NYU CHEM GA 2600: Statistical Mechanics Midterm

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Instructions: This midterm is a take-home, and you can use whatever reference materials you want. However, you should work on the midterm yourself, and not with others in the class, so that I can assess each student's learning individually.

Also, please note that use of any resource that answers questions for you (e.g. Chegg) is definitely cheating. Please keep in mind that you are bound by NYU's honor policy (https://cas.nyu.edu/content/nyu-as/cas/academic-integrity.html).

Your solutions should be written out as cleanly as you can (on paper, or using a tablet) and then uploaded as a PDF to brightspace before 5PM NYC time on Friday, November 5.

1. **A little more lattice gas. (45 pts total)** In the last homework, you compute the energy for a lattice gas with N molecules on N_l lattice sites, each with volume v. This system is in the microcanonical ensemble, and N and N_l are big enough that you can use Sterling's approximation if needed.

   (a) What is the entropy of this system if any number of molecules are allowed to be on any lattice site and explain why (ideal gas, no volume exclusion) (15 pts).

   (b) Compute the pressure from this entropy. How does this formula connect to what you might expect? (10 pts)

   (c) Going back to the case of volume exclusion, compute the pressure from the entropy. Does this pressure contain a term that is like what you got in the previous case? It may not look like it, but expand your result in the limit of small density $\rho = N/V$ or $\rho = N/N_l$ to produce the equivalent of the virial expansion we had in class. What is the second virial coefficient in this case? (20 pts).

2. **Grand-canonical ensemble (50 pts total).** So far we have learned about the constant N, V, E ensemble and N, V, T ensemble. Here you will learn about the constant μ, V, T ensemble, where chemical potential is fixed instead of particle number.

(a) Sketch a system and bath where particles/molecules can flow between them, and the total N,V,E are conserved for the combined system (10 pts).

(b) Show for this ensemble that the weight of a given state is proportional to $e^{-\beta(E_{sys}-\mu N_{sys})}$. Do this in an analogous way to how we derived the Boltzmann weights, except this time Taylor expand the entropy simultaneously in terms of E and N (15 pts).

(c) Explain in words why the grand-canonical partition function is given by $\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{N_{tot}} \int d\vec{X} e^{-\beta(H(\vec{X})-\mu N)}$. What is the dimension of $\vec{X}$ here? (10 pts)

(d) Show why $\langle N \rangle = k_B T \frac{\partial \ln(\mathcal{Z})}{\partial \mu}$ (5 pts)

(e) Write a formula for the variance of N analogous to the one we derived for the variance of E in the canonical ensemble (10 pts)

3. **Three-state polymer model (55 pts).** A simple model for a polymer in solution is one where the angle between successive monomers can be in one of three states (analogous to trans, gauche+, gauche-). As in the figure, we can call these three options *straight (s)*, *left (l)*, *right (r)*, and each link has length l. Let the energy for each bend be equal to either $\epsilon_s = 0$, $\epsilon_l = \epsilon_r = \epsilon$. This system is at constant temperature (canonical ensemble).

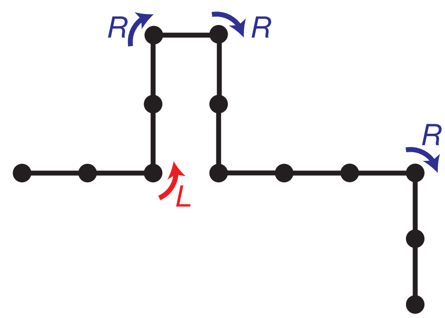


Figure 1: Example microstate of a three-state polymer model with $N = 13$, $N_r = 3$, $N_l = 1$.

(a) For a polymer with N monomers as in the cartoon, compute the partition function. Do this by writing the partition function for each bend separately and use the fact that all of the bends are independent (15 pts).

(b) Compute the average energy of the polymer (15 pts).

