

DEPARTMENT OF PHYSICS  
INDIAN INSTITUTE OF TECHNOLOGY, MADRAS

PH5080 Statistical Physics

Problem Set 6

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**Critical Exponents in the van der Waals gas**

**Some history**

The Nobel Prize in Physics 1910 was awarded to Johannes Diderik van der Waals “*for his work on the equation of state for gases and liquids*”. The matter around us assumes different forms: solid, fluid or gaseous. The relationship between the volume, pressure and temperature of gases has been formulated since the 17th century. In 1873, Johannes van der Waals formulated an equation of state that applies to both gases and liquids. In it he introduced the idea that molecules attract one another to explain why the laws governing gases do not apply under high pressure. In 1880, he formulated the principle that a gas can be fully described if the critical temperature at which the gas liquefies is known.

[http://www.nobelprize.org/nobel\\_prizes/physics/laureates/1910/waals-facts.html](http://www.nobelprize.org/nobel_prizes/physics/laureates/1910/waals-facts.html)

This might explain why we have paid a lot of attention to the van der Waals gas. Actually, this problem set shows that there is even more!

The van der Waals equation of state is given by

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_B T .$$

We saw in class that the Helmholtz free energy for the van der Waals gas takes the form

$$F(T, V, N) = -Nk_B T \left[ \log \left( \frac{V - Nb}{N} \right) + \frac{3}{2} \log \left( \frac{2\pi m k_B T}{h^2} \right) + 1 \right] - \frac{N^2 a}{V} .$$

1. Define the **critical** point on  $PV$  isotherms to be the temperature  $T = T_c$  where an inflection point appears on the  $PV$  curve, i.e.,

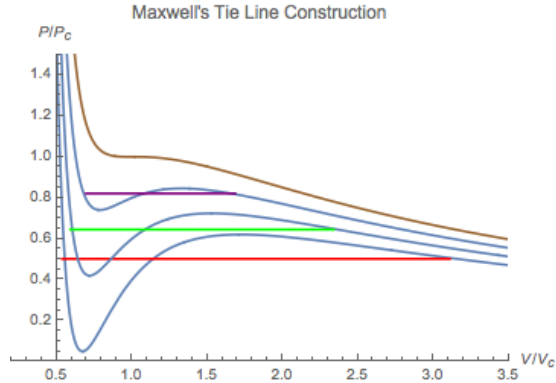
$$\frac{\partial P}{\partial V} = 0 \quad \text{and} \quad \frac{\partial^2 P}{\partial V^2} = 0 .$$

Let  $(P_c, V_c, T_c)$  denotes the inflection point in the  $PV$  diagram at the critical temperature. Show that

$$P_c = \frac{a}{27b^2} , \quad V_c = 3Nb , \quad k_B T_c = \frac{8a}{27b} .$$

Define the **reduced variables** by  $p = P/P_c$ ,  $t = T/T_c$  and  $v = V/V_c$ .

In the figure below, we plot isotherms for various values of  $T < T_c$  with the corresponding Maxwell tie line.



2. Show that the specific entropy,  $s = S/N$  in reduced variables is given by

$$s = k_B \log t^{3/2} (3v - 1) + \text{constant} .$$

Hence compute  $c_v = T(\partial s / \partial T)_v$  and show that as  $T \rightarrow T_c$ , the specific heat goes as  $c_v \sim (T - T_c)^\alpha$ , with critical exponent  $\alpha = 0$ .

3. Show that the pressure, in reduced variables, is given by

$$p(v, t) = -\frac{3}{v^2} + \frac{8t}{3v - 1} , \tag{1}$$

and show that as  $T \rightarrow T_c$  (or  $t \rightarrow 1$ ) the isothermal compressibility  $\kappa_T$  goes as  $(T - T_c)^{-\gamma}$  with critical exponent  $\gamma = 1$ .

4. Next show that at  $T = T_c$ , i.e., on the critical isotherm, one has as  $V \rightarrow V_c$

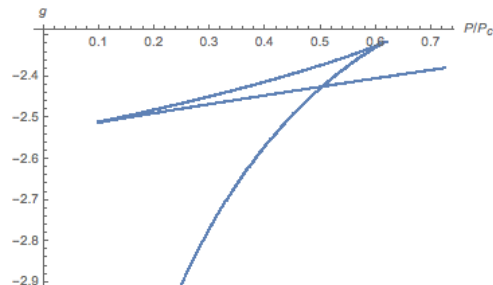
$$(p - 1) \sim (v - 1)^\delta \quad \text{or} \quad (P - P_c) \sim (V - V_c)^\delta ,$$

with the critical exponent  $\delta = 3$ .

5. Verify that, in terms of reduced variables, the chemical potential of a van der Waals gas is given by

$$\frac{\mu(v, t)}{k_B T_c} = -t \log(3v - 1) + \frac{t}{3v - 1} - \frac{9}{4v} + \text{a function of } t . \tag{2}$$

In the figure below, we plot  $\mu = g = G/N$  as a function of pressure at  $T = 0.85T_c$ .



6. We wish to show that as  $T \rightarrow T_c^-$ , one has

$$(v_g - v_\ell) \sim (T_c - T)^\beta ,$$

with  $\beta = 1/2$ . It is not as simple to obtain this exponent! So we shall go through the process and then simplify to obtain the value of  $\beta$ .

On the coexistence curve, where the liquid and gas phases can coexist, the pressures of the two phases and chemical potentials must be equal. These conditions imply

$$-\frac{3}{v_\ell^2} + \frac{8t}{3v_\ell - 1} = -\frac{3}{v_g^2} + \frac{8t}{3v_g - 1} , \quad (3)$$

$$-t \log(3v_\ell - 1) + \frac{t}{3v_\ell - 1} - \frac{9}{4v_\ell} = -t \log(3v_g - 1) + \frac{t}{3v_g - 1} - \frac{9}{4v_g} . \quad (4)$$

where  $v_\ell$  and  $v_g$  denote the specific volumes of the gas and liquid phases. Let us make an assumption that as  $t \rightarrow 1^-$ , one has for some non-zero and positive  $\varepsilon$ , that

$$v_\ell \sim 1 - \frac{\varepsilon}{2} \quad \text{and} \quad v_g \sim 1 + \frac{\varepsilon}{2} .$$

Substitute this into both of the above equations and expand to third-order<sup>1</sup> in  $\varepsilon$  and show that both of them give

$$v_g - v_\ell \equiv \varepsilon \sim 4(1 - t)^{1/2} ,$$

which implies that  $\beta = 1/2$ . Since both equations are simultaneously valid, our assumption is justified.

Notice that these exponents are identical to what we get from the mean field solution to the Ising model. The exponents for the vdW gas are not quite correct – they correspond the *mean field* result – this misses out on fluctuations and the correct values are slightly different.

Model	$\alpha$	$\beta$	$\gamma$	$\delta$
vdW	0	1/2	1	3
3d Ising	0.1	0.33	1.24	4.79

Most real gases fall in the **universality** class of the the 3d Ising Model for which the exponents can be numerically determined.

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<sup>1</sup>I suggest the use of symbolic manipulation packages such as Sympy or Mathematica or Maxima to carry out this computation! All figures were generated using Mathematica.