{T^2}{T_C^2} - \frac{2T^2}{T_C^2} \right] \\
&= \frac{H_0^2}{2\pi T_C} \left(\frac{T}{T_C} - \frac{3T^3}{T_C^3} \right) \quad (3.56)
\end{aligned}$$

For sufficiently low T , the cubic term will be smaller than the linear one so that $c_n > c_s$ in the coexistence region. At $T = T_C$, we have

$$(c_n - c_s)_{T=T_C} = -\frac{H_0^2}{\pi T_C}$$

Note also that

$$(s_n - s_s)_{T=0} = 0$$

in agreement with the 3rd law.

Integrating (3.57) at fixed T gives

$$g(T, H) = g(T, 0) - \frac{1}{4\pi} \int_0^H B dH \quad (3.58)$$

Using $B_n = H$ and $B_s = 0$, we have

$$g_n(T, H) = g_n(T, 0) - \frac{1}{8\pi} H^2 \quad (3.59)$$

$$g_s(T, H) = g_s(T, 0) \quad \text{for } H \leq H_C \quad (3.60)$$

Finally, with the help that, on the coexistence curve,

$$g_n(T, H_C) = g_s(T, H_C) \quad (3.61)$$

we can combine (3.59-60) into

$$\begin{aligned}
g_s(T, 0) &= g_s(T, H_C) = g_n(T, H_C) \\
&= g_n(T, 0) - \frac{1}{8\pi} H_C^2 \quad (3.62)
\end{aligned}$$

Thus, the **condensation energy** is

$$g_n(T, 0) - g_s(T, 0) = \frac{1}{8\pi} [H_C(T)]^2$$

with

$$g_n(T_C, 0) - g_s(T_C, 0) = 0$$

3.F. Helium Liquids

- 3.F.1. [Liquid \$He^4\$](#)
- 3.F.2. [Liquid \$He^3\$](#)
- 3.F.3. [Liquid \$He^3\$ - \$He^4\$ Mixtures](#)

3.F.1. Liquid He^4

The phase diagram of He^4 is shown in Fig.3.15 and should be compared with that of a typical classical fluid shown in Fig.3.4. Salient points of interest are

1. The solid phase appears only for pressures above 25atm even as $T \rightarrow 0$.
2. There are 2 liquid phases separated by a λ -line near $T \approx 2K$. A λ -line is a line of λ -points, so called because the graph of C vs T near a λ -point looks like the letter λ . (see Fig.3.16)
3. The high temperature liquid phase is called the ***He I*** or **normal** phase. Its behavior is similar to a classical fluid.
4. The low temperature liquid phase is called the ***He II*** or **superfluid** phase. It's the first discovered example of a quantum fluid.
5. *He II* exhibits frictionless flow and can leak through cracks impermeable to *He* gas. Hence the name superfluid. [cf. superconductor]
6. The *He I-II* transition is continuous with broken gauge symmetry. The order parameter is the macroscopic superfluid wave function.
7. The slopes of *g-l* and *s-l* coexistence curves goes to zero as $T \rightarrow 0$, in accordance with the 3rd law.

3.F.2. Liquid He^3

He^3 has only 3/4 of the mass of He^4 . Hence,

$$T_{Boiling}[He^3] = \frac{3}{4} T_{Boiling}[He^4] \quad P_{Solidification}[He^3] = \frac{4}{3} P_{Solidification}[He^4]$$

The phase diagram of He^3 is shown in 2 scales in Figs.3.17-8.

The minimum in the l - s coexistence curve in Fig.3.17 is due to the spin contribution to the entropy which makes $\Delta S = S_{liquid} - S_{solid}$ change sign at $T \approx 0.3K$. Since

$\Delta V \approx const$ along the coexistence curve, the minimum follows directly from the Clausius- Clapeyron equation $\left(\frac{dP}{dT}\right)_{coex} = \frac{T\Delta S}{\Delta V}$.

The superfluid phases (see Fig.3.18) appears only for $T \leq 0.0027K$ so that they are not discernible in Fig.3.17. Since He^3 is a fermion, a (Bose-Einstein) condensation into the superfluid phase requires a pairing mechanism. Depending on the angular momenta of the bounded pairs, different superfluid phases results.

1. The high temperature A-phase is anisotropic.
2. The low temperature B-phase is more or less isotropic.
3. A third phase appears under magnetic field.
4. Transition between normal & superfluid is continuous.
5. Transition between the A and B phases is 1st order.

3.F.3. Liquid He^3 - He^4 Mixtures

In a mixture of He^3 - He^4 , one expects to find two types of phase transitions, namely, the superfluid and the binary. This is shown in the phase diagram in Fig.3.19 with x_3 indicating the molar fraction of He^3 .

The λ -line, extending from ($T = 2.19K$, $x_3 = 0$) to the tricritical point at ($T = 0.87K$, $x_3 = 0.67$), denotes the 2nd order superfluid phase transition.

The tricritical point is also the critical point of the 1st order binary phase transition. Thus, below $T = 0.87K$, the mixture can segregate into coexisting He^3 rich and He^4 rich regions. This can be observed using NMR technique.