(c) Using the fact that the energy is connected to the number of bent links, write the average number of straight, left, and right links $\langle N_s \rangle$, $\langle N_r \rangle$, $\langle N_l \rangle$ (5 pts).

(d) Sketch a plot of how $\langle N_r \rangle$, and $\langle N_l \rangle$ depend on temperature, and show what the limiting value is at 0 and infinite temperature on the sketch (10 pts).

(e) Compute the heat capacity of this polymer (10 pts).

4. **Statistical mechanical perturbation theory (50 pts total).** Sometimes in statistical mechanics, we cannot exactly compute the partition function or sample easily for

our system which has Hamiltonian H. However, we can solve the problem for a similar Hamiltonian H_0. In this case, we can make a prediction for averages under our true Hamiltonian based on information from our 'easy' Hamiltonian. *For the canonical ensemble,* and observable O,

(a) Show that $\langle O(\vec{X})\rangle = \langle O(\vec{X})e^{-\beta(H(\vec{X})-H_0(\vec{X}))}\rangle_0 / \langle e^{-\beta(H(\vec{X})-H_0(\vec{X}))}\rangle_0$, where $\langle\cdot\rangle$ means an average with respect to H and $\langle\cdot\rangle_0$ means an average with respect to Hamiltonian H_0. (10 pts)

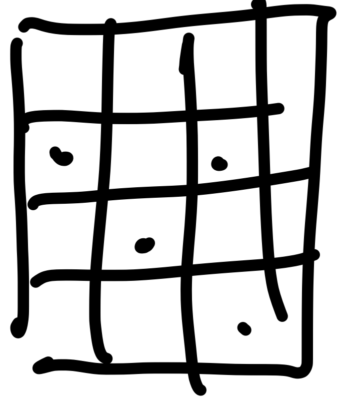
(b) Just as you may have seen in Quantum Mechanical perturbation theory, sometimes we can write $H(X) = H_0(X) + \lambda V(X)$ where λ is a constant. Similar to the previous item, show that $Z/Z_0 = \langle e^{-\beta\lambda V(X)}\rangle_0$, where Z and Z_0 are the partition functions with respect to H and H_0 respectively. (10 pts)

(c) Show that the difference in Helmholtz free energy between a system with Hamiltonian H and one with H_0 is $\Delta A = -k_B T \ln(\langle e^{-\beta\lambda V(X)}\rangle_0)$. (5 pts)

(d) Expanding the exponential for small λ and then using the Taylor series for $\ln(1+x)$ show that for small λ, $\Delta A \approx \lambda\langle V(X)\rangle_0 + \beta\lambda^2/2[\langle V(X)^2\rangle_0 - \langle V(X)\rangle_0^2]$. This is part of what is called a *cumulant expansion*. (15 pts)

(e) An alternative way to find the difference between the state with $\lambda = 0$ and $\lambda = 1$ is called *thermodynamic integration*. Note that Z for Hamiltonian H depends explicitly on λ. Show that $A(\lambda) = -k_B T \ln Z(\lambda)$ implies $\frac{\partial A(\lambda)}{\partial \lambda} = \langle V(X)\rangle_\lambda$. And that therefore $\Delta A = \int_0^1 \langle V(X)\rangle_\lambda d\lambda$. (10 pts)

①



$V = N_\ell \cdot v$

N molecules

a) if a molecule can be on any sites, then there are N_ℓ places for mc 1, N_ℓ for mc 2 · N_ℓ places for mc 3 . . . .

