3.H. Critical Exponents

In a phase transition, an entire system suddenly changes into another form of substantially different physical attributes. This, by itself, already makes the phenomenon fascinating. Furthermore, measurements showed that critical phenomenon has certain universality so that different systems behave essentially the same way. This, of course, attracts a lot of theoretical interests.

3.H.1. Definition of Critical Exponents

The transition point of a continuous phase transition is called a critical point. Value of a physical quantity at that point is called a critical value and denoted by a subscript C.

The "distance" from a critical point is measured by a dimensionless parameter

$$\epsilon = \frac{T - T_C}{T_C} \tag{3.80}$$

where T_C is the critical temperature. Now, measurements showed that the order parameter and response functions take the form

$$f(\epsilon) = \begin{cases} \epsilon^{\lambda} g(\epsilon) & \text{for } T > T_C \\ (-\epsilon)^{\lambda'} g'(\epsilon) & \text{for } T < T_C \end{cases} \tag{3.81}$$

where $g(\epsilon)$ is finite and nonzero at $\epsilon = 0$ and λ is called the critical exponent of f on the high temperature side; and analogously for the primed variables on the low temperature side. Since the primed and unprimed variables have the same mathematical structure, it suffices to carry our discussion in terms of the unprimed ones. The logarithm of (3.81) gives

$$\ln f(\epsilon) = \lambda \ln \epsilon + \ln g(\epsilon)$$

$$\rightarrow \quad \lambda = \lim_{\epsilon \to 0_+} \frac{\ln f(\epsilon)}{\ln \epsilon} \qquad \left[\lim_{\epsilon \to 0_+} \frac{\ln g(\epsilon)}{\ln \epsilon} = 0 \text{ since } g(0) \text{ is finite.} \right] \tag{3.82}$$

where $\epsilon \to 0_+$ means ϵ goes to 0 on the positive side to keep $\ln \epsilon$ real.

Thus,

$$\lim_{\epsilon \to 0_+} f \propto \epsilon^{\lambda} \to \infty \qquad \text{if} \qquad \lambda < 0$$

$$\lim_{\epsilon \to 0_+} f = 0 \qquad \text{if} \qquad \lambda > 0 \tag{3.82a}$$

The case $\lambda = 0$ warrants further attention. First of all, using the L'Hospital rule, we have

$$\lim_{\epsilon \to 0_+} \frac{\ln(\ln \epsilon)}{\ln \epsilon} = \lim_{\epsilon \to 0_+} \left(\frac{1/(\epsilon \ln \epsilon)}{1/\epsilon} \right) = \lim_{\epsilon \to 0_+} \frac{1}{\ln \epsilon} = 0$$

so that (3.82) can be satisfied by

$$f(\epsilon) = A \; | \ln \epsilon | + B \tag{3.82c}$$

where A & B are constants and $| \ln \epsilon |$ is used since $\ln \epsilon < 0$ for $\epsilon < 1$. Thus, besides the obvious solution $f(\epsilon) = g(\epsilon)$ that has a finite value at $\epsilon = 0$, we also have the solution (3.82c) that diverges there.

In general, for $\lambda \geq 0$, even if $f(0)$ is finite, f can still be non-analytic there, i.e.,

$$\left. \frac{d^j f}{d \epsilon^j} \right|_{\epsilon = 0} \quad \text{is finite only for } j < n \tag{3.83a}$$

Reminder: a function $f(x)$ is non-analytic at x_0 if f has no Taylor expansion at $x = x_0$.

This non-analyticity can be classified by the auxiliary exponent

$$\tilde{\lambda} = n + \lim_{\epsilon \to 0_+} \frac{\ln \left| \frac{d^n f}{d\epsilon^n} \right|}{\ln \epsilon} \tag{3.83}$$

where n is defined in (3.83a).