The tricritical point is so called because it is actually the intersect of 3 lines of 2nd order transitions. [see R. B. Griffith, Phys. Rev. Lett. 24, 715 (1970)]

3.G. Landau Theory

	1 st order transition	Continuous transition
1 st derivatives of G	Discontinuous at transition point	Continuous
Order parameter	Discontinuous across coexistent curve (except at the critical point)	Continuous
Symmetry	May or may not be broken	Always broken

The Ginzburg-Landau theory is a mean field theory that describes an order-disorder transition. Thus, the low temperature, or ordered, phase is characterized by a nonzero order parameter η , which vanishes in the high temperature, or disordered phase. In a continuous transition, there is also an accompanying change of symmetries with the ordered phase having the lower symmetries. The molar free energy φ is assumed to be analytic (i.e., a Taylor series expansion exists) so that near the transition point where η is small, we can write

$$\varphi(T, Y, \eta) \approx \varphi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_3(T, Y)\eta^3 + \alpha_4(T, Y)\eta^4 \quad (3.63a)$$

where terms $O(\eta^5)$ are neglected and we have set $\alpha_1 = 0$ so that the disordered phase $\eta = 0$ is always a local minimum. In the presence of an external force conjugate to η , (3.63a) is generalized to

$$\begin{aligned} \psi(T, Y, f) &= \varphi(T, Y, \eta) - f\eta \\ &\approx \varphi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_3(T, Y)\eta^3 + \alpha_4(T, Y)\eta^4 - f\eta \end{aligned} \quad (3.63)$$

3.G.1. [Continuous Phase Transitions](#)

3.G.2. [First Order Transitions](#)

3.G.1. Continuous Phase Transitions

Since η is a real scalar, if α_j is a complex number, vector, or tensor of odd rank, we must have $\alpha_j = 0$ for all odd j because any term containing odd powers of η can never be a real scalar. In which case, eq(3.63a) simplifies to

$$\varphi(T, Y, \eta) = \varphi_0(T, Y) + \alpha_2(T, Y)\eta^2 + \alpha_4(T, Y)\eta^4 \quad (3.64)$$

where, to ensure (formal) global stability, we must have

$$\alpha_4(T, Y) > 0 \quad (3.66)$$

[$\alpha_4 < 0$ implies global minima of φ at $\eta \rightarrow \pm\infty$]

For fixed Y and T , each equilibrium state (phase) is a minimum of φ so that

$$\left(\frac{\partial \varphi}{\partial \eta} \right)_{TY} = 0 \quad \left(\frac{\partial^2 \varphi}{\partial \eta^2} \right)_{TY} > 0 \quad (3.65)$$

i.e.,

$$2\alpha_2\eta + 4\alpha_4\eta^3 = 0 \quad 2\alpha_2 + 12\alpha_4\eta^2 > 0 \quad (3.65a)$$

There are 2 solutions to eq(3.65a), namely,

$$\eta = 0 \quad \text{with } \alpha_2 > 0 \quad (3.65b)$$

and

$$\eta^2 = -\frac{\alpha_2}{2\alpha_4} \quad \text{with } \alpha_2 < 0 \quad (3.65c)$$

Obviously, (3.65b) and (3.65c) correspond to the disordered ($T > T_c$) and ordered ($T < T_c$) states, respectively. Thus, the transition, or critical, point satisfies

$$\alpha_2(T, Y) = 0 \quad (3.65d)$$

For a given Y , let $T_c(Y)$ be the solution of eq(3.65d), i.e.,

$$\alpha_2[T_c(Y), Y] = 0 \quad (3.65e)$$

Thus, $T_c(Y)$ describes a coexistence curve in the Y - T plane. The conditions

(3.65b,c,e) are guaranteed if we write

$$\alpha_2(T, Y) = \alpha_0(T, Y)[T - T_c(Y)] \quad (3.67)$$

where $\alpha_0 > 0$ is expected to be slowly varying in the neighborhood of the transition point. Hence, eq(3.65c) becomes,

$$\eta = \pm \sqrt{\frac{\alpha_0}{2\alpha_4}(T_C - T)} \quad (3.69)$$

Putting everything into (3.64) gives

$$\varphi(T, Y, \eta) = \begin{cases} \varphi_0(T, Y) & \text{for } T > T_C \\ \varphi_0(T, Y) - \frac{\alpha_0^2}{4\alpha_4}(T_C - T)^2 & \text{for } T < T_C \end{cases} \quad (3.70)$$

Heat Capacity

Since φ is the Gibbs free energy, the molar heat capacity is given by,

$$c_Y = -T \left(\frac{\partial^2 \varphi}{\partial T^2} \right)_Y \quad (3.71)$$

so that

$$c_Y = \begin{cases} c_{Y0} & \text{for } T > T_C \\ c_{Y0} + \frac{\alpha_0^2}{2\alpha_4} & \text{for } T < T_C \end{cases} \quad (3.71a)$$

where

$$c_{Y0} = -T \left(\frac{\partial^2 \varphi_0}{\partial T^2} \right)_Y$$

Thus, there is a discontinuity at T_C of magnitude

$$\Delta c_Y = c_Y(T_C^-) - c_Y(T_C^+) = \frac{\alpha_0^2}{2\alpha_4} \quad (3.72)$$

which gives the c_Y vs T plot a shape of a λ (see Fig.3.21) and hence the reason for calling the critical point a λ -point.