$\Rightarrow \# = N_\ell \cdot N_\ell \cdot \ldots N_\ell = N_\ell^N$

But! indistinguishable so $\Omega = N_\ell^N / N!$

$$S = k_B \ln \Omega = N k_B \ln N_\ell - k_B \ln N!$$

b) $S = N k_B \ln [V/v] - k_B \ln N!$

$= N k_B \ln V - N k_B \ln v - k_B \ln N!$

$$P/T = \left(\frac{\partial S}{\partial V}\right)_{N,E} = N k_B \cdot \frac{1}{V} \Rightarrow P = \frac{N k_B T}{V}$$

ideal gas law!

c) with volume exclusion

$$\Omega = \binom{N_\ell}{N} = \frac{N_\ell!}{N!\,(N_\ell - N)!}$$

$$S = k_B \ln \Omega \approx k_B \Big[N_\ell \ln N_\ell - \cancel{N_\ell} - N \ln N + \cancel{N} - (N_\ell - N)\ln(N_\ell - N) + \cancel{(N_\ell - N)} \Big]$$

$$= k_B \big[N_\ell \ln N_\ell - N \ln N - (N_\ell - N)\ln(N_\ell - N) \big]$$

$$P/T = \frac{\partial S}{\partial V} = \frac{1}{v}\frac{\partial S}{\partial N_\ell} = k_B \Big[\cancel{\frac{N_\ell}{N_\ell}} + 1 \cdot \ln N_\ell - \cancel{\frac{(N_\ell - N)}{(N_\ell - N)}} - 1 \cdot \ln(N_\ell - N) \Big]$$

$$\Rightarrow \frac{P v}{k_B T} = \ln\left[\frac{N_\ell}{N_\ell - N}\right] \Rightarrow \underline{P = \frac{k_B T}{v} \cdot \ln\left[\frac{N_\ell}{N_\ell - N}\right]}$$

but, we can expand this log, how?

$$P = \frac{k_B T}{v} \ln\left[\frac{N_\ell}{N_\ell - N}\right]$$

$$= -\frac{k_B T}{v} \ln\left[\frac{N_\ell - N}{N_\ell}\right] = -\frac{k_B T}{v} \ln\left[1 - \frac{N}{N_\ell}\right]$$

small

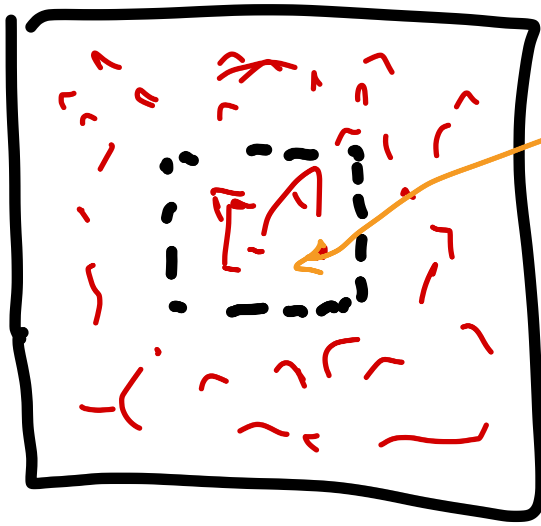
$$\approx -\frac{k_B T}{v}\left[-\frac{N}{N_\ell} - \frac{1}{2}\left(\frac{N}{N_\ell}\right)^2 - \frac{1}{3}\left(\frac{N}{N_\ell}\right)^3 \cdots\right]$$

$$= \frac{N k_B T}{V} + \frac{1}{2} k_B T v \left[\frac{N}{V}\right]^2 + \frac{1}{3} k_B T v^2 \left[\frac{N}{V}\right]^3 + \cdots$$

$$\beta P \approx \rho + \frac{1}{2} v \rho^2 + \cdots$$

second virial coefficent is $\frac{v}{2}$,
half the volume taken up by one molecule

2a)



