Advanced Statistical Mechanics: Assignment #1

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Aditya Vijaykumar

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Problem 1

Part (a)
Given that

$$\begin{aligned}
X &= \frac{\sum_{i=1}^N X_i}{\sigma\sqrt{N}} \\
\langle X \rangle &= \frac{\sum_{i=1}^N \langle X_i \rangle}{\sigma\sqrt{N}} = \frac{\sum_{i=1}^N 0}{\sigma\sqrt{N}} = 0 \\
\sqrt{\langle X^2 \rangle} &= \frac{\sqrt{\sum_{i=1}^N \sum_{j=1}^N \langle X_i X_j \rangle}}{\sigma\sqrt{N}} \\
&= \frac{\sqrt{\sum_{i=1}^N \sum_{j=1}^N \langle X_i^2 \rangle \delta_{ij}}}{\sigma\sqrt{N}} \Longleftarrow \quad \text{independent variables, hence covariance is zero} \\
&= \frac{\sqrt{\sum_{i=1}^N \sigma^2}}{\sigma\sqrt{N}} \\
\sigma_X &= \frac{\sqrt{N\sigma^2}}{\sigma\sqrt{N}} = 1
\end{aligned}$$

Part (b)
Let $x, y-x, 1-y$ be the lengths of the 3 sticks after breaking. Triangle inequality gives us the following conditions on the stick,

$$\begin{aligned}
x < 1-x &\implies x < \frac{1}{2} \\
y-x < x+1-y &\implies y-x > \frac{1}{2} \\
1-y < y &\implies y > \frac{1}{2}
\end{aligned}$$

In the unit square of the $x-y$ plane, we need to find the intersection of the above regions. The first and last regions have an intersection of are$\frac{1}{4}$ in the plane, and the second region automatically includes this intersection. Hence the required probability is $\frac{1}{4}$.
Part (c)
The histograms are plotted below,
Part (d)
In our case, in time interval dt, the walker can go left with probability αdt, right with probability αdt and

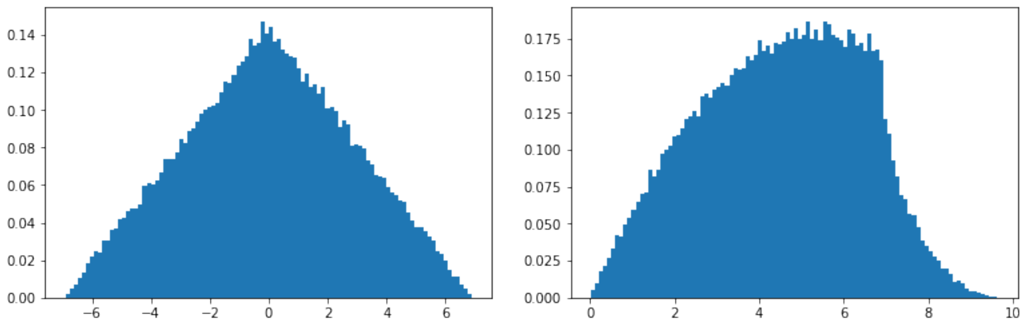

Figure 1: L : Trace Distribution, R: Eigenvalue Spacing Distribution for Uniform case

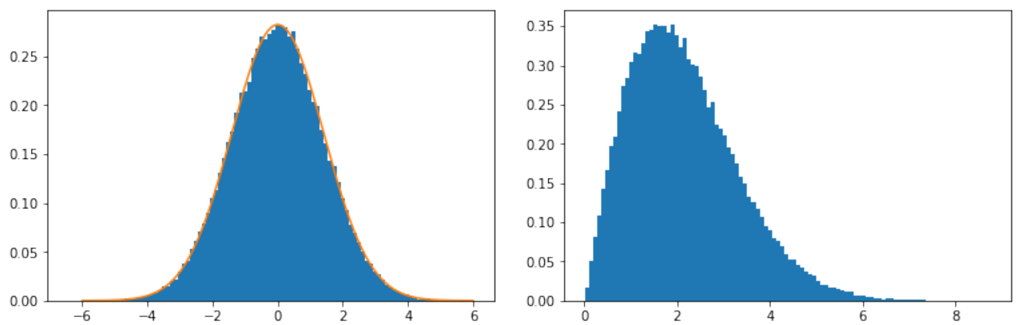

Figure 2: L : Trace Distribution, R: Eigenvalue Spacing Distribution for Normal case