For example, let

$$f(\epsilon) = 1 - \epsilon^p$$

then

$$\lambda = \lim_{\epsilon \to 0_+} \frac{\ln(1 - \epsilon^p)}{\ln \epsilon} = \lim_{\epsilon \to 0_+} \frac{-\epsilon^p}{\ln \epsilon} = 0$$

$$\frac{df}{d\epsilon} = -p\,\epsilon^{p-1} \qquad \frac{d^2 f}{d\epsilon^2} = -p\,(p-1)\,\epsilon^{p-2} \qquad \dots \qquad \frac{d^n f}{d\epsilon^n} = -p\,(p-1)\dots(p-n+1)\,\epsilon^{p-n}$$

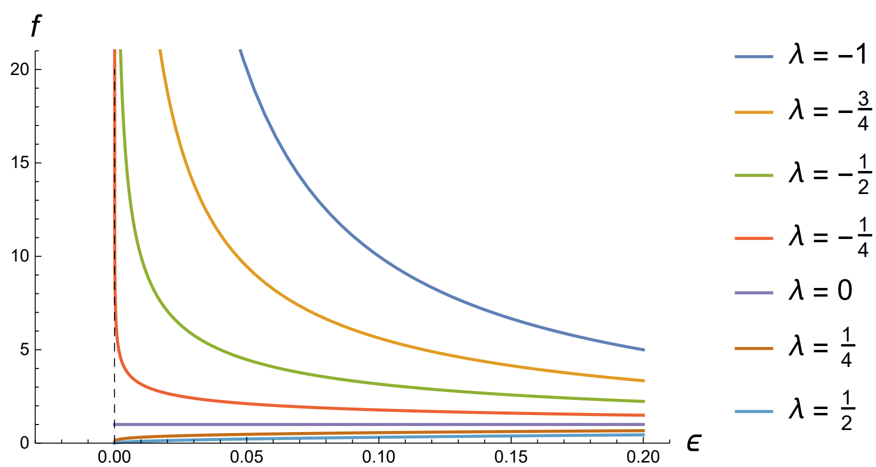
Let p be a non-integer with the integral part $[p]$. Then

$$\left.\frac{d^n f}{d\epsilon^n}\right|_{\epsilon=0} \quad \text{diverges if} \quad p - n < 0 \quad \text{or} \quad n > [p]$$

so that

$$\begin{aligned}
\tilde{\lambda} &= [p] + 1 + \lim_{\epsilon \to 0_+} \frac{\ln \left| \frac{d^{[p]+1} f}{d\epsilon^{[p]+1}} \right|}{\ln \epsilon} \\
&= [p] + 1 + \lim_{\epsilon \to 0_+} \frac{\ln \left| \epsilon^{p-[p]-1} \right|}{\ln \epsilon} \\
&= p
\end{aligned}$$

Now, on the theoretical side, the scaling theory [see §8.C] implies that the Gibbs function, as a function of ϵ, is non-analytic at the critical point. Thus, its derivatives, which include all response functions as well as the order parameter, are all non-analytic there. Hence the necessity of $\tilde{\lambda}$.



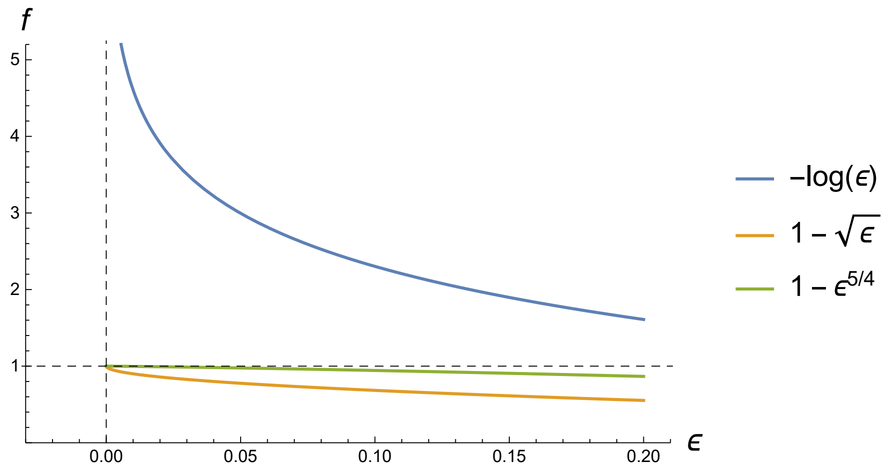


Fig.3.26. Plots of $f(\epsilon)$.

