NYU CHEM GA 2600: Statistical Mechanics Midterm

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Instructions: This midterm is open book/open note. No electronic devices besides a calculator. Please write your name on each page and try to write your solutions legibly. Try to use scratch paper for figuring things out.

1. **van der Waal's Equation of State (50 pts total)**. In class we showed that you can approximate the pressure of a non-ideal gas by

$$P = \frac{nRT}{V - nb} - a\frac{n^2}{V^2} \tag{1}$$

   (a) Describe in words the meanings of the terms a and b. (10 pts)

   (b) Example system - Real data says that 1 mole of carbon dioxide at 373 K occupies 536 mL when at 50.0 atm. *What is the calculated value of the pressure for CO_2 at 373 K in a box of sized 536 mL using:*

      i. The ideal gas equation (remember, n is the number of moles of gas such that $Nk_B = nR$, and R=0.08206 L atm / (K mol)). (5 pts)

      ii. The van der Waal's equation, with a = 3.61 $\text{L}^2\text{atm/mol}^2$ and $b = 0.0428\text{L/mol}$. (5 pts)

   In both cases, compute the percent deviation from the true pressure. (5 pts each)

   (c) The Canonical partition function corresponding to our van der Waal's equation of state is

$$Q(N,V,T) = \frac{1}{N!}\left(2\pi m k_B T/h^2\right)^{3N/2}(V - Nb)^N e^{aN^2/(Vk_BT)} \tag{2}$$

   Compute the *average energy* and the *heat capacity* from this partition function. (20 pts)

2. **Maxwell-Boltzmann distribution (90 points total)**. The Maxwell-Boltzmann distribution gives the probability of a particle having velocity v in an ideal gas with constant (N, V, T). For 1-dimension, it is given by:

$$P(v) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{mv^2}{2k_B T}} \tag{3}$$

   (a) Some properties of a particle in 1 dimension:

      i. For a particle in a 1D box of length L, write the Canonical partition function, and do the all the integrals to find a constant factor related to what is seen in Eqn. 3 (15 pts).

      ii. Using Eqn. 3, what is the average velocity of a particle, i.e. $\langle v \rangle = \int_{-\infty}^{\infty} vP(v)dv$ (10 pts).

      iii. Using Eqn. 3, what is the mean-squared velocity of a particle, i.e. $\langle v^2 \rangle$ (Hint: remember how we solved similar problems in the first homework). (10 pts)

      iv. What is the variance of the velocity of a particle? (10 pts)

      v. Sketch the 1-D Maxwell-Boltzmann probability distribution (Eqn. 3). (5 pts)

   (b) In three dimensions, the probability of finding a velocity vector is given by the product of the probabilities in each direction, i.e.

$$P(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_B T}} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{m\vec{v}^2}{2k_B T}} \tag{4}$$

   Changing to spherical coordinates, the probability distribution for the speed $s = \sqrt{v_x^2 + v_y^2 + v_z^2}$ is given by:

$$P(s) = 4\pi s^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{ms^2}{2k_B T}} \tag{5}$$

   Reminder: since we're in spherical coordinates, the average of a variable A is only an integral over positive speeds:

$$\langle A \rangle = \int_0^{\infty} ds A(s) P(s) \tag{6}$$

      i. Sketch the 3D Maxwell-Boltzmann probability distribution for speed (Eqn. 5). (10 points)

      ii. What is the root-mean-squared speed ($\sqrt{\langle s^2 \rangle}$)? (15 pts)

      iii. What is the most probable speed? How does this compare to the root-mean-squared speed? Hint: solve $\frac{dP(s)}{ds} = 0$. (15 pts)

3. **One dimensional lattice model (60 points total)**. In the homework, we studied N independent 2 level systems. In this problem, we will line up all of our N systems and call each one a "site" on a lattice. An example state of a system of size $N = 9$ might look like the following:

State (n_i):	1	0	0	1	1	0	0	0	1
Site (i):	1	2	3	4	5	6	7	8	9

Figure 1: An example configuration of a lattice with $N = 9$ states.

Site i can have a value either $n_i = 0$ or $n_i = 1$ (in the example above, $n_1 = 1, n_4 = 1, n_5 = 1$ and $n_9 = 1$).

In one dimension, define the energy of a given state as

$$H = \sum_{i=1}^{N} \mu n_i - \sum_{i=1}^{N-1} J n_i n_{i+1} \tag{7}$$

Every time a site has value $n_i = 1$, the energy goes up by μ, and when 2 sites next to each-other have value $n_i = 1$ and $n_{i+1} = 1$, then the energy goes down by J. The energy of the configuration in Fig. 1 is $H = 4\mu - J$.

(a) List all configurations for a lattice of length $N = 3$ and their corresponding energies. (16 points)

(b) How many configurations does a lattice of length N have? (4 points)

(c) Write the Canonical partition function of a system of size N at temperature T (20 points).