can stay at the same position with probability $1 - 2\alpha dt$. So then, at position i and time $t + dt$,

$$
\begin{aligned}
P(i, t + dt) &= P(i, t)(1 - 2\alpha dt) + (P(i + 1, t) + P(i - 1, t))\alpha dt \\
\frac{\partial P(i, t)}{\partial t} &= -2P(i, t)\alpha + (P(i + 1, t) + P(i - 1, t))\alpha
\end{aligned}
$$

We solve the above equation by writing down the Fourier series. Every step away from ith site will introduce factors of e^{jk} in the Fourier space,

$$
\frac{\partial P(k, t)}{\partial t} = (-2\alpha + e^{jk} + e^{-jk})P(k, t)
$$

We know that $P(x, t = 0) = \delta_{x,0} \implies P(k, t = 0) = 1$ and then the solution to the above equation is,

$$
\begin{aligned}
P(k, t) &= e^{(-2\alpha + e^{jk} + e^{-jk})t} \\
&= e^{-2\alpha t} \sum_{x=-\infty}^{\infty} e^{2jkx \cos k} \\
P(k, t) &= e^{-2\alpha t} \sum_{x=-\infty}^{\infty} e^{2jkx} I_x(t)
\end{aligned}
$$

From which we can see by inverse Fourier, $P(x, t) = e^{-2\alpha t} I_x(t)$, where $I_x(t)$ is the Bessel function of the first kind.

Part (e)

Let's say the random walker takes x steps rightward and y steps leftward. For this walker to be at r after

N steps, $x + y = N$ and $x - y = r \implies x = \dfrac{N+r}{2}$ and $y = \dfrac{N-r}{2}$. The probability $P(r,N)$ is then,

$$\begin{aligned}P(r,N) &= \binom{N}{r}\frac{1}{2^x}\frac{1}{2^y}\\ &= \binom{N}{x}\frac{1}{2^N}\end{aligned}$$

For very large N,

$$\begin{aligned}\binom{n}{x} = \frac{N!}{x!y!} &= \frac{N!}{\left(\dfrac{N+r}{2}\right)!\left(\dfrac{N-r}{2}\right)!}\\ &= \frac{e^{-N}N^N}{(N+r)^{(N+r)/2}(N-r)^{(N-r)/2}2^{-N}e^{-N}}\\ &= \frac{N^N}{(1+r/N)^{(N+r)/2}(1-r/N)^{(N-r)/2}2^{-N}N^N}\\ P(r,N) &= \frac{1}{(1+r/N)^{(N+r)/2}(1-r/N)^{(N-r)/2}}\\ P(r,N) &= [(1+r/N)^{(1+r/N)}(1-r/N)^{(1-r/N)}]^{-N/2}\end{aligned}$$

Comparing with the form $P(r,N) = e^{-N\phi(r/N)}$, we get,

$$\phi(x) = \frac{(1+x)\ln(1+x) + (1-x)\ln(1-x)}{2}$$

Problem 2

Part (a)

For constant number of particles,

$$dU = -PdV + TdS + hdM$$

The enthalpy E is defined as $E = U + PV$,

$$\begin{aligned}dE &= dU + PdV + VdP = -PdV + TdS + hdM + PdV + VdP\\ &= TdS + hdM + VdP\end{aligned}$$

The Helmholtz Potential A is defined as $A = U - TS$,

$$\begin{aligned}dA &= dU - TdS - SdT = -PdV + TdS + hdM - TdS - SdT\\ &= -PdV + hdM - SdT\end{aligned}$$

The Gibbs Potential $G = E - TS$,

$$\begin{aligned}dG &= TdS + hdM + VdP - TdS - SdT\\ &= hdM + VdP - SdT\end{aligned}$$

As all the quantities are related by Legendre Transforms, knowledge of one of the quantities is enough to calculate all the others.