Superfluid

The normal- superfluid transition of He^4 is continuous.

The order parameter is the macroscopic superfluid (complex) wave function Ψ so that

$$\varphi(T, P, \Psi) \simeq \varphi_0(T, P) + \alpha_2 |\Psi|^2 + \alpha_4 |\Psi|^4 \quad (3.73)$$

with $\alpha_2 = (T - T_C)\alpha_0$. Similar to (3.69), we have

$$|\Psi|^2 = \frac{\alpha_0}{2\alpha_4}(T_c - T) \quad \Rightarrow \quad \Psi = e^{i\theta} \sqrt{\frac{\alpha_0}{2\alpha_4}(T_c - T)}$$

where the phase θ is a real number that can be set to zero when current flow is absent.

External Force

In the presence of an external force f that couples to the order parameter η , the relevant free energy is [see (3.64)]

$$\psi(T, Y, f) = \varphi_0(T, Y) + \alpha_2 \eta^2 + \alpha_4 \eta^4 - f \eta \quad (3.74)$$

which implies the Legendre transform (for equilibrium states),

$$\begin{aligned} \varphi(T, Y, \eta) &= \psi(T, Y, f) - f \frac{\partial \psi}{\partial f} \\ &= \psi(T, Y, f) + f \eta \end{aligned}$$

where $\frac{\partial \psi}{\partial f} = -\eta$. Typical plots of ψ can be found in Fig.3.22.

For fixed T, Y , and f , the equilibrium phases are minima of ψ so that

$$\left(\frac{\partial \psi}{\partial \eta} \right)_{TYf} = 2\alpha_2 \eta + 4\alpha_4 \eta^3 - f = 0 \quad (3.75)$$

$$\left(\frac{\partial^2 \psi}{\partial \eta^2} \right)_{TYf} = 2\alpha_2 + 12\alpha_4 \eta^2 > 0$$

See Fig.3.22 for a few typical solutions. Note that (3.75) is simply the assertion that

for equilibrium states, f is indeed the force conjugate to η , i.e., $f = \left(\frac{\partial \varphi}{\partial \eta} \right)_{TY}$.

More interesting is the susceptibility

$$\chi(f) = \left(\frac{\partial \eta}{\partial f} \right)_{TY} = - \left(\frac{\partial^2 \psi}{\partial f^2} \right)_{TY}$$

with the implicit assumption that all quantities take on their equilibrium values.

Taking the partial derivative of eq(3.75) gives

$$2\alpha_2 \left(\frac{\partial \eta}{\partial f} \right)_{TY} + 12\alpha_4 \eta^2 \left(\frac{\partial \eta}{\partial f} \right)_{TY} - 1 = 0$$

$$\Rightarrow \chi(f) = \frac{1}{2\alpha_2 + 12\alpha_4\eta^2} \quad (3.76)$$

For $f = 0$, eq(3.65b,c) gives

$$\eta = \begin{cases} 0 & \text{for } T > T_C \\ \pm \sqrt{-\frac{\alpha_2}{2\alpha_4}} & \text{for } T < T_C \end{cases} \quad (3.76a)$$

so that with $\alpha_2 = (T - T_C)\alpha_0$, we have

$$\chi(0) = \begin{cases} \frac{1}{2\alpha_2} = \frac{1}{2(T - T_C)\alpha_0} & \text{for } T > T_C \\ -\frac{1}{4\alpha_2} = \frac{1}{4(T_C - T)\alpha_0} & \text{for } T < T_C \end{cases} \quad (3.77)$$

which exhibits a divergence at $T = T_C$.

Paramagnetic-Ferromagnetic Transition

In a para- to ferro- magnetic transition, critical values are called Curie values.

The order parameter is the magnetization vector \mathbf{M} .

The symmetry that is broken is the rotational symmetry. Thus,

$$\varphi(T, \mathbf{M}) = \varphi_0(T) + \alpha_2 \mathbf{M} \cdot \mathbf{M} + \alpha_4 (\mathbf{M} \cdot \mathbf{M})^2$$

$$\psi(T, \mathbf{H}) = \varphi_0(T) + \alpha_2 \mathbf{M} \cdot \mathbf{M} + \alpha_4 (\mathbf{M} \cdot \mathbf{M})^2 - \mathbf{H} \cdot \mathbf{M} \quad (3.78)$$

For $\mathbf{H} = 0$, the analog of (3.76a) is

$$\mathbf{M} = \begin{cases} 0 & \text{for } T > T_C \\ \pm \hat{\mathbf{M}} \sqrt{\frac{\alpha_0}{2\alpha_4} (T_C - T)} & \text{for } T < T_C \end{cases}$$

where $\hat{\mathbf{M}}$ is a unit vector.

