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.

The test has 3 parts worth 200 points. *The test also has two bonus questions. Do not start these unless you have tried all the other problems!*

1. **Einstein's model for finding the heat-capacity of a crystal (50 points total + 50 bonus points)**. A famous problem in the early 1900's was to understand the low temperature behavior of the heat capacity of a solid. The first model for this was proposed by Einstein in 1906, and although it is not quite right, we can reproduce the Einstein model using what we know already from class.

   The model is: There are N atoms in the crystal bonded harmonically to their lattice site in 3D. Einstein supposed each of the 3N dimensions could be thought of as an *independent* and *distinguishable* quantum harmonic oscillator. The energy levels of a quantum harmonic oscillator are

$$E(n) = \hbar\omega(n + \frac{1}{2}), \text{with } n = 0, 1, ... \tag{1}$$

   (a) **Canonical ensemble** Let's find the heat capacity in the *Canonical* ensemble at temperature T (and $\beta = (k_B T)^{-1}$).

      i. Write the partition function for a single quantum harmonic oscillator (5 pts)

      ii. Perform the sum over states and find a simple expression in terms of a hyperbolic trig function, using info from the equation sheet (15 pts)

      iii. What is the partition function of the full Einstein crystal, in terms of the partition function of single quantum harmonic oscillator, and why (5 pts) [Hint: this should be a very simple answer]

iv. Show (10 pts) that the average energy of the Einstein crystal is

$$\langle E \rangle = \frac{3N\hbar\omega}{2} \frac{1}{\tanh(\frac{\beta\hbar\omega}{2})} \tag{2}$$

v. Show (15 pts) that the heat capacity of the Einstein crystal is

$$C_V = 3Nk_B \left(\frac{\beta\hbar\omega}{2}\right)^2 \frac{1}{\sinh^2(\frac{\beta\hbar\omega}{2})} \tag{3}$$

(b) **Bonus - Microcanonical ensemble. Only if you have time** Let's find the heat capacity in the *Microcanonical ensemble*. It turns out that the number of ways do distribute q quanta of energy into $N' = 3N$ oscillators is

$$\Omega(N', V, E) = \frac{(q + N' - 1)!}{q!(N' - 1)!} \tag{4}$$

and the total energy of the system is

$$E = \frac{3N\hbar\omega}{2} + q\hbar\omega = \frac{N'\hbar\omega}{2} + q\hbar\omega \tag{5}$$

i. Using the fact that $N' \gg 1$ and Sterling's approximation, find the simplest expression you can for the entropy of this system (10 pts).

ii. Compute the temperature from the entropy, using the fact that $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)$ and $\left(\frac{\partial S}{\partial E}\right) = \left(\frac{\partial S}{\partial q}\frac{\partial q}{\partial E}\right)$ and for this system $\frac{\partial q}{\partial E} = (\hbar\omega)^{-1}$. (15 pts)

iii. Solve for q as a function of T, showing that $q = \frac{N'}{e^{\beta\hbar\omega} - 1}$. (5 pts)

iv. Using this, find the energy as a function only of N and β (10 pts)

v. Using this function of the energy, find the heat capacity of the solid, which should agree with Eq. 3. (10 pts)

2. **Simulations (100 Points total)**.

(a) **Molecular dynamics**. Suppose you are simulating a particle in a harmonic oscillator in 1d, with mass 1 and spring constant 1, so that

$$H(q, p) = \frac{p^2}{2m} + \frac{kq^2}{2} = \frac{mv^2}{2} + \frac{q^2}{2} \tag{6}$$

i. Write Hamilton's equations of motion for this system and simplify (10 pts)

ii. Suppose $k = m = 1$ and initially, $q(0) = 1$ and $p(0) = 0$. Manually perform 2 iterations of the Velocity Verlet algorithm [Tuckerman Page 100], with time step $\Delta t = 0.1$, to find the position and momentum/velocity at times t=0.1 and 0.2. *Show all your steps, and underline your final values at these 2 times*. (25 pts)

iii. Sketch the potential, and explain why your new $q's$ and $v's$ make physical sense (10 pts).