Part (b)

C_x and κ_x are defined as follows,

$$C_x = \left.\frac{\mathrm{d}Q}{\mathrm{d}T}\right|_{x=const.} \qquad \kappa_x = -\left.\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P}\right|_{x=const.}$$

Consider the following,

$$C_P = T\left.\frac{\mathrm{d}S}{\mathrm{d}T}\right|_{P=const} = -T\frac{\partial^2 G}{\partial T^2} \implies \frac{\partial^2 G}{\partial T^2} < 0 \implies G(T) \text{ is concave}$$
$$C_V = T\left.\frac{\mathrm{d}S}{\mathrm{d}T}\right|_{V=const} = -T\frac{\partial^2 A}{\partial T^2} \implies \frac{\partial^2 A}{\partial T^2} < 0 \implies A(T) \text{ is concave}$$
$$\kappa_T = -\left.\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P}\right|_{T=const.} = -\frac{1}{V}\frac{\partial^2 G}{\partial P^2} \implies \frac{\partial^2 G}{\partial P^2} < 0 \implies G(P) \text{ is concave}$$
$$\kappa_T = -\left.\frac{1}{V}\frac{\mathrm{d}V}{\mathrm{d}P}\right|_{T=const.} = \frac{1}{V}\frac{1}{\frac{\partial^2 A}{\partial V^2}} \implies \frac{\partial^2 A}{\partial V^2} > 0 \implies A(V) \text{ is convex}$$

Problem 3

Given $S_{Gibbs} = -\sum_a p_\alpha \log p_\alpha$, which we have to maximize under $\sum_\alpha p_\alpha = 1$. We use the method of Lagrange multipliers, $f(p_\alpha) = -\sum_a p_\alpha \log p_\alpha + \lambda(\sum_\alpha p_\alpha - 1)$,

$$\frac{\mathrm{d}f}{\mathrm{d}p_\gamma} = -\log p_\gamma - 1 + \lambda = 0$$
$$\implies \lambda = 1 + \log p_\gamma \implies p_\gamma = constant = \frac{1}{N}$$

where N is the number of microstates. Hence, we have shown that the all microstates are equally likely in microcanonical ensemble.
Similarly, we proceed to carry out the calculation for canonical ensemble and grand canonical ensemble. In this case, $f(p_\alpha) = -\sum_a p_\alpha \log p_\alpha + \lambda_1(\sum_\alpha p_\alpha - 1) + \lambda_2(\sum_\alpha p_\alpha E_\alpha - \langle E\rangle)$,

$$\frac{\mathrm{d}f}{\mathrm{d}p_\gamma} = -\log p_\gamma - 1 + \lambda_1 + \lambda_2 E_\gamma = 0$$
$$\implies p_\gamma = \exp(\lambda_1 - 1)\exp(\lambda_2 E_\gamma)$$

which is the expression for probability in the canonical ensemble *ie.* some normalization times $\exp(\beta E_\gamma)$.
For the grand canonical ensemble, $f(p_\alpha) = -\sum_a p_\alpha \log p_\alpha + \lambda_1(\sum_\alpha p_\alpha - 1) + \lambda_2(\sum_\alpha p_\alpha E_\alpha - \langle E\rangle) + \lambda_3(\sum_\alpha N_\alpha p_\alpha - \langle N\rangle)$,

$$\frac{\mathrm{d}f}{\mathrm{d}p_\gamma} = -\log p_\gamma - 1 + \lambda_1 + \lambda_2 E_\gamma + \lambda_3 N_\gamma = 0$$
$$\implies p_\gamma = \exp(\lambda_1 - 1)\exp(\lambda_2 E_\gamma + \lambda_3 N_\gamma)$$

