Homework 1

*Submit a **single file** (pdf or zip) online using the dropbox submission link for the appropriate deadline. Acknowledge any references you use as well as any other students with whom you collaborate.*

1 Critical exponent for the coexistence boundary

When you computed the critical exponents for the van der Waals model you worked under the assumption that

$$|v_l - 1| \sim |v_g - 1| \quad (t \to 0-). \tag{1}$$

Let's show that this is indeed the case for all models that *behave like the van der Waals gas.*

We'll work with a state equation $P = f(T, V)$ that has the same features as the van der Waals one, and define

$$v_l = 1 - x, \quad v_g = 1 + y, \quad x, y \geq 0. \tag{2}$$

To make things simpler we will assume that we are working with reduced variables, so $v_{\mathrm{c}} = 1$.

(a) Show that if

$$\begin{cases} \frac{\partial P}{\partial v}(T,1) = a(T) \\ \frac{\partial^2 P}{\partial v^2}(T,1) = 2b(T) \\ \frac{\partial^3 P}{\partial v^3}(T,1) = 6c(T) \end{cases} \tag{3}$$

with $a(T), b(T) \neq 0$ when T is close to T_{c} but $T \neq T_{\mathrm{c}}$, then the two equations

$$P(T, v_l) = P(T, v_g) \tag{4}$$

$$\left.\frac{G}{N}\right|_{v=v_l} = \left.\frac{G}{N}\right|_{v=v_g} \tag{5}$$

specifying v_l and v_g can be written up to cubic order in x, y as

$$a(x+y) + b(y^2 - x^2) + c(x^3 + y^3) = 0 \tag{6}$$

$$a(x+y) + (b + a/2)(y^2 - x^2) + (c + 2b/3)(x^3 + y^3) = 0. \tag{7}$$

Hint: $g = G/N$ *can be written as*

$$g(T, v) = A(T) + P(T, v)v - \int_1^v P \, \mathrm{d}v \tag{8}$$

for some function $A(T)$.

(b) The two equations above can be combined to obtain

$$3a(y^2 - x^2) + 4b(x^3 + y^3) = 0. \tag{9}$$

Show that the only consistent solution is

$$y = x + O(x^2). \tag{10}$$

2 Dietrici equation of state

In this question you'll see some evidence of critical exponents being universal, i.e., they don't depend on the specific details about the interactions. You'll work with a gas described by the Dietrici equation of state

$$P(v-b) = kT\exp\left(-\frac{a}{kTv}\right), \quad a, b > 0. \tag{11}$$

You can convince yourself by plotting the isotherms that the overall behaviour is the same as the van der Waals gas (this equation also needs to be fixed with Maxwell's construction).

I recommend using Mathematica to do the calculations as it can get messy otherwise. Feel free to include your Mathematica results instead of writing them out by hand.

(a) Find the critical point and show that in terms of the reduced variables

$$P_r = \frac{T_r}{2v_r - 1}e^{2-2/T_r v_r}. \tag{12}$$

Use the reduced equation for the rest of the question. Feel free to drop the r subscript.

(b) Find the critical exponent δ and γ.

(c) Use the result from the previous question to find the critical exponent β like you did for the van der Waals gas.

Hint: expand P_r to linear order in t and cubic order in x before solving $P_r(T_r, v_l) = P_r(T_r, v_g)$ for t.