(b) **Parallel Tempearutre Replica Exchange Simulation**. Suppose you can run simulations of this same classical Harmonic oscillator Hamiltonian at constant temperature. If you run simulation with $m = k = 1$ at 2 temperatures, $k_B T_1 = 1$ and $k_B T_2 = 2$, what is the acceptance rule for exchanging the following two configurations (20 pts):

i. $p_1 = 1, q_1 = 1$

ii. $p_2 = \sqrt{5}, q_2 = 1$

(c) **Monte Carlo Simulations**. Consider doing a Monte Carlo simulation of the Einstein model in the Canonical ensemble from Problem 1a. There are 3N independent oscillators which start with occupation numbers $(n_1, n_2, ..., n_{3N})$.

i. What is the Metropolis Acceptance Rule for changing the occupation number of an arbitrary site X from $n_X^{initial} \to n_X^{final}$? (15 pts)

ii. For every material, we can fit an "Einstein Temperature" $T_E = \hbar\omega/k_B$. For example, T_E(Li)=469.4 K and T_E(Na)=191.9 K. Compute the acceptance rate for *increasing* the occupation number of an arbitrary oscillator by one (i.e. $n_X \to n_X + 1$) at T=300K and T=77K for both lithium and sodium crystals [i.e. for 4 different cases] (20 pts).

3. **Experiment Directed Simulation (50 points total + 30 bonus points)**. In the seminar last week, Andrew White presented the Experiment Directed Simulation method, for incorporating data directly into molecular simulations. That work follows directly from what we learned in class.

Suppose our original simulation system has energy function $U(\vec{q})$, and $f(\vec{q})$ is an observable function we are interested in measuring from simulation. We do an experiment and find the correct value of $\langle f \rangle$ for our system is $\hat{f}$, which does not quite agree with what we measure from simulation.

Then there exists a λ^* such that $\langle f \rangle_{\lambda^*} = \hat{f}$, where

$$\langle f \rangle_\lambda = \frac{\int d\vec{q} f(\vec{q}) e^{-\beta U(\vec{q}) + \lambda f(\vec{q})}}{Z_\lambda} \tag{7}$$

and $Z_\lambda = \int d\vec{q} e^{-\beta U(\vec{q}) + \lambda f(\vec{q})}$.

(a) **Rule for learning unknown parameters.** We want to find the λ that minimizes the error in $\langle f \rangle_\lambda$. This is done by minimizing the observed squared error.

Show that (25 pts):

$$\frac{\partial}{\partial \lambda}(\langle f \rangle_\lambda - \hat{f})^2 = 2(\langle f \rangle_\lambda - \hat{f})\mathrm{Var}_\lambda(f) \tag{8}$$

In practice, λ is updated until the squared error is minimized, and $\lambda \to \lambda^*$.

(b) **Solving for λ where error is small**. If the error in $\langle f \rangle$ is small, then λ^* will be small. In this situation, it is possible to find an approximation for λ^* from an un-modified simulation ($\lambda = 0$).

Without loss of generality, assume $\hat{f} = 0$ (we can always define $g(\vec{q}) = f(\vec{q}) - \hat{f}$, such that $\hat{g} = 0$).

i. Start by assuming $0 = \hat{f} = \langle f \rangle_{\lambda^*}$. Using Eq. 7, expand the exponential for small λ^* to first order in λ^*, to show (15 pts)

$$\lambda^* = -\frac{\langle f \rangle_{\lambda=0}}{\langle f^2 \rangle_{\lambda=0}} \tag{9}$$

ii. What do you get if you now expand to second order in λ^* and solve for λ^*? (10 pts)

(c) **Bonus - Deriving the EDS probability density. Only if you have time (30 bonus pts)**. In the homework we showed you can derive the Boltzmann distribution by maximum entropy and Lagrange multipliers.

EDS is derived in the same way, but with distributions. Let $P_0(\vec{q})$ be the Boltzmann distribution (i.e. NVT-ensemble) and $P(\vec{q})$ is a new distribution where the average of f is $\hat{f}$.

We can define the relative entropy $S[P(\vec{q})] = -\int d\vec{q} P(\vec{q}) \ln\left(P(\vec{q})/P_0(\vec{q})\right)$ and set the constraints $\int d\vec{q} P(\vec{q}) = 1$ and $\int d\vec{q} P(\vec{q}) f(\vec{q}) = \hat{f}$.

Maximize S subject to these constraints over the family of distributions $P(\vec{q})$ and show that you get the distribution corresponding to Eq. 7.

To do this, you take the derivative with respect to the function $P(\vec{q})$, and you will just need to know the following facts:

i. If $f[g(x)] = \int dx g(x) h(x)$, then $\frac{\delta f}{\delta g(x)} = h(x)$.

ii. If $f[g(x)] = \int dx \ln(g(x)) g(x)$, then $\frac{\delta f}{\delta g(x)} = 1 + \ln(g(x))$.