The heat capacity exhibits the shape as shown in Fig.3.23.

3.G.2. First Order Transitions

If η is a scalar, or tensor of even rank, odd power terms of η can also be scalars if properly constructed. Transitions in such systems are 1st order. For simplicity, we shall assume η to be a scalar and write,

$$\varphi(T, Y, \eta) \approx \varphi_0(T, Y) + \alpha_2 \eta^2 + \alpha_3 \eta^3 + \alpha_4 \eta^4 \quad (3.79)$$

where $\alpha_4 > 0$ for global stability. The equilibrium conditions are

$$\left(\frac{\partial \varphi}{\partial \eta} \right)_{TY} = 2\alpha_2 \eta + 3\alpha_3 \eta^2 + 4\alpha_4 \eta^3 = 0 \quad (a)$$

$$\left(\frac{\partial^2 \varphi}{\partial \eta^2} \right)_{TY} = 2\alpha_2 + 6\alpha_3 \eta + 12\alpha_4 \eta^2 > 0 \quad (b)$$

Solutions to (a) are

$$\eta = 0$$

and

$$2\alpha_2 + 3\alpha_3 \eta + 4\alpha_4 \eta^2 = 0 \quad (c)$$

$$\Rightarrow \eta = \frac{1}{8\alpha_4} \left(-3\alpha_3 \pm \sqrt{D} \right) \quad (d)$$

where the discriminant is $D = 9\alpha_3^2 - 32\alpha_2\alpha_4$.

As before, the disordered case $\eta = 0$ requires $\alpha_2 > 0$ or $T > T_C$ to satisfy (b).

If we follow the procedure of the last section, we can obtain from (d) an expression

for η for the ordered phase valid for $\alpha_2 < 0$ or $T < T_C$. Obviously, this would be a continuous phase transition.

On the other hand, as shown in Fig.3.24, we can adjust α_3 to produce another minimum at $\eta = \eta_D$ lower than that at $\eta = 0$ for the case $\alpha_2 > 0$. Obviously, transition to this new minimum will result in a discontinuous change in the slope of φ and hence signifies a 1st order phase transition. Furthermore, since we are still in the region $T > T_C$, this transition precedes that for the continuous one at $T = T_C$ so that the latter is never observed. Again with reference to Fig.3.24, the onset of this 1st order transition (curve D) happens when both minima have the same value, i.e.,

$$\varphi(T, Y, \eta_D) = \varphi_0(T, Y)$$

$$\Rightarrow \alpha_2 \eta^2 + \alpha_3 \eta^3 + \alpha_4 \eta^4 = 0 \quad \Rightarrow \quad \alpha_2 + \alpha_3 \eta + \alpha_4 \eta^2 = 0 \quad (e)$$

Thus, the new phase is determined by conditions (b,c,e).

Now, $4(e) - (c)$ gives

$$2\alpha_2 + \alpha_3\eta = 0 \quad \Rightarrow \quad \eta = -\frac{2\alpha_2}{\alpha_3}$$

$$(c) - 2(e) \Rightarrow \quad \alpha_3\eta + 2\alpha_4\eta^2 = 0 \quad \Rightarrow \quad \eta = -\frac{\alpha_3}{2\alpha_4}$$

Combining these 2 expressions, we also have $\alpha_2 = \frac{\alpha_3^2}{4\alpha_4}$.

Combining (e) with condition (b) gives

$$-5\alpha_2 - 3\alpha_3\eta > 0$$

or, simply, $\alpha_2 > 0$. Since $\alpha_4 > 0$, the sign of η is determined by that of α_3 .

3.H. Critical Exponents

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3.H.1. Definition Of Critical Exponents

The "distance" from a critical point is usually measured in terms of the reduced parameter

$$\varepsilon = \frac{T - T_C}{T_C} \quad (3.80)$$

The **critical exponent** of a thermodynamic function f is defined as

$$\lambda = \lim_{\varepsilon \rightarrow 0} \frac{\ln|f(\varepsilon)|}{\ln|\varepsilon|} \quad (3.82)$$

which implies f can be written in the form

$$f(\varepsilon) = A\varepsilon^\lambda (1 + B\varepsilon^y + \dots) \quad y > 0 \quad (3.81)$$

since

$$\ln f \rightarrow \lambda \ln \varepsilon \quad \text{as } \varepsilon \rightarrow 0$$

Thus, as $\varepsilon \rightarrow 0$,

1. $\lambda < 0 \Rightarrow |f| \rightarrow \infty$
2. $\lambda > 0 \Rightarrow |f| \rightarrow 0$
3. $\lambda = 0$. A modified exponent λ' is defined as

$$\lambda' = j + \lim_{\varepsilon \rightarrow 0} \frac{\ln|f^{(j)}(\varepsilon)|}{\ln|\varepsilon|} \quad (3.83)$$

where j is the smallest integer such that $\frac{d^j f}{d\varepsilon^j} = f^{(j)}$ diverges.