U_{sys} const

$N_{tot}, V_{tot}, \mathcal{E}_{tot}$ const

b) $N_{tot} = N_{sys} + N_{bath}$

$\mathcal{E}_{tot} = \mathcal{E}_{sys} + \mathcal{E}_{bath}$

$$S_{bath}(N_{bath}, V_{bath}, \mathcal{E}_{bath})$$

$$\approx S_{bath}(N_{tot}, V_{bath}, \mathcal{E}_{tot})$$

$$+ \underbrace{(\mathcal{E}_{bath} - \mathcal{E}_{tot})}_{-\mathcal{E}_{sys}} \underbrace{\left(\frac{\partial S_{bath}}{\partial \mathcal{E}_{bath}}\right)_{N,V}}_{\frac{1}{T}}$$

$$+ \underbrace{(N_{bath} - N_{tot})}_{-N_{sys}} \underbrace{\left(\frac{\partial S_{bath}}{\partial N_{bath}}\right)_{V,\mathcal{E}}}_{-\frac{\mu}{T}}$$

+ higher order terms

so $S_{bath} \approx \text{const} - \frac{E_{sys}}{T} + \frac{\mu N_{sys}}{T}$

$\quad \| $

$k_B \ln \Omega_{bath}$

weigh of each state $\propto \Omega_{bath}$ so

weight $\propto e^{-E_{sys}/k_BT + \mu N_{sys}/k_BT} = e^{-\beta[E - \mu N]}$

c) The partition function is a sum over all state weights, the normalization constant for the probability dist.

Here, N_{sys} is discrete so we use a simple sum over all states [0 to N_{tot} so]

The integral is over all configurations of N particles. So $\vec{x}$ has dimension $6N$, different for each term in the Σ

Also $\mathcal{H}(x) = E_{sys}$

d) $\langle N \rangle = \sum_N \int d\vec{x}_{\substack{\uparrow \\ \text{dim } 6N}} \; N \; P(\vec{x})$

$$= \sum_N \int d\vec{x} \, N \, e^{-\beta(\mathcal{H}(x) - \mu N)} / Z$$

$$\frac{\partial \ln Z}{\partial \mu} = \sum_N \int d\vec{x} \, \beta N \, e^{-\beta(\mathcal{H}(x) - \mu N)} / Z$$

so $\langle N \rangle = k_B T \dfrac{\partial \ln Z}{\partial \mu}$

c) $\mathrm{Var}\, N = \langle N^2 \rangle - \langle N \rangle^2$

$\partial \ln Z / \partial \mu$ has 3 terms that depend on N (including Z)

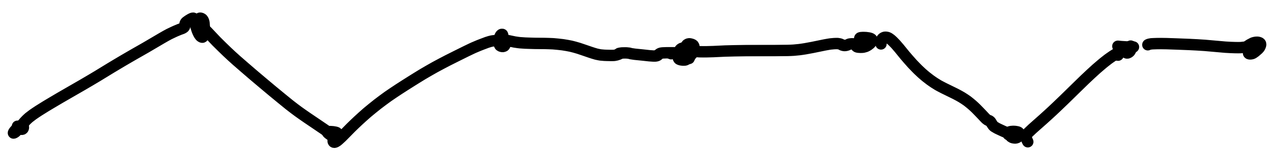
$$\frac{\partial \ln Z}{\partial \mu} = \sum_N \int d\vec{x} \, \beta N e^{-\beta(\mathcal{H}(x) - \mu N)} / Z$$

$$\frac{\partial^2 \ln Z}{\partial \mu^2} = \frac{Z \sum_N \int d\vec{x} \, \beta^2 N^2 e^{-\beta(\mathcal{H}(x) - \mu N)} - \sum_N \int dx \, \beta N e^{-\beta(\mathcal{H}(x) - \mu N)} \cdot \sum_N \int dx \, \beta N \cdots}{Z^2}$$

so $$\frac{\partial^2 \ln Z}{\partial \mu^2} = \langle \beta^2 N^2 \rangle - \langle \beta N \rangle^2$$
$$= \beta^2 \left(\langle N^2 \rangle - \langle N \rangle^2 \right)$$
$$= \beta^2 \, \mathrm{Var}(N)$$

$$\mathrm{Var}(N) = (k_B T)^2 \frac{\partial^2 \ln Z}{\partial \mu^2}$$

3a)