Code

In[ ]:=
```
f[ϵ_] := 1 - ϵ^λ
Table[Derivative[n][f][ϵ], {n, 5}]
```

Out[ ]=
```
{-ϵ^(-1+λ) λ, -ϵ^(-2+λ) (-1 + λ) λ, -ϵ^(-3+λ) (-2 + λ) (-1 + λ) λ,
 -ϵ^(-4+λ) (-3 + λ) (-2 + λ) (-1 + λ) λ, -ϵ^(-5+λ) (-4 + λ) (-3 + λ) (-2 + λ) (-1 + λ) λ}
```

In[ ]:=
```
fL = Table[ϵ^λ, {λ, -1, 1/2, 1/4}];

leg = Table["λ = " <> ToString[λ, TraditionalForm], {λ, -1, 1/2, 1/4}];

Plot[fL, {ϵ, 0, .2},
    PlotRange → {{-.03, .21}, {0, 21}},
    AxesOrigin → {-.03, 0},
    AxesLabel → {"ϵ", "f"},
    PlotLegends → leg,
    Epilog → {Dashed, Line[{{0, 0}, {0, 20}}]}
    ]
```

In[ ]:=
```
fL0 = {-Log[ϵ], 1 - ϵ^(1/2), 1 - ϵ^(5/4)};
Plot[fL0, {ϵ, 0, .2},
    PlotRange → {{-.03, .21}, {0, 5.2}},
    AxesOrigin → {-.03, 0},
    AxesLabel → {"ϵ", "f"},
    PlotLegends → fL0,
    Epilog → {Dashed, Line[{{0, 0}, {0, 20}}], Line[{{-1, 1}, {1, 1}}]}
    ]
```

3.H.2. Critical Exponents for Pure PVT Systems

The are 4 commonly used critical exponents for a pure PVT system.

(a) The critical exponent δ, also called the degree of the critical isotherm, is defined by

$$\frac{P - P_C}{P_C} = A_\delta \left| \frac{\rho - \rho_C}{\rho_C} \right|^\delta \operatorname{sgn}(\rho - \rho_C) \qquad \text{at} \quad T = T_C \tag{3.84}$$

where A_δ is a constant. Typical experimental values are, $6 > \delta \gtrsim 4$.

(b) The critical exponents β, also called the degree of the coexistence curve, is defined by

$$\frac{\rho_l - \rho_g}{\rho_C} = A_\beta (-\epsilon)^\beta \tag{3.85}$$

where A_β is a constant. Typical experimental value gives $\beta = \frac{1}{3}$.

[See Guggenheim's formula (3.27) of §3.D.3.]

(c) The critical exponents α & α' for the heat capacity at constant volume C_V is defined by

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

where A_α & A_α' are constants. Typical experimental values are $\alpha \approx \alpha' \approx 0.1$.
A logarithmic divergence is possible [see Ex.3.4].

(d) The critical exponents γ & γ' for the isothermal compressibility κ_T is defined by

$$\frac{\kappa_T}{\kappa_{TC}} = \begin{cases} A_\gamma' (-\epsilon)^{-\gamma'} & \text{for} \quad T < T_C \quad \& \quad \rho = \rho_l(T) \text{ or } \rho_g(T) \\ A_\gamma \epsilon^{-\gamma} & \text{for} \quad T > T_C \quad \& \quad \rho = \rho_C \end{cases} \tag{3.87}$$

where A_γ & A_γ' are constants. Typical experimental values are $\gamma' \approx 1.2$ & $\gamma \approx 1.3$.

Thermodynamic stability imposes inequality relations between the critical exponents. For example, using

$$\rho = \frac{m}{v} \quad \rightarrow \quad d v = -\frac{m}{\rho^2} d\rho \qquad [\, m = \text{molar mass} \,]$$

and

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \quad \rightarrow \quad \left(\frac{\partial P}{\partial v}\right)_T = -\frac{1}{v \kappa_T} = -\frac{\rho}{m \kappa_T}$$

we can write (3.40) of §3.D.3 as

$$c_v = x_g \left[c_{vg} + T \frac{m}{\kappa_T^g \rho_g^3} \left(\frac{\partial \rho_g}{\partial T}\right)_{\text{coex}}^2 \right] + x_l \left[c_{vl} + T \frac{m}{\kappa_T^l \rho_l^3} \left(\frac{\partial \rho_{gl}}{\partial T}\right)_{\text{coex}}^2 \right] \tag{3.88}$$