(d) Suppose we want to simulate a system with $N = 9$ using Metropolis Monte Carlo. A move is flipping a site's value from 1 to 0 or 0 to 1. We will start in the configuration given in Fig. 1. Write the Metropolis acceptance rule for the following moves (20 points total):

i. Changing the value of site 7 to a 1

ii. Changing the value of site 5 to a 0

iii. Changing the value of site 6 to a 1

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1a) "a" quantifies how attracted molecules/atoms are to eachother 5

"b" quantifies how much space they take up 5

b) i) $P = \frac{nRT}{V} = \frac{(1\,mol)(0.08206\,\frac{L\,atm}{K\,mol})(373\,K)}{(.536\,L)}$

$= \underline{57.1\ atm}$ 5

$\%\ error = \left|\frac{57.1 - 50}{50}\right| \times 100 = \underline{14.2\ \%}$ 5

ii) $P = \frac{(1\,mol)(.08206\,\frac{L\,atm}{K\,mol})(373\,K)}{(.536\,L - .0428\,L)} - \frac{3.61\,L^2\,atm}{mol^2}\left(\frac{1\,mol^2}{(.536\,L)^2}\right)$

$= 62.06\ atm - 12.56\ atm$

$= \underline{49.5\ atm}$ 5

$\%\ error = \left|\frac{49.5\ atm - 50\ atm}{50\ atm}\right| \times 100 = \underline{1.0\ \%}$ 5

$\boxed{30}$

c) $Q = 1/N! \left(\frac{2\pi m}{h^2}\right)^{3N/2} \cdot \beta^{-3N/2} \cdot (V-Nb)^N \cdot \exp\left(\frac{aN^2}{V}\beta\right)$

no β dependence

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[-\frac{3N}{2}\log\beta + \frac{aN^2}{V}\beta + \text{"const"}\right]$$

$$= \frac{3}{2}N \cdot \frac{1}{\beta} + \frac{aN^2}{V}$$

$$= \underline{3/2\, N k_B T + aN^2/V}$$

15

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = \underline{\frac{3}{2} N k_B}$$

5

2) a) i) $Q = \frac{1}{h} \cdot \int_{-\infty}^{\infty} dp \int_0^L dq \exp\left(-\frac{1}{k_B T}\left(p^2/2m\right)\right)$

$$= L/h \int_{-\infty}^{\infty} dp\, e^{-\frac{1}{2mk_BT}\cdot p^2} \qquad \int_{-\infty}^{\infty} dx\, e^{-\alpha x^2} = \sqrt{\pi/\alpha}$$

$$= \boxed{\frac{L}{h} \cdot \sqrt{2\pi m k_B T}}$$

15

35

Note: to get full prob dist, count weight of all states w/ velocity v

$P(v) = \frac{1}{h}\int dp' dq'\, e^{-\beta \mathcal{H}(p', q')} \delta(v'-v)/Q$, let $p' = mv'$

$P(v) = \frac{Lm}{h}\int dv' e^{-\beta \cdot \frac{1}{2}mv'^2} \delta(v'-v)/Q = \frac{Lm}{h} e^{-\beta/2\, mv^2}/Q$

$$= \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{mv^2}{2k_BT}}$$

ii) $\langle v \rangle \propto \int_{-\infty}^{\infty} dv \; v e^{-mv^2/2k_BT} = \int_0^{\infty} v e^{-mv^2/2k_BT} dv + \int_{-\infty}^{0} v e^{-mv^2/2k_BT} dv$

odd/even

$v' = -v$
$v' = -dv'$

this is enough to say $= 0$

$$= \int_0^{\infty} v e^{-mv^2/2k_BT} dv - \int_0^{\infty} v' e^{-mv'^2/2k_BT} dv' = \underline{\underline{0}}$$

10

iii) $\langle v^2 \rangle = \int_{-\infty}^{\infty} v^2 P(v) dv$

$$= \sqrt{\frac{m}{2\pi k_BT}} \int_{-\infty}^{\infty} v^2 e^{-\frac{m}{2k_BT} v^2} dv$$

remember $\int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = -\frac{d}{da} \sqrt{\pi}\, a^{-1/2} = \frac{\sqrt{\pi}}{2} a^{-3/2}$

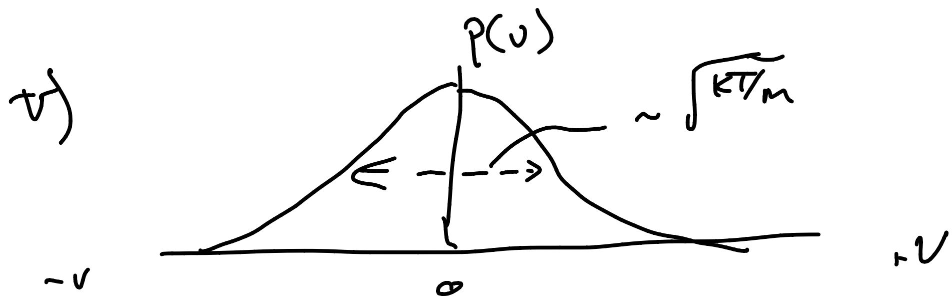
$$= \left(\frac{m}{2\pi k_BT}\right)^{1/2} \cdot \frac{\pi^{1/2}}{2} \cdot \left(\frac{2k_BT}{m}\right)^{3/2}$$