N monomers $\rightarrow$ $N-1$ independent links

$\rightarrow$ $N-2$ independent bends

$$Z = Z_0^{(N-2)}$$

$$Z_0 = \sum_{i=1}^{3} e^{-\beta \epsilon_i} = 1 + e^{-\beta \epsilon_L} + e^{-\beta \epsilon_R}$$
$$= 1 + 2e^{-\beta \epsilon}$$

$$Z = \left(1 + 2e^{-\beta \epsilon}\right)^{(N-2)}$$

b) $\langle E \rangle = -\dfrac{\partial \ln Z}{\partial \beta}$

$$= -(N-2) \cdot \frac{1}{1+2e^{-\beta\epsilon}} \cdot -2\epsilon e^{-\beta\epsilon}$$

$$= (N-2) \cdot 2\epsilon \cdot \frac{e^{-\beta\epsilon}}{1+2e^{-\beta\epsilon}}$$

c) $E = (N_L + N_R) \cdot \epsilon$

$$\langle E \rangle = \langle N_L + N_R \rangle \cdot \epsilon$$

$$= 2\langle N_L \rangle \epsilon \text{ or } 2\langle N_R \rangle \epsilon$$

by symmetry

So $\langle N_L \rangle = \langle N_R \rangle = (N-2) \dfrac{e^{-\beta\epsilon}}{1+2e^{-\beta\epsilon}}$

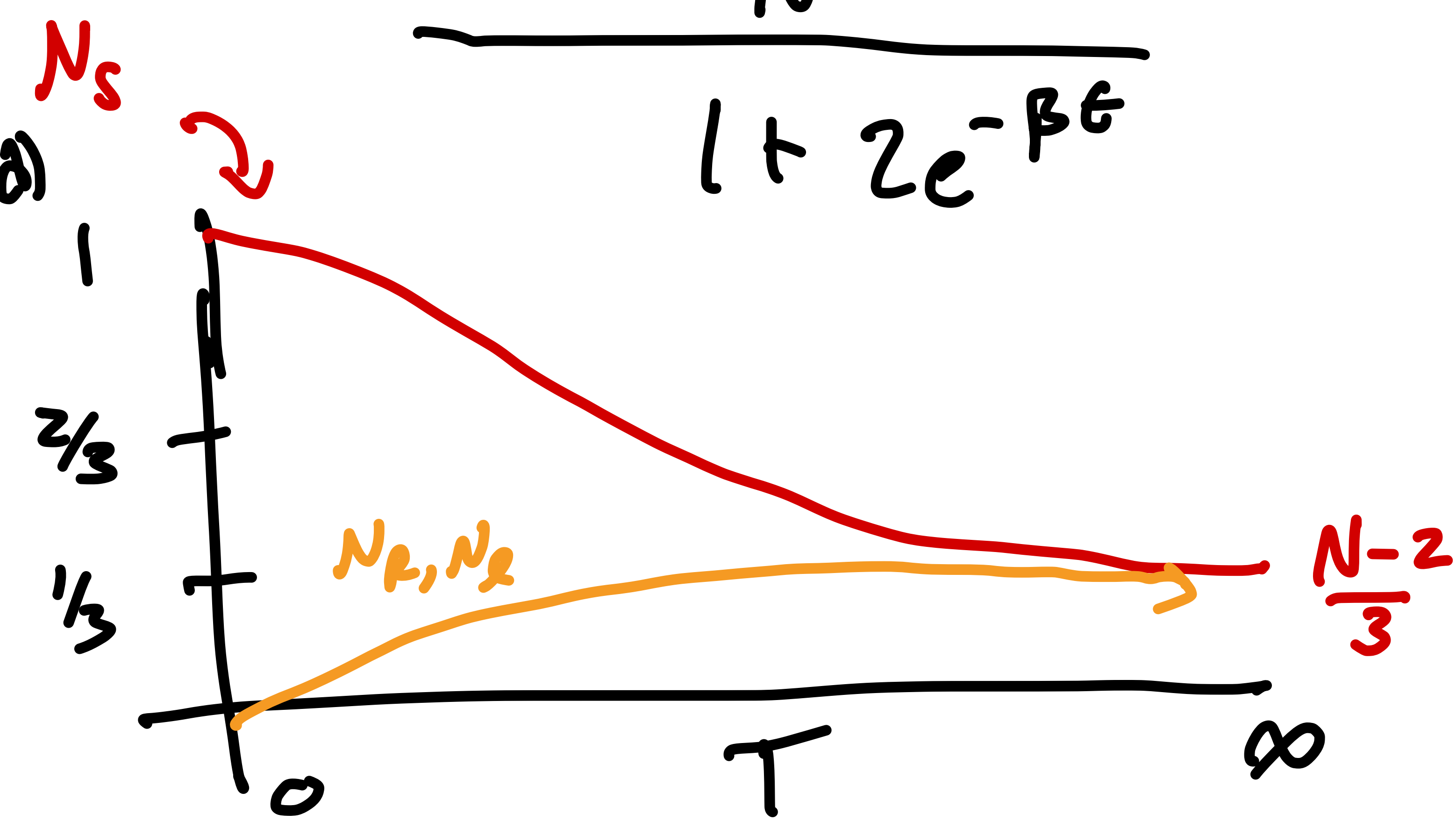
$$\langle N_S \rangle = N - \langle N_L \rangle - \langle N_R \rangle$$