For example, if $f(\varepsilon) = A + B\varepsilon^y$, we have

$$\lambda = \lim_{\varepsilon \rightarrow 0} \frac{\ln|A|}{\ln|\varepsilon|} = \lim_{x \rightarrow \infty} \frac{\ln|A|}{-x} = 0$$

If y is a positive fraction, we have $j = 1$ and $f' = By\varepsilon^{y-1}$ so that

$$\lambda' = 1 + \lim_{\varepsilon \rightarrow 0} \frac{\ln|\varepsilon|^{y-1}}{\ln|\varepsilon|} = y$$

Another example is the logarithmic divergence $f(\varepsilon) = A \ln \varepsilon + B$ which gives

$$\lambda = \lim_{\varepsilon \rightarrow 0} \frac{\ln|\ln \varepsilon|}{\ln|\varepsilon|} = \lim_{x \rightarrow \infty} \frac{\ln x}{-x} = \lim_{x \rightarrow \infty} \frac{x^{-1}}{-1} = 0$$

where we've used the L'Hospital rule. Since $f' = \frac{A}{\varepsilon}$, we have $j = 1$ and

$$\lambda' = 1 + \lim_{\varepsilon \rightarrow 0} \frac{\ln|\varepsilon|^{-1}}{\ln|\varepsilon|} = 0$$

Typical plots of f vs ε can be found in Fig.3.26.

3.H.2. The Critical Exponents For Pure *PVT* Systems

There are 4 critical exponents of interest.

(a) Degree of the Critical Isotherm,

$$\frac{P - P_C}{P_C^0} \equiv A_\delta \left| \frac{\rho - \rho_C}{\rho_C} \right|^\delta \text{sign}(\rho - \rho_C) \quad T = T_C \quad (3.84)$$

where the subscript 0 denotes properties of the ideal gas.

Experimentally, $6 > \delta \geq 4$.

(b) Degree of the Coexistence Curve,

$$\frac{\rho_l - \rho_g}{\rho_C} = A_\beta (-\varepsilon)^\beta \quad T < T_C \quad (3.85)$$

where $\rho_l - \rho_g$ is the order parameter. Experimentally, $\beta \approx 0.34$.

(c) Critical Exponent of the Heat Capacity, α, α'

$$C_V = \begin{cases} A_\alpha' (-\varepsilon)^{-\alpha'} & \text{for } T < T_C \\ A_\alpha (+\varepsilon)^{-\alpha} & \text{for } T > T_C \end{cases} \quad \rho = \rho_C \quad (3.86)$$

Experimentally, $\alpha \approx \alpha' \approx 0.1$.

(d) Isothermal Compressibility,

$$\frac{\kappa_T}{\kappa_T^0} = \begin{cases} A_\gamma' (-\varepsilon)^{-\gamma'} & \text{for } T < T_C \\ A_\gamma (+\varepsilon)^{-\gamma} & \text{for } T > T_C \end{cases} \quad (3.87)$$

Experimentally, $\gamma' \approx 1.2$ and $\gamma \approx 1.3$.

Exponent Inequalities

Using

$$\left(\frac{\partial P}{\partial v} \right)_T = -\frac{1}{v\kappa_T} = -\frac{\rho}{m\kappa_T} \quad \text{and} \quad \frac{\partial v}{\partial T} = \frac{\partial}{\partial T} \left(\frac{m}{\rho} \right) = -\frac{m}{\rho^2} \frac{\partial \rho}{\partial T}$$

where ρ is the mass density and m is the molar weight, we can rewrite eq(3.40) as

$$c_v = x_g c_{v_g} + x_l c_{v_l} + \frac{x_g T_0}{\kappa_T^g \rho_g^3} \left(\frac{\partial \rho_g}{\partial T} \right)_{\text{coex}}^2 + \frac{x_l T_0}{\kappa_T^l \rho_l^3} \left(\frac{\partial \rho_l}{\partial T} \right)_{\text{coex}}^2 \quad (3.88)$$

where c now denotes specific heat (molar heat capacity / m). Since all terms on the

right are positive, we have

$$c_v \geq \frac{x_g T_0}{\kappa_T^g \rho_g^3} \left(\frac{\partial \rho_g}{\partial T} \right)_{coex}^2 \quad (3.89)$$

Now, when the critical point is approached from below, we have

$$c_v \propto (-\varepsilon)^{-\alpha'} \quad [\text{from (3.86)}]$$

$$\rho \rightarrow \rho_C$$

$$\kappa_T \propto (-\varepsilon)^{-\gamma'} \quad [\text{from (3.87)}]$$

$$\left[\frac{\partial(\rho_l - \rho_g)}{\partial T} \right]_{coex} \propto (-\varepsilon)^{\beta-1} \quad [\text{from (3.85)}]$$

Taking the square of the last gives

$$\left(\frac{\partial \rho_l}{\partial T} - \frac{\partial \rho_g}{\partial T} \right)_{coex}^2 \propto (-\varepsilon)^{2\beta-2}$$