Owing to thermodynamic stability requirements, $\kappa_T > 0$ so that every term in (3.88) is positive. Therefore,

$$c_v \geq x_g T \frac{m}{\kappa_T^g \rho_g^3} \left(\frac{\partial \rho_g}{\partial T}\right)_{\text{coex}}^2 \tag{3.89a}$$

or

$$\tilde{c}_v \geq x_g T \frac{1}{\kappa_T^g \rho_g^3} \left(\frac{\partial \rho_g}{\partial T}\right)_{\text{coex}}^2 \tag{3.89}$$

where

$$\tilde{c}_v = \frac{c_v}{m} = \frac{C_V}{n\, m} = \frac{C_V}{M} = \text{specific heat at constant volume}$$

As $T \rightarrow T_C$ along the coexistence curve,

$$\rho_g \rightarrow \rho_C$$

$$\kappa_T^g \propto (-\epsilon)^{-\gamma'} \qquad \text{[(3.87) used.]}$$

$$\left(\frac{\partial \rho_g}{\partial T}\right)_{\text{coex}} \propto -\rho_C \frac{\partial}{\partial T}\left(\frac{T_C - T}{T_C}\right)^{\beta} \qquad \text{[(3.85) used assuming } \left(\frac{\partial \rho_l}{\partial T}\right)_{\text{coex}} \approx -\left(\frac{\partial \rho_g}{\partial T}\right)_{\text{coex}} \text{.]}$$

$$\propto \rho_C (-\epsilon)^{\beta - 1}$$

$$c_V \propto (-\epsilon)^{-\alpha'}$$

(3.89) then becomes

$$(-\epsilon)^{-\alpha'} \geq A \frac{T_C}{\rho_C} (-\epsilon)^{\gamma' + 2\beta - 2} \qquad (3.90)$$

where $A > 0$ is a product of x_g, κ_T^0 and the proportionality constants in the definitions of the critical exponents. Taking the logarithm gives

$$\ln(-\epsilon)^{-\alpha'} \geq \ln\left(A \frac{T_C}{\rho_C}\right) + \ln(-\epsilon)^{\gamma' + 2\beta - 2}$$

Since

$$\ln(-\epsilon) \to -\infty \qquad \text{as} \qquad \epsilon \to 0_-$$

the finite constant term can be dropped so that

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

$$\to \quad -\alpha' \,|\ln(-\epsilon)|\, \leq (\gamma' + 2\beta - 2)\, |\ln(-\epsilon)|$$

and hence the Rushbrook inequality,

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

Putting in the experimental values

$$\alpha' = 0.1 \qquad \beta = \frac{1}{3} \qquad \gamma' = 1.2$$

we have

$$\alpha' + \gamma' + 2\beta \approx 2.0$$

In[ ]:=
```
.1 + 2 × 1/3 + 1.2
```

Out[ ]=
```
1.96667
```

Since mean field theories such as the van der Waals or Ginzburg-Landau theories can usually be solved exactly, critical exponents easily follow. However, agreement with experiment is generally poor. The correct approach is Wilson’s renormalization group theory [see §8.D].

Ex.3.4.

Compute the critical exponents, α, β, δ & γ for a van der Waals fluid.

Answer

Since we are interested in the neighborhood of the critical point, we use the difference variables

$$\epsilon = \overline{T} - 1 \qquad \omega = \overline{v} - 1 \qquad \pi = \overline{P} - 1 \qquad [\,\overline{X} = \frac{X}{X_C}\,] \qquad (1a)$$

to rewrite the reduced vdW equation [see (3.44)]

$$\overline{P} = \frac{8\,\overline{T}}{3\,\overline{v} - 1} - \frac{3}{\overline{v}^2}$$

as

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

or

$$\pi = \frac{8\,\epsilon + 16\,\epsilon\,\omega + 8\,\epsilon\,\omega^2 - 3\,\omega^3}{2 + 7\,\omega + 8\,\omega^2 + 3\,\omega^3} \qquad (2)$$

$$= 4\,\epsilon - 6\,\epsilon\,\omega + 9\,\epsilon\,\omega^2 - \frac{3}{2}(1 + 9\,\epsilon)\,\omega^3 + O(\omega^4) \qquad (5)$$

Code

In[∘]:=
```
8 (1 + ϵ)/(2 + 3 ω) - 3/(1 + ω)^2 - 1 // Together
```

Out[∘]=
$$\frac{8 \in + 16 \in \omega + 8 \in \omega^2 - 3\,\omega^3}{(1+\omega)^2\,(2 + 3\,\omega)}$$