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(1)(a)

(i) $q = \sum_{\epsilon} e^{-\beta \epsilon} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)}$

(ii) $q = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n = e^{-\beta\hbar\omega/2} \Big/ 1 - e^{-\beta\hbar\omega}$

$$= \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$$

(iii) $Q = q^{3N}$ (independent & distinguishable)

(iv) $$E = -\frac{\partial \log Q}{\partial \beta} = -3N \frac{\partial \log q}{\partial \beta} = 3N \frac{\partial \log \sinh(\beta\hbar\omega/2)}{\partial \beta}$$

$$= 3N \cdot \frac{1}{\sinh(\beta\hbar\omega/2)} \cdot \frac{\partial \sinh(\beta\hbar\omega/2)}{\partial \beta}$$

$$= \frac{3N\hbar\omega}{2} \frac{\cosh(\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)} = \frac{3N\hbar\omega}{2} \cdot \frac{1}{\tanh(\beta\hbar\omega/2)}$$

(v) $$C_V = \frac{\partial \mathcal{E}}{\partial T} = \frac{d\beta}{dT}\frac{\partial \mathcal{E}}{\partial \beta} = -\frac{1}{k_B T^2}\frac{\partial \mathcal{E}}{\partial \beta}$$

$$\frac{\partial \mathcal{E}}{\partial \beta} = \frac{3N\hbar\omega}{2}\frac{\partial}{\partial \beta}\left[\tanh\left(\frac{\beta\hbar\omega}{2}\right)\right]^{-1}$$

$$= -\frac{3N\hbar\omega}{2}\cdot\frac{1}{\tanh\left(\frac{\beta\hbar\omega}{2}\right)^2}\cdot \operatorname{sech}^2\left(\frac{\beta\hbar\omega}{2}\right)\cdot\frac{\hbar\omega}{2}$$

$$= -3N\left(\frac{\hbar\omega}{2}\right)^2\cdot\frac{1}{\sinh^2\left(\frac{\beta\hbar\omega}{2}\right)}$$

$$C_V = 3Nk_B\left(\frac{\beta\hbar\omega}{2}\right)^2\cdot\frac{1}{\sinh^2(\beta\hbar\omega/2)}$$ ✓

Bonus:

(b) $S = k_B \log \Omega(N', V, \mathcal{E})$

(i) $$= k_B \log\frac{[q+N'-1]!}{q!\,(N'-1)!} \approx k_B \log \frac{[q+N']!}{q!\,N'!} \quad \text{b/c } N' \gg 1$$

$$= k_B\log((q+N')!) - k_B \log q! - k_B \log N'!$$

this also assumes q is large

$$= k_B\left[(q+N')\log(q+N') - (\cancel{q+N'}) - q\log q + \cancel{q} - N'\log N' + \cancel{N'}\right]$$

$$= k_B\left[\left(q\log\left(\frac{q+N'}{q}\right) + N'\log\left(\frac{q+N'}{N'}\right)\right)\right]$$

$$= k_B\left[q\log\left(1+N'/q\right) + N'\log\left(q/N'+1\right)\right]$$

(ii) $\frac{1}{T} = \left(\frac{\partial S}{\partial \mathcal{E}}\right) = \left(\frac{\partial S}{\partial q}\right) \cdot \left(\frac{\partial \mathcal{E}}{\partial q}\right)^{-1} = \frac{1}{\hbar\omega} \frac{\partial S}{\partial q}$

$$\frac{\partial S}{\partial q} = k_B \left[q \cdot \frac{1}{1 + N'/q} \cdot - \frac{N'}{q^2} + \log(1 + N'/q) \right.$$

$$\left. + N' \cdot \frac{1}{q/N' + 1} \cdot \frac{1}{N'} \right] = k_B \log(1 + N'/q)$$

$$\frac{1}{T} = \frac{k_B}{\hbar\omega} \log(1 + N'/q)$$

$$\Rightarrow 1 + N'/q = e^{\beta\hbar\omega}$$

iii. $$\Rightarrow q = \frac{N'}{e^{\beta\hbar\omega} - 1}$$

iv. $$\mathcal{E} = \frac{3N\hbar\omega}{2} + \frac{3N\hbar\omega}{e^{\beta\hbar\omega} - 1}$$

v. $$C_V = -\frac{1}{k_B T^2} \frac{\partial \mathcal{E}}{\partial \beta} = -\frac{3N\hbar\omega}{k_B T^2} \cdot -1 \frac{\hbar\omega\, e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

$$= 3N \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

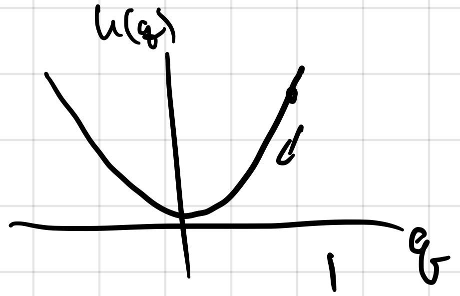
$$= 3N \left(\frac{\hbar\omega}{k_B T}\right)^2 \cdot \frac{1}{(e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2})}$$