On the other hand, $\left(\frac{\partial \rho_l}{\partial T} + \frac{\partial \rho_g}{\partial T} \right)_{coex}^2$ is expected to be regular, [see (3.26)], so that

$$\begin{aligned} \frac{1}{4} \left[\left(\frac{\partial \rho_l}{\partial T} - \frac{\partial \rho_g}{\partial T} \right)_{coex}^2 + \left(\frac{\partial \rho_l}{\partial T} + \frac{\partial \rho_g}{\partial T} \right)_{coex}^2 \right] &= \frac{1}{2} \left[\left(\frac{\partial \rho_l}{\partial T} \right)_{coex}^2 + \left(\frac{\partial \rho_g}{\partial T} \right)_{coex}^2 \right] \\ &= \left(\frac{\partial \rho}{\partial T} \right)_{coex}^2 \propto (-\varepsilon)^{2\beta-2} \end{aligned}$$

Putting everything into (3.89), we have

$$c_v = A_1 (-\varepsilon)^{-\alpha'} \geq \frac{A_2}{\kappa_T} \left(\frac{\partial \rho}{\partial T} \right)_{coex}^2 = A_3 (-\varepsilon)^{\gamma'+2\beta-2} \quad (3.90)$$

where the A_j 's are constants. Since $0 < -\varepsilon < 1$, we have

$$\ln(-\varepsilon) = -|\ln(-\varepsilon)| < 0$$

Thus, the singular part of the logarithm of (3.90) gives

$$\alpha' |\ln(-\varepsilon)| \geq -(\gamma' + 2\beta - 2) |\ln(-\varepsilon)|$$

$$\Rightarrow \alpha' + \gamma' + 2\beta \geq 2 \quad (3.92)$$

which is known as the **Rushbrook inequality**.

3.H.3. Exercise 3.4

Compute ε , ω , and π for a van der Waals fluid.

Answer

For convenience, we set

$$\varepsilon = \frac{T - T_C}{T_C} = \bar{T} - 1 \quad \omega = \frac{v - v_C}{v_C} = \bar{v} - 1 \quad \pi = \frac{P - P_C}{P_C} = \bar{P} - 1$$

so that the reduced van der Waals equation

$$\left(\bar{P} + \frac{3}{\bar{v}^2} \right) (3\bar{v} - 1) = 8\bar{T}$$

can be rewritten as

$$\left(\pi + 1 + \frac{3}{(\omega + 1)^2} \right) (3\omega + 2) = 8(\varepsilon + 1) \quad (1)$$

Solving for π gives

$$\pi = -1 - \frac{3}{(\omega + 1)^2} + \frac{8(\varepsilon + 1)}{3\omega + 2}$$

Using

$$-(\omega + 1)^2 (3\omega + 2) = -2 - 7\omega - 8\omega^2 - 3\omega^3$$

$$-3(3\omega + 2) = -9\omega - 6$$

$$8(\omega + 1)^2 (\varepsilon + 1) = 8 + 16\omega + 8\omega^2 + 8\varepsilon + 16\varepsilon\omega + 8\varepsilon\omega^2$$

we have

$$\pi = \frac{8\varepsilon + 16\varepsilon\omega + 8\varepsilon\omega^2 - 3\omega^3}{2 + 7\omega + 8\omega^2 + 3\omega^3} \quad (2)$$

The Degree of the Critical Isotherm

Rewriting (3.84) in the present notation gives

$$\pi \propto |\bar{p} - 1|^\delta = \left| \frac{1}{\bar{v}} - 1 \right|^\delta \propto \omega^\delta \quad \text{at } \varepsilon = 0$$

Eq(2) thus gives

$$\pi = \frac{-3\omega^3}{2 + 7\omega + 8\omega^2 + 3\omega^3} \propto \omega^3$$

so that $\delta = 3$.

The Isothermal Compressibility Exponent

Rewriting (3.87) in the present notation gives

$$\kappa_T \propto \varepsilon^{-\gamma} \quad \text{at} \quad \omega = 0$$

where

$$\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \propto \left(\frac{\partial w}{\partial \pi} \right)_\varepsilon = \left(\frac{\partial \pi}{\partial \omega} \right)_\varepsilon^{-1}$$

Using (2), we have

$$\begin{aligned} \left(\frac{\partial \pi}{\partial \omega} \right)_\varepsilon &= \frac{16\varepsilon + 16\varepsilon\omega - 9\omega^2}{2 + 7\omega + 8\omega^2 + 3\omega^3} - \frac{(8\varepsilon + 16\varepsilon\omega + 8\varepsilon\omega^2 - 3\omega^3)(7 + 16\omega + 9\omega^2)}{(2 + 7\omega + 8\omega^2 + 3\omega^3)^2} \\ &= 8\varepsilon - 14\varepsilon = -6\varepsilon \quad \text{for} \quad \omega = 0 \end{aligned}$$

Hence, $\kappa_T \propto \varepsilon^{-1}$ so that $\gamma = 1$.