which is the expression for probability in the canonical ensemble *ie.* some normalization times $\exp(\beta E_\gamma + \mu N_\gamma)$.
Part (b)
We first write down the partition function for a classical ideal gas,

$$Z = \frac{1}{h^{3N}N!}\prod_{i=1}^{N}\int d^3q_i d^3p_i \exp\left(-\beta p_i^2/2m\right)$$
$$= \frac{1}{h^{3N}N!}\prod_{i=1}^{N} V\left(\frac{2\pi m}{\beta}\right)^{3/2}$$
$$= \frac{V^N}{h^{3N}N!}\left(\frac{2\pi m}{\beta}\right)^{3N/2}$$

Problem 3 continued on next page. . .

So then, the probability is given by,

$$
\begin{aligned}
P(N=N) &= \sum_{\epsilon_i} \frac{e^{\beta\mu N} e^{-\beta\epsilon_i}}{Z} \\
&= \frac{e^{\beta\mu N}}{e^{\langle N\rangle}} \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \\
&= \frac{e^{-\langle N\rangle}\langle N\rangle^N}{N!}
\end{aligned}
$$

Problem 4

$$
\begin{aligned}
f_\nu(z) &= \frac{1}{\Gamma(\nu)}\int_0^\infty \mathrm{d}x \frac{x^{\nu-1}}{z^{-1}e^x+1} \\
&= \frac{1}{\Gamma(\nu)}\left[\frac{x^\nu}{\nu(z^{-1}e^x+1)}\bigg|_0^\infty - \int_0^\infty \mathrm{d}x\frac{x^\nu}{\nu}\frac{\mathrm{d}z^{-1}e^x+1}{\mathrm{d}x}\right] \\
&= -\frac{1}{\Gamma(\nu+1)}\left[\mathrm{d}x x^\nu \frac{\mathrm{d}z^{-1}e^x+1}{\mathrm{d}x}\right]
\end{aligned}
$$

We change the variables to $x = \ln z + t$ and get,

$$
\begin{aligned}
f_\nu(z) &\approx -\frac{1}{\Gamma(\nu+1)}\int_{-\infty}^{\infty} dt(\ln z+t)^\nu \frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{z^{-1}ze^t+1}\right) \\
&\approx -\frac{1}{\Gamma(\nu+1)}\int_{-\infty}^{\infty} dt\sum_m \frac{\nu!}{m!(\nu-m)!}t^m(\ln z)^{\nu-m}\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{1}{e^t+1}\right) \\
&\approx \frac{1}{\Gamma(|\nu-m|+1)}\int_{-\infty}^{\infty} dt\sum_m (\beta\mu)^{\nu-m} I_m
\end{aligned}
$$

Part (b)

$$
\begin{aligned}
N &= \frac{V}{\lambda^3} f_{3/2} \\
&= \frac{V}{\lambda^3}\left(\frac{(\beta\mu)^{3/2}}{\Gamma(5/2)} + \left(\frac{(\beta\mu)^{-1/2}}{\Gamma(3/2)}2f_2^-(1)\right)\right) \\
&= \frac{V\beta^{-3/2}}{(2\pi m)^{-3/2}}\left(\frac{4\mu^3/2}{3} + 4\mu^{-1/2}\beta^2 f_2^-(1)\right) \\
&= \frac{4V\mu^{3/2}}{3\pi(2m\pi)^{3/2}} + \frac{4V\mu^{-1/2}\beta f_2(1)}{\pi(2m\pi)^{3/2}}
\end{aligned}
$$