$$= (N-2) - \frac{2(N-2)\, e^{-\beta\epsilon}}{1+2e^{-\beta\epsilon}}$$

$$= \frac{(N-2)\left(1+2e^{-\beta\epsilon}\right) - 2(N-2)\,e^{-\beta\epsilon}}{1+2e^{-\beta\epsilon}}$$

$$= \frac{N-2}{1+2e^{-\beta\epsilon}}$$

d)



e) $C_v = -k_B \beta^2 \frac{\partial E}{\partial \beta}$

$$E = (N-2) \cdot 2\epsilon \cdot \frac{e^{-\beta\epsilon}}{1+2e^{-\beta\epsilon}}$$

$$\partial E/\partial \beta = (N-2) \cdot 2\epsilon \cdot \frac{\left[(1+2e^{-\beta\epsilon}) \cdot (-\epsilon e^{-\beta\epsilon}) - e^{-\beta\epsilon}(-2\epsilon e^{-\beta\epsilon})\right]}{(1+2e^{-\beta\epsilon})^2}$$

$$= 2(N-2)\epsilon^2 \frac{\left[-e^{-\beta\epsilon} - 2e^{-2\beta\epsilon} + 2e^{-2\beta\epsilon}\right]}{(1+2e^{-\beta\epsilon})^2}$$

$$C_v = 2k_B \beta^2 \epsilon^2 (N-2) \frac{e^{-\beta\epsilon}}{(1+2e^{-\beta\epsilon})^2} \qquad \times \frac{e^{2\beta\epsilon}}{e^{2\beta\epsilon}}$$

or $= 2k_B \beta^2 \epsilon^2 (N-2) \cdot \frac{e^{+\beta\epsilon}}{(e^{2\beta\epsilon}+2)^2}$

4 a)

Note: $1 = e^{-\beta \mathcal{H}_0(x)} e^{+\beta \mathcal{H}_0(x)}$

$$\langle O \rangle = \frac{\int dx\, O(x)\, e^{-\beta \mathcal{H}(x)}}{\int dx\, e^{-\beta \mathcal{H}(x)}} \qquad \frac{e^{\beta \mathcal{H}(x)} \cdot e^{-\beta \mathcal{H}_0(x)} \Big/ \int dx\, e^{-\beta \mathcal{H}_0(x)}}{e^{\beta \mathcal{H}(x)}\, e^{-\beta \mathcal{H}_0(x)} \Big/ \int dx\, e^{-\beta \mathcal{H}_0(x)}}$$

