# Physics 114 Statistical Mechanics Spring 2021

# Week 12 Reading and Problem Assignment

## Overview:

This week, we study transitions between different equilibrium phases of matter. Knowing the chemical potential allows us to trace out coexistence curves on a phase diagram. We will use the historically important model of a van der Waals fluid, in order to study the liquid-gas phase transition. We'll derive that the enthalpy change, or "latent heat" of transition, determines the slope of the phase coexistence curve between any two phases on a P-T diagram.

Now, systems have interparticle interactions which can't be neglected (which can thus make a system undergo a phase transition). The potential energy, $u(r_i, r_j)$ between particles $i$ and $j$ thus factors into a fluid's statistical properties. We will learn how to write *virial series* for pressure (and other quantities like free energy). These are *series with the density $N/V$ as the expansion parameter.* A virial series is used when a gas is not dilute enough to be ideal, but not dense enough to be a liquid.

## Suggested Reading:

*Note: This is a bit less than what is listed on our P114 Syllabus for Week 12.*

G&T Sections

- 7.3, 7.4
- 8.1-8.3

B&B Sections

- 26.1
- 26.3, 26.4
- 28.1-28.7

Schroeder Section

- 5.3

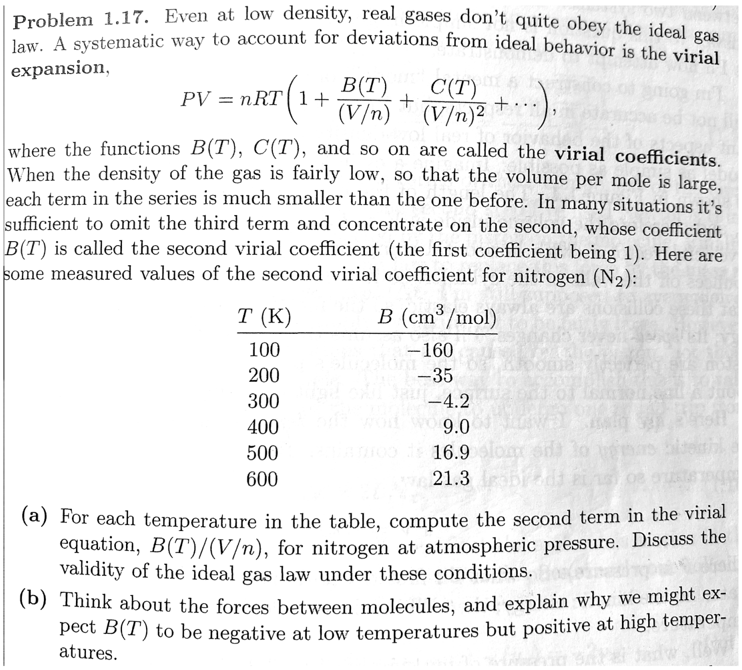
## Warmup Problems:

### W1 Second virial coefficient:

Do Schroeder Problem 1.17 Parts (a), (b) shown below.

*Notes: i) The symbol $n$ means the number of moles of gas.*

*ii) Since $B$ is already a coefficient in a density expansion, you may use the ideal*



**Problem 1.17.** Even at low density, real gases don't quite obey the ideal gas law. A systematic way to account for deviations from ideal behavior is the **virial expansion**,

$$PV = nRT\left(1 + \frac{B(T)}{(V/n)} + \frac{C(T)}{(V/n)^2} + \cdots\right),$$

where the functions $B(T)$, $C(T)$, and so on are called the **virial coefficients**. When the density of the gas is fairly low, so that the volume per mole is large, each term in the series is much smaller than the one before. In many situations it's sufficient to omit the third term and concentrate on the second, whose coefficient $B(T)$ is called the second virial coefficient (the first coefficient being 1). Here are some measured values of the second virial coefficient for nitrogen ($N_2$):

| $T$ (K) | $B$ (cm$^3$/mol) |
|---|---|
| 100 | −160 |
| 200 | −35 |
| 300 | −4.2 |
| 400 | 9.0 |
| 500 | 16.9 |
| 600 | 21.3 |

(a) For each temperature in the table, compute the second term in the virial equation, $B(T)/(V/n)$, for nitrogen at atmospheric pressure. Discuss the validity of the ideal gas law under these conditions.

(b) Think about the forces between molecules, and explain why we might expect $B(T)$ to be negative at low temperatures but positive at high temperatures.

*gas equation of state to calculate $n/V$.*

**W2 Diamond or Graphite?** Schroeder Problem 5.24

## Problems to discuss in our meeting

**Note:** The * means that these problems are to be handed in. They are due the day after we meet.

### 1 The vapor pressure equation:

i) Write a solution to Schroeder Problem 5.35

*Note that this problem is already done for us as Example, 7.3 in G&T :-)*

ii) Schroeder Problem 5.36 part (a)

### 2 Critical exponents for the van der Waals gas:

i) Briefly explain the meaning of "reduced units" for the van der Waals equation, and the related concept of "the law of corresponding states".

ii) G&T Problem 7.18

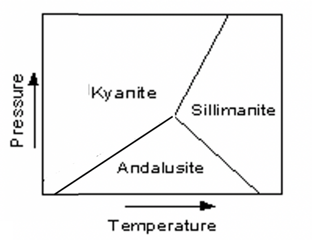
### 3* One more critical exponent for the van der Waals gas:

B&B Problem 26.1

### 4 Phases and a triple point for an aluminosilicate:

i) Schroeder 5.29 parts (a) - (c). (Below is a qualitative phase diagram.)

*ii) Optional ... if you have time:* Schroeder 5.39, which uses the answers from i).



**5* The van der Waals isotherm and the Maxwell construction:**

i) Schroeder Problem 5.52

*ii) Optional ... if you have time:* Plot $G(t, v)$ vs. $v$ for $t = 0.95$. Do you get a curve that looks something like G&T Fig. 7.6 with minima in the right places?

**6 $B_2(T)$ for a toy potential:** G&T Problem 8.30

*Note: If you have an old edition of the book, there may be a typo in Eq. (8.205). The lower limit for $u(r) = -\epsilon$ is $\sigma$ (not 0).*

**7* Changing the freezing point with physics:**

i) B&B Problem 28.1

ii) For my saltwater aquarium I use Instant Ocean$^{\text{TM}}$, a combination of salts and minerals. I add these to pure water, so that the solution has a mole fraction of $x_B = 0.22$. By how much does this change the freezing temperature as compared to pure water ... and does it raise or lower it?

**8 Numerical calculation of virial stuff:**

Use a computer to calculate and plot the second virial coefficient for a gas of molecules interacting via the Lennard-Jones (LJ) potential. This potential is given in G&T as Eq. (8.2). For a LJ potential: the parameter $\epsilon$ is the "attractive strength" and $\sigma$ is the "size" of the particles. (If you are doing this problem using Schroeder, these parameters are called $u_o$ and $r_o$.)

Use values of $kT/\epsilon$ ranging from 1-7. On the same graph, plot the data for nitrogen given in our first warmup problem. Can you find LJ parameters $\sigma$ and $\epsilon$ so as to obtain a good fit?