In[∘]:=
```
Denominator[%] // Expand
```

Out[∘]= $2 + 7\,\omega + 8\,\omega^2 + 3\,\omega^3$

In[∘]:=
```
%% + O[ω]^4
```

Out[∘]=
$$4 \in - 6 \in \omega + 9 \in \omega^2 + \left(-\frac{3}{2} - \frac{27 \in}{2}\right)\omega^3 + O[\omega]^4$$

(a) δ

In terms of the difference variables, (3.84) becomes

$$\pi = -A_\delta \mid \overline{\rho} - 1 \mid^\delta \qquad \text{at } \epsilon = 0_+ \text{ so that } \rho \lesssim \rho_C$$

$$= -A_\delta \left|\frac{1}{\overline{v}} - 1\right|^\delta = -A_\delta \left|\frac{1}{\omega + 1} - 1\right|^\delta = -A_\delta \left|\frac{\omega}{\omega + 1}\right|^\delta$$

$$\approx -A_\delta\,\omega^\delta + O\left(\omega^{\delta+1}\right)$$

Comparing with (5) at $\epsilon = 0_+$, namely,

$$\pi = -\frac{3}{2}\,\omega^3 + O\left(\omega^4\right) \qquad (3)$$

we have

$$\delta = 3$$

(b) γ

In terms of the difference variables,

$$\kappa_T = -\frac{P_C}{\overline{v}}\left(\frac{\partial\,\overline{v}}{\partial\,\overline{P}}\right)_T = -\frac{P_C}{\overline{v}}\left(\frac{\partial\,\omega}{\partial\,\pi}\right)_\epsilon \qquad \kappa_{T\,C} = -P_C\left(\frac{\partial\,\omega}{\partial\,\pi}\right)_0$$

and (3.87) gives

$$\left(\frac{\partial\,\omega}{\partial\,\pi}\right)_\epsilon \propto \epsilon^{-\gamma} \qquad \text{for } \epsilon\to 0_+ \;\; \& \;\; \omega = 0 \tag{4a}$$

Differentiating (5) gives

$$\left(\frac{\partial\,\pi}{\partial\,\omega}\right)_\epsilon = -6\,\epsilon \qquad \text{for } \omega = 0 \tag{4}$$

Comparing (4) with (4a) gives

$$\gamma = 1$$

(c) β

Using

$$\frac{\rho_l - \rho_g}{\rho_C} = \overline{\rho}_l - \overline{\rho}_g = \frac{1}{\overline{v}_l} - \frac{1}{\overline{v}_g} = \frac{1}{1+\omega_l} - \frac{1}{1+\omega_g}$$

$$\approx \omega_g - \omega_l \approx 2\,\omega_g \qquad \text{for } \epsilon \to 0_-$$

(3.85) becomes

$$\omega_g = \frac{1}{2} A_\beta\,(-\epsilon)^\beta \tag{5a}$$

Now, v_g & v_l are the largest & smallest real solutions to the vdW equation with $P = P_{\text{coex}}(T)$ [see Fig.3.9 of §3.D.4]. In terms of (5), we have

$$\pi_{\text{coex}} = 4\,\epsilon - 6\,\epsilon\,\omega_g + 9\,\epsilon\,\omega_g^2 - \frac{3}{2}(1+9\,\epsilon)\,\omega_g^3 + O(\omega^4) \tag{7a}$$

$$= 4\,\epsilon - 6\,\epsilon\,\omega_l + 9\,\epsilon\,\omega_l^2 - \frac{3}{2}(1+9\,\epsilon)\,\omega_l^3 + O(\omega^4)$$

$$= 4\,\epsilon + 6\,\epsilon\,\omega_g + 9\,\epsilon\,\omega_g^2 + \frac{3}{2}(1+9\,\epsilon)\,\omega_g^3 + O(\omega^4) \qquad [\,\omega_l \approx -\omega_g \text{ for } \epsilon\to 0_- \text{ used.}\,] \tag{7b}$$

Comparing (7a) & (7b) gives

$$6\,\epsilon\,\omega_g + \frac{3}{2}(1+9\,\epsilon)\,\omega_g^3 = 0 \tag{7c}$$

Since

$$\omega_g \ge 0 \qquad \text{if} \qquad \epsilon \ne 0$$

the only solution to (7c) is

$$\omega_g = \sqrt{\frac{-4\,\epsilon}{1+9\,\epsilon}} \approx 2\sqrt{-\epsilon} \qquad \text{for } \epsilon\to 0_- \tag{11}$$