The Degree of the Coexistence Curve

Rewriting (3.85) in the present notation gives

$$\bar{\rho}_l - \bar{\rho}_g = \frac{1}{\bar{v}_l} - \frac{1}{\bar{v}_g} = \frac{\bar{v}_g - \bar{v}_l}{\bar{v}_l \bar{v}_g} = \frac{\omega_g - \omega_l}{\bar{v}_l \bar{v}_g} = A_\beta (-\varepsilon)^\beta$$

or

$$\omega_g - \omega_l \propto (-\varepsilon)^\beta \quad (\text{a})$$

along the coexistence curve. Now, the intercepts (points C and G in Fig.3.9) of an isotherm $T_0 < T_C$ with the coexistence curve is given by the Maxwell construction as

$$\int_C^G v dP = 0 \quad (6)$$

where the integral is along the isotherm $T = T_0$. In terms of the present notation, we have

$$\int_C^G (1 + \omega) d\pi = 0 \quad (6a)$$

where is given by (2) with $\varepsilon = \varepsilon_0 = \frac{T_0}{T_C} - 1$. In the vicinity of the critical point, (2)

can be written as

$$\begin{aligned}
\pi &= \left(4\varepsilon + 8\varepsilon\omega + 4\varepsilon\omega^2 - \frac{3}{2}\omega^3\right) \left(1 + \frac{7}{2}\omega + 4\omega^2 + \frac{3}{2}\omega^3\right)^{-1} \\
&= \left(4\varepsilon + 8\varepsilon\omega + 4\varepsilon\omega^2 - \frac{3}{2}\omega^3\right) \left[1 - \frac{7}{2}\omega + \left(\frac{49}{4} - 4\right)\omega^2 + \left(-\frac{343}{8} - \frac{3}{2}\right)\omega^3 + \dots\right] \\
&\simeq 4\varepsilon + 8\varepsilon\omega + 4\varepsilon\omega^2 - \frac{3}{2}\omega^3 - \frac{7}{2}\omega(4\varepsilon + 8\varepsilon\omega) + \frac{33}{4}\omega^2(4\varepsilon) + \dots \\
&\simeq 4\varepsilon - 6\varepsilon\omega + 9\varepsilon\omega^2 - \frac{3}{2}\omega^3 + \dots \quad (5)
\end{aligned}$$

where only terms $\varepsilon^n \omega^m$ with $n + m \leq 3$ are kept. For fixed $\varepsilon = \varepsilon_0$, we have

$$d\pi \simeq \left(-6\varepsilon_0 + 18\varepsilon_0\omega - \frac{9}{2}\omega^2 + \dots\right) d\omega \quad (5a)$$

so that (6a) becomes

$$\begin{aligned}
&\int_C^G (1 + \omega) \left(-6\varepsilon_0 + 18\varepsilon_0\omega - \frac{9}{2}\omega^2 + \dots\right) d\omega = 0 \\
\Rightarrow &\int_C^G \left(-6\varepsilon_0 + 12\varepsilon_0\omega - \frac{9}{2}\omega^2 + \dots\right) d\omega = 0 \\
&\left[-6\varepsilon_0\omega + 6\varepsilon_0\omega^2 - \frac{3}{2}\omega^3 + \dots\right]_C^G = 0 \\
&-6\varepsilon_0(\omega_g - \omega_l) + 6\varepsilon_0(\omega_g^2 - \omega_l^2) - \frac{3}{2}(\omega_g^3 - \omega_l^3) + \dots = 0 \quad (9)
\end{aligned}$$

where, by definition, $\omega = \omega_g$ at G and $\omega = \omega_l$ at C [see Fig.3.8-9].

Now, both G and C are at the same temperature and pressure so that (5) gives

$$\begin{aligned}
4\varepsilon_0 - 6\varepsilon_0\omega_g + 9\varepsilon_0\omega_g^2 - \frac{3}{2}\omega_g^3 + \dots &= 4\varepsilon_0 - 6\varepsilon_0\omega_l + 9\varepsilon_0\omega_l^2 - \frac{3}{2}\omega_l^3 + \dots \\
\Rightarrow -6\varepsilon_0(\omega_g - \omega_l) + 9\varepsilon_0(\omega_g^2 - \omega_l^2) - \frac{3}{2}(\omega_g^3 - \omega_l^3) + \dots &= 0 \quad (8)
\end{aligned}$$

This is compatible with (9) only if

$$\begin{aligned}
9\varepsilon_0(\omega_g^2 - \omega_l^2) &= 6\varepsilon_0(\omega_g^2 - \omega_l^2) \\
\Rightarrow \omega_g^2 &= \omega_l^2 \quad (8a)
\end{aligned}$$

Since $\omega_g = \frac{v_g - v_C}{v_C} \geq 0$ and $\omega_l = \frac{v_l - v_C}{v_C} \leq 0$, eq(8a) implies

$$\omega_g = -\omega_l \geq 0 \quad (8b)$$

Either (8) or (9) then gives

$$-12\varepsilon_0\omega_g - 3\omega_g^3 \simeq 0$$

$$\Rightarrow \quad \omega_g = 0 \quad \text{or} \quad \omega_g^2 = -4\varepsilon_0$$

Thus, slightly away from the critical point, we have

$$\omega_g = 2\sqrt{-\varepsilon_0} \quad (11)$$

where $\varepsilon_0 < 0$ since $T_0 < T_C$. Comparing with condition (a) gives $\beta = \frac{1}{2}$.