$\sinh^2\left(\frac{\beta\hbar\omega}{2}\right)$

② (a) (i) $\dot{q} = \frac{\partial H}{\partial p} = p/m = v$

$$\dot{p} = -\frac{\partial H}{\partial q} = -kq \quad \text{(Hooke's law)}$$

(ii)



$q(0) = 1$

$p(0) = 0 = v$

$$F = -\frac{\partial H}{\partial q} = -q$$

Step 1 $q(0.1) = q(0) + 0.1 \cdot \underset{\text{velocity}}{0} + \frac{.01}{2} \cdot \underset{\text{force}}{(-1)}$

$= 1 - 0.005 = \underline{0.995}$

$f(0.1) = -q(0.1) = -0.995$

Step 2 $v(0.1) = \underbrace{v(0)}_{0} + \frac{.1}{2}(\underbrace{-1}_{f(0)} - 0.995)$

$= \underline{-0.09975}$

Step 3 $q(0.2) = q(0.1) + 0.1 v(0.1) + \frac{.01}{2} \cdot (-0.995)$

$= 0.995 + 0.1(-0.09975) + 0.005(-0.995)$

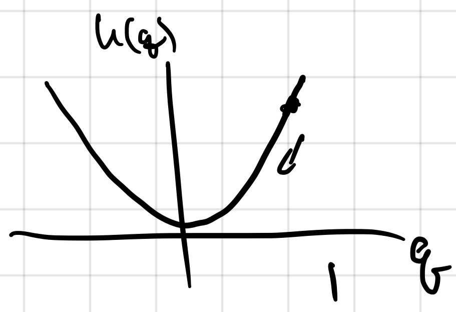
$= \underline{0.980}$

$f(0.2) = -0.980$

Step4: $v(0.2) = \underbrace{v(0.1)}_{-0.09975} + .05(-0.995 - 0.980)$

$$= -1.985$$

iii)



Makes sense, at max position, then position decreases, velocity increases (accelleration) force starts high & decreases

(b) Acceptance rate =

$$\min\left(1, \exp\left(\left(\frac{1}{kT_2} - \frac{1}{kT_1}\right)(\varepsilon_2 - \varepsilon_1)\right)\right)$$

$$\varepsilon_2 = p_2^2/2 + q_2^2/2 = \frac{5}{2} + 1/2 = 3$$

$$\varepsilon_1 = p_1^2/2 + q_1^2/2 = 1$$

$$\frac{1}{k_B T_2} - \frac{1}{k_B T_1} = \frac{1}{2} - 1 = -\frac{1}{2}$$

$$\text{rate} = \exp\left(-\frac{1}{2} \cdot 2\right) = \exp(-1) \approx 0.368$$

c) (i) rule =

$$\min(1, \exp(-\beta \Delta E))$$

$$\Delta E = \hbar\omega(n_x^{final} + \tfrac{1}{2}) - \hbar\omega(n_x^{init} + 1/2)$$

$$= \hbar\omega(n_x^{final} - n_x^{init})$$

$$\text{rule} = \min\left(1, \exp\left(-\frac{\hbar\omega}{k_B T}(n_x^{final} - n_x^{init})\right)\right)$$

ii) increasing by 1, $\Rightarrow$ $n_x^{final} - n_x^{initial} = 1$

$$\text{rate} = \exp\left(-\left(\frac{\hbar\omega}{k_B}\right) \cdot \frac{1}{T} \cdot (1)\right)$$

$$= \exp\left(-T_E/T\right)$$

	rate@ 300K		rate @ 77K	
Li	$e^{-469.4/300}$	$= 0.209$	$e^{-469.4/77}$	$= 0.002$
Na	$e^{-191.9/300}$	$= 0.529$	$e^{-191.9/77}$	$= 0.083$