Comparing (11) with (5a) gives

$$\beta = \frac{1}{2}$$

(d) α

In terms of the difference variables, (3.40) of §3.D.3 becomes

$$c_V = x_g\left[c_{V_g} - T\,\frac{P_C\,v_C}{T_C^2}\left(\frac{\partial\,\pi}{\partial\,\omega}\right)_{\omega=\omega_g}\left(\frac{d\,\omega_g}{d\,\epsilon}\right)^2\right] + x_l\left[c_{V_l} - T\,\frac{P_C\,v_C}{T_C^2}\left(\frac{\partial\,\pi}{\partial\,\omega}\right)_{\omega=\omega_l}\left(\frac{d\,\omega_l}{d\,\epsilon}\right)^2\right] \qquad [\text{ For } \epsilon < 0.\,]$$

Reminder: since v is to be kept constant, the path of measuring c_v is a vertical line $v = v_C$ in the v-P plane that passes through the critical point, with

$$v = x_g v_g + x_l v_l \qquad \text{for} \quad T < T_C \qquad \rightarrow \qquad 0 = x_g\, d v_g + x_l\, d v_l$$

(3.40) accounts for the fact that v_g & v_l must change as one moves along the coexistence curve when the temperature changes [see Fig.3.7 of §3.D.3].

Just above the critical point,

$$c_v(T_C^+) = c_{v_g}$$

and just below the critical point,

$$c_v(T_C^-) = c_{v_g} - Z_C R (1 - \epsilon) \left[x_g \left(\frac{\partial \pi}{\partial \omega} \right)_{\omega = \omega_g} \left(\frac{d\, \omega_g}{d \epsilon} \right)^2 + x_l \left(\frac{\partial \pi}{\partial \omega} \right)_{\omega = \omega_l} \left(\frac{d\, \omega_l}{d \epsilon} \right)^2 \right]_{\epsilon = 0_-} \tag{12a}$$

where

$$x_g + x_l = 1, \qquad c_{v_g} \approx c_{v_l} \quad \text{as} \quad \epsilon \to 0_-$$

and

$$Z_C = \frac{P_c v_c}{R T_c} = \frac{3}{8}$$

is the compressibility factor at the critical point [see §3.D.4].

Using (5), we have

$$\left(\frac{\partial \pi}{\partial \omega} \right)_\epsilon = -6 \epsilon + 18 \epsilon \omega - \frac{9}{2} (1 + 9 \epsilon) \omega^2 + O(\omega^3)$$

$$\rightarrow \left(\frac{\partial \pi}{\partial \omega} \right)_{\omega = \omega_g} = -6 \epsilon - 36 (-\epsilon)^{3/2} + 18 (1 + 9 \epsilon) \epsilon + \ldots \qquad \text{[(11) used.]}$$

$$= 12 \epsilon - 36 (-\epsilon)^{3/2} + 162 \epsilon^2 + \ldots \tag{13a}$$

$$\left(\frac{\partial \pi}{\partial \omega} \right)_{\omega = \omega_l} = -6 \epsilon + 36 (-\epsilon)^{3/2} + 18 (1 + 9 \epsilon) \epsilon + \ldots \qquad [\ \omega_l \approx -\omega_g \text{ used.}]$$

$$= 12 \epsilon + 36 (-\epsilon)^{3/2} + 162 \epsilon^2 + \ldots \tag{13b}$$

$$\left(\frac{d\, \omega_g}{d \epsilon} \right)^2 = \left(\frac{d\, \omega_l}{d \epsilon} \right)^2 = -\frac{1}{\epsilon} \qquad \text{[(11) used.]} \tag{13c}$$

(12a) thus becomes

$$c_v(T_C^-) \approx c_{v_g} + Z_C R (1 - \epsilon) \left[12 + (x_l - x_g) (-\epsilon)^{1/2} + 162 \epsilon + \ldots \right]$$

$$\approx c_{v_g} + \frac{9}{2} R + O(\epsilon) \tag{14a}$$

and

$$c_v(T_C^-) - c_v(T_C^+) = \frac{9}{2} R + O(\epsilon) \tag{14}$$

Since both $c_v(T_C^+)$ & $c_v(T_C^-)$ are finite, (3.86) gives

$$\alpha = \alpha' = 0$$