10

$$= \frac{1}{2} \cdot \frac{2k_BT}{m} = \underline{\underline{k_BT/m}}$$

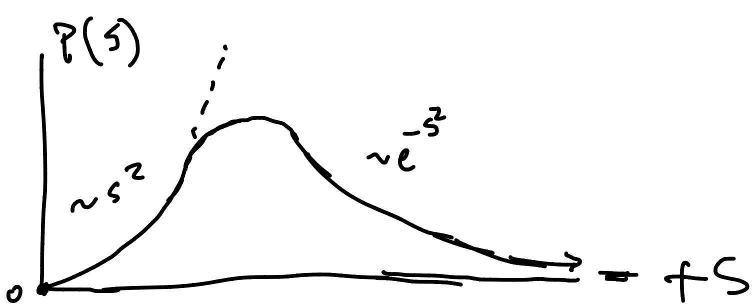
iv) $Var(v) = \langle v^2 \rangle - \langle v^2 \rangle = k_BT/m - 0 = k_BT/m$ 10

v)



5

b) i)



10

$\boxed{45}$

ii) $\langle s^2\rangle = \int_0^\infty ds \quad s^2 \, P(s)$

$$= 4\pi \cdot \left(\frac{m}{2\pi k_B T}\right)^{3/2} \underbrace{\int_0^\infty ds\, s^4 \, e^{-ms^2/2k_BT}}_{I}$$

I is even so

$$2I = I + I = \int_0^\infty ds s^4 \cdots + \int_{-\infty}^0 ds s^4 \cdots$$

$$= \int_{-\infty}^\infty ds\, s^4 \, e^{-ms^2/2k_BT}$$

remember $\displaystyle\int_{-\infty}^\infty dx\, x^4 e^{-ax^2} = -\frac{d}{da}\left(\frac{\sqrt{\pi}}{2} a^{-3/2}\right)$

$$= +\tfrac{3}{2} \frac{\sqrt{\pi}}{2} a^{-5/2}$$

$$= \frac{3}{4}\sqrt{\pi}\, a^{-5/2}$$

so "a" $= \frac{m}{2k_BT}$

$$2I = \frac{3}{4}\sqrt{\pi}\left(\frac{2k_BT}{m}\right)^{5/2}$$

$$\langle s^2\rangle = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2} \cdot \frac{3}{8}\sqrt{\pi} \cdot \left(\frac{2k_BT}{m}\right)^{5/2}$$

$$= 3\pi \cdot \frac{k_BT}{m} \cdot \frac{\pi}{\pi} = 3\frac{k_BT}{m}$$

RMS speed $= \sqrt{3k_BT/m}$

15

$\boxed{15}$

iii) most probable speed, $\frac{dP(s)}{ds} = 0$

$$0 = \frac{d}{ds}\left(4\pi s^2 \cdot \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-ms^2/2k_BT}\right)$$

$$= \frac{d}{ds}\left(s^2 e^{-ms^2/2k_BT}\right)$$ (divide by const on both sides)

$$= s^2 \cdot \left(-\frac{m}{2k_BT}\frac{d}{ds}s^2\right)e^{-ms^2/2k_BT} + e^{-ms^2/2k_BT}\frac{d}{ds}(s^2)$$

$$= \underbrace{2s^3 \cdot \frac{-m}{2k_BT}}\, e^{-ms^2/2k_BT} + e^{-ms^2/2k_BT} \cdot 2s$$

move to other side & divide by $2se^{-ms^2/2k_BT}$

$$\Rightarrow s^2 \cdot \frac{m}{2k_BT} = 1$$

$$\Rightarrow s = \sqrt{2k_BT/m}$$

12

most probable

$$S_{\text{most prob}} = \sqrt{\cancel{2}/3} \cdot \sqrt{\langle s^2 \rangle}$$ (most prob is smaller)

3

$\boxed{15}$

3) a) for $N=3$, there are 8 configs

cfg	energy
000	0
100, 010, 001	μ
101	2μ
110, 011	$2\mu - J$
111	$3\mu - 2J$

16

b) Every box has 2 configs & all independent so # configs =

$$\underbrace{2 \times 2 \times \cdots \times 2}_{N} = \prod_{i=1}^{N} 2 = 2^N$$

4

20

c) $$Z = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \sum_{n_N=0}^{1} \exp\left(-\frac{1}{k_B T}\left[\sum_{i=1}^{N} \mu n_i - \sum_{i=1}^{N-1} J n_i n_{i+1}\right]\right)$$

d) Metropolis acceptance prob $= \min\left[1, \underbrace{\exp(-\beta \Delta E)}_{5}\right]$

i) $\Delta E = +\mu$ 5

ii) $\Delta E = -\mu + J$ 5

iii) $\Delta E = +\mu - J$ 5

$\boxed{60}$