$$= \frac{\int dx \left[O(x)\, e^{-\beta[H - H_0]}\right] e^{-\beta \mathcal{H}_0(x)} \Big/ \int dx\, e^{-\beta \mathcal{H}_0(x)}}{\int dx \left(e^{-\beta[H - H_0]}\right) e^{-\beta \mathcal{H}_0(x)} \Big/ \int dx\, e^{-\beta \mathcal{H}_0(x)}}$$

$$= \left\langle O e^{-\beta(H - H_0)} \right\rangle_0 \Big/ \left\langle e^{-\beta(H - H_0)} \right\rangle_0$$

b) $$Z/Z_0 = \frac{\int dx\, e^{-\beta \mathcal{H}(x)}}{\int dx\, e^{-\beta \mathcal{H}_0(x)}}$$

$\mathcal{H} = \mathcal{H}_0 + \lambda V$

$$= \frac{\int dx\, e^{-\beta[H_0 + \lambda V]}}{\int dx\, e^{-\beta H_0}}$$

$$= \int dx\, e^{-\beta\lambda V(x)} \cdot \frac{e^{-\beta \mathcal{H}_0(x)}}{Z_0}$$

$$= \left\langle e^{-\beta\lambda V(x)} \right\rangle_0$$

✓

c) $$A - A_0 = -k_B T \ln Z - (-k_B T \ln Z_0)$$

$$= -k_B T \ln (Z/Z_0)$$

$$= -k_B T \ln \left\langle e^{-\beta\lambda V} \right\rangle_0$$

✓

$$\Delta A = -k_BT \ln \langle e^{-\beta\lambda V}\rangle_0$$

$$\approx -k_BT \ln \left(\left\langle 1-\beta\lambda V + \frac{\beta^2\lambda^2V^2}{2} + \cdots \right\rangle_0\right)$$

$$= -k_BT\ln\left[1+\left\langle -\beta\lambda V+\frac{\beta^2\lambda^2V^2}{2}+\cdots\right\rangle_0\right]$$

$$\ln(1+x)\approx x - \frac{x^2}{2}+\frac{x^3}{3}\cdots$$

$$\approx -k_BT\Big[\left\langle -\beta\lambda V + \frac{\beta^2\lambda^2V^2}{2}+\cdots\right\rangle_0$$
$$- \left\langle -\beta\lambda V + \frac{\beta^2\lambda^2V^2}{2}+\cdots\right\rangle_0^2 + \cdots\Big]$$

$$\approx +k_BT\left(\beta\lambda\langle V\rangle_0 - \frac{\beta^2\lambda^2}{2}\langle V^2\rangle_0 + \frac{\beta^2\lambda^2\langle V^2\rangle_0}{2} + O(\lambda^3)\right)$$

note, typo in question

$$= \lambda\langle V\rangle_0 - \frac{\beta\lambda^2}{2}\left[\langle V^2\rangle_0 - \langle V^2\rangle_0\right] + O(\lambda^3)$$

e) $A(\lambda) = -k_B T \ln Z(\lambda)$

$$= -k_B T \ln \int dx\, e^{-\beta \mathcal{H}_0 - \beta \lambda V(x)}$$

$$\frac{\partial A}{\partial \lambda} = -k_B T \cdot \frac{\int dx\, (-\beta V(x)) e^{-\beta \mathcal{H}_0 - \beta \lambda V(x)}}{\int dx\, e^{-\beta \mathcal{H}_0 - \beta \lambda V(x)}}$$

$$= \int dx\, V(x) e^{-\beta \mathcal{H}(x,\lambda)} \Big/ Z(\lambda)$$

$$= \langle V(x) \rangle_\lambda$$

so $A_1 - A_0 = \int_0^1 \frac{\partial A}{\partial \lambda} d\lambda$

$$= \int_0^1 \langle V(x) \rangle_\lambda \, d\lambda \quad \checkmark$$