(3) (a) $\mathcal{E}rror = (\langle f\rangle_\lambda - \hat{f})^2$

$$\frac{\partial \mathcal{E}rror}{\partial \lambda} = 2(\langle f\rangle_\lambda - \hat{f})\frac{\partial}{\partial\lambda}(\langle f\rangle_\lambda - \hat{f})$$

$$\frac{\partial}{\partial\lambda}(\langle f\rangle_\lambda - \hat{f}) = \frac{\partial}{\partial\lambda}\langle f\rangle_\lambda$$

$$\frac{\partial}{\partial\lambda}\langle f\rangle_\lambda = -\frac{1}{Z_\lambda^2}\frac{\partial Z_\lambda}{\partial\lambda}\cdot\int dq\, f(q) e^{-\beta u(q)+\lambda f(q)}$$

$$+\frac{1}{Z_\lambda}\int dq\, f(q)^2 e^{-\beta u(q)+\lambda f(q)}$$

$$\& \frac{\partial Z_\lambda}{\partial\lambda} = \int dq\, f(q) e^{-\beta u(q)+\lambda f(q)} = Z_\lambda \langle f\rangle_\lambda$$

$$\frac{\partial}{\partial\lambda}\langle f\rangle_\lambda = \langle f^2\rangle_\lambda - \langle f\rangle_\lambda^2 = \mathrm{Var}_\lambda(f)$$

so $$\frac{\partial \mathcal{E}rror}{\partial\lambda} = 2(\langle f\rangle_\lambda - \hat{f})\,\mathrm{Var}_\lambda(f) \checkmark$$

(b) Eq 7:

$$0 = \langle f \rangle_{\lambda^*} = \frac{\int d\vec{q}\, f(q)\, e^{-\beta u(q) + \lambda^* f(q)}}{Z_{\lambda^*}}$$

multiply by $Z^* > 0$ & expand

$$\Rightarrow 0 = \int d\vec{q}\, f(q)\, e^{-\beta u(q)} \left[1 + \lambda^* f(q) + \lambda^{*2}/2\, f^2(q) + \dots \right]$$

multiply by Z_0 / Z_0

$$\Rightarrow 0 = \langle f \rangle + \lambda^* \langle f^2 \rangle + \lambda^{*2}/2 \langle f^3 \rangle + \dots$$

@ first order

$$\lambda^* = -\langle f \rangle / \langle f^2 \rangle$$

[Note:

if $\langle f \rangle$ bigger than zero, $\lambda^* < 0$

so in eq 7, cfgs with $f(q) > 0$

have lower weight $[e^{\lambda f(q)} < 1]$

and the opposite is true for $\langle f \rangle < 0$]

at second order

$$0 = \langle f \rangle + \lambda^* \langle f^2 \rangle + \lambda^{*2}/_2 \langle f^3 \rangle$$

which can be solved by the quadratic formula

w/ $a = \langle f^3 \rangle/_2$ $b = \langle f^2 \rangle$ $c = \langle f \rangle$

$$\Rightarrow \lambda^* = \frac{-\langle f^2 \rangle \pm \sqrt{\langle f^2 \rangle^2 - 2\langle f^3 \rangle \langle f \rangle}}{\langle f^3 \rangle}$$

(c) $L = S - \lambda_1 \int dq\, P(q) - \lambda_2 \int dq\, P(q) f(q)$

$$\frac{\delta L}{\delta P(q)} = \frac{\delta S}{\delta P(q)} - \lambda_1 - \lambda_2 f(q) = 0$$

$$\frac{\delta S}{\delta P(q)} = \frac{\delta}{\delta P(q)} \left[\int dq \left[-P(q) \ln P(q) + P(q) \ln P_0(q) \right] \right]$$

$$= -\ln P(q) - 1 + \ln P_0(q)$$

$$\Rightarrow \ln P(q) = \ln P_0(q) - 1 - \lambda_1 - \lambda_2 f(q)$$

$$\Rightarrow P(q) = P_0(q)\, e^{-1-\lambda_1-\lambda_2 f(q)}$$

$$= e^{-\beta u(q)} \cdot \frac{1}{Z} e^{-1-\lambda_1} \; e^{-\lambda_2 f(q)}$$

$$\Rightarrow P(q) = \frac{e^{-\beta u(q) - \lambda_2 f(q)}}{Z_{\lambda_2}}$$

$$Z_{\lambda_2} = \int dq\, e^{-\beta u(q) - \lambda_2 f(q)}$$

let $\lambda_2 = \lambda$ & this matches eq 7