The Heat Capacity Exponent

Rewriting (3.86) in the present notation gives

$$c_v \propto \begin{cases} (-\varepsilon)^{-\alpha'} & \text{for } \varepsilon < 0 \\ (+\varepsilon)^{-\alpha} & \text{for } \varepsilon > 0 \end{cases} \quad \text{at } \omega = 0$$

Now, as one approaches the critical point along the isochore $\omega = 0$, one gets [see (3.88)],

$$c_v = \begin{cases} x_g c_{v_g} + x_l c_{v_l} + \frac{x_g T_0}{\kappa_T \rho_g^3} \left(\frac{\partial \rho_g}{\partial T} \right)_{coex}^2 + \frac{x_l T_0}{\kappa_T \rho_l^3} \left(\frac{\partial \rho_l}{\partial T} \right)_{coex}^2 & \text{for } \varepsilon < 0 \\ c_{v_g} & \text{for } \varepsilon > 0 \end{cases}$$

Very close to the critical point, the liquid and vapor phases merges so that

$$c_v \simeq \begin{cases} c_{v_g} + \left[\frac{T_0}{\kappa_T \rho^3} \left(\frac{\partial \rho}{\partial T} \right)^2 \right]_{coex} & \text{for } \varepsilon \simeq 0^- \\ c_{v_g} & \text{for } \varepsilon \simeq 0^+ \end{cases}$$

Thus, there is a discontinuity at the critical point,

$$\Delta = c_v(T_C^-) - c_v(T_C^+) = \left[\frac{T_0}{\kappa_T \rho^3} \left(\frac{\partial \rho}{\partial T} \right)^2 \right]_{crit} \quad \text{with } v = v_C$$

Now,

$$\frac{\partial \rho}{\partial T} = \frac{\rho_C}{T_C} \frac{\partial \bar{\rho}}{\partial \bar{T}} = \frac{\rho_C}{T_C} \frac{\partial}{\partial \bar{T}} \left(\frac{1}{\bar{v}} \right) = \frac{\rho_C}{T_C} \frac{\partial}{\partial \varepsilon} \left(\frac{1}{\omega + 1} \right)$$

$$= -\frac{\rho_c}{T_c(\omega+1)^2} \frac{\partial \omega}{\partial \varepsilon} \simeq \frac{\rho_c}{T_c(\omega+1)^2} \frac{2}{\omega}$$

where eq(11) was used to obtain the last equality. Thus

$$\frac{1}{\rho^3} \left(\frac{\partial \rho}{\partial T} \right)^2 \simeq \frac{(\omega+1)^3}{\rho_c^3} \left[\frac{\rho_c}{T_c(\omega+1)^2} \frac{2}{\omega} \right]^2 = \frac{4}{T_c^2 \rho_c (\omega+1) \omega^2}$$

Similarly,

$$\begin{aligned} \kappa_T &= -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T = -\frac{1}{P_C \bar{v}} \left(\frac{\partial \bar{v}}{\partial \bar{P}} \right)_T \\ &= -\frac{1}{P_C(\omega+1)} \left(\frac{\partial \omega}{\partial \pi} \right)_\varepsilon = -\frac{1}{P_C(\omega+1)} \left(\frac{\partial \pi}{\partial \omega} \right)_\varepsilon^{-1} \end{aligned}$$

Using (5a), we have

$$\left(\frac{\partial \pi}{\partial \omega} \right)_\varepsilon \simeq -6\varepsilon + 18\varepsilon\omega - \frac{9}{2}\omega^2 + \dots$$

so that

$$\frac{1}{\kappa_T} \simeq P_C(1+\omega) \left(6\varepsilon - 18\varepsilon\omega + \frac{9}{2}\omega^2 + \dots \right)$$

Putting everything together, we have

$$\Delta \simeq \left[T_C(\varepsilon+1) \frac{4}{T_C^2 \rho_c (\omega+1) \omega^2} P_C(1+\omega) \left(6\varepsilon - 18\varepsilon\omega + \frac{9}{2}\omega^2 + \dots \right) \right]_{crit}$$

where *crit* means $\omega = 2\sqrt{-\varepsilon}$ with $\varepsilon = 0$. Thus

$$\begin{aligned} \Delta &\simeq \frac{4P_C}{T_C \rho_c} \left(6\frac{\varepsilon}{\omega^2} - 18\frac{\varepsilon}{\omega} + \frac{9}{2} + \dots \right) \\ &\simeq \frac{4P_C}{T_C \rho_c} \left(-\frac{3}{2} + 9\sqrt{-\varepsilon} + \frac{9}{2} + \dots \right) \end{aligned}$$

Using $\frac{P_C}{T_C \rho_C} = \frac{3}{8}R$, we have

$$\Delta \simeq \frac{9}{2}R \quad (14)$$

Since the jump is finite, we have $\alpha = \alpha' = 0$.