$$
\begin{aligned}
E &= \frac{3V(\beta)^{-5/2}}{2\lambda^3} f_{5/2}(z) \\
&= \frac{3V\beta^{-5/2}}{2(2\pi m)^{-3/2}}\left[\frac{(\beta\mu)^{5/2}}{\Gamma(7/2)} + \frac{(\beta\mu)^{1/2}}{\Gamma(3/2)}(2f_2^-(1))\right] \\
&= \frac{3V}{2(2\pi m)^{-3/2}}\left[\frac{(\mu)^{5/2}}{\Gamma(7/2)} + \frac{(\beta)^{-2}(\mu)^{1/2}}{\Gamma(3/2)}(2f_2^-(1))\right] \\
C_V &= \lim_{T\to 0}\frac{\partial E}{\partial T} = \frac{3V\mu^{1/2}(2\pi m)^{3/2}}{\Gamma(3/2)}k_B^2 T
\end{aligned}
$$

Problem 5

Part (b)
We are given,

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N-1} u(x_i - x_{i-1}) + v(x_1) + v(x_N)$$

One can write the expression of the partition function as follows,

$$\begin{aligned} Z &= \frac{1}{N!} \prod_i^N \int\int \frac{\mathrm{d}p_i \,\mathrm{d}x_i}{h} \exp(-\beta H_N) \\ &= \frac{1}{N! h^N} \prod_i^N \int \mathrm{d}p_i \exp\!\left(-\beta p_i^2/2m\right) \prod_i \int \mathrm{d}x_i \exp\left(-\beta \sum_{i=1}^{N-1} u(x_i - x_{i-1})\right) \\ &= \frac{1}{N! h^N} \left(\frac{2\pi m}{\beta}\right)^{N/2} \prod_i \int \mathrm{d}x_i \exp\left(-\beta \sum_{i=1}^{N-1} u(x_i - x_{i-1})\right) \end{aligned}$$

Consider,

$$\begin{aligned} \prod_i \int \mathrm{d}x_i \exp\left(-\beta \sum_{i=1}^{N-1} u(x_i - x_{i-1})\right) &= \prod_{i\neq 1} \int \mathrm{d}x_i \exp\left(-\beta \sum_{i=1}^{N-1} u(x_i - x_{i-1}) + v(x_i)\right) \int_{-\infty}^{\infty} \mathrm{d}x_1 e^{-\beta u(x_2 - x_1) + v(x_1)} \\ &= \prod_{i\neq 1} \int \mathrm{d}x_i \exp\left(-\beta \sum_{i=1}^{N-1} u(x_i - x_{i-1}) + v(x_i)\right) \int_{a/2}^{x_2 - a} \mathrm{d}x_1 \\ &= \prod_{i\neq 1} \int \mathrm{d}x_i \exp\left(-\beta \sum_{i=1}^{N-1} u(x_i - x_{i-1}) + v(x_i)\right) (x_2 - 1.5a) \end{aligned}$$

We have done one integral, and we now similarly separate out integrals over the other x_i's. The constant terms will integrate to zero, while the terms involving x_i's can be simply integrated as power functions. After N integrals, one will be left with,

$$\begin{aligned} &\int_{(N-a/2)}^{L-a/2} \mathrm{d}x_N \frac{1}{(N-1)!} \exp(\beta u(x_N - x_{N-1}) - \beta v(x_N)) \left(x_N - \frac{N-1}{2} a\right)^{N-1} \\ &\qquad = \int_{(N-a/2)}^{L-a/2} \mathrm{d}x_N \frac{1}{(N-1)!} (x_N - (N-0.5)a)^{N-1} \\ &\qquad = \frac{1}{N!} \left(L - \frac{a}{2} - Na + \frac{a}{2}\right)^N \\ &\qquad = \frac{1}{N!} (L - Na)^N \end{aligned}$$

Hence, the full partition function of the problem, $Z_N = \dfrac{1}{\lambda^N N!^2} (L - Na)^N$
Now that we have the partition function, $A = -k_B T \log Z_N$,

$$\begin{aligned} \therefore P = -\frac{\partial A}{\partial L} &= \frac{k_B T}{Z_N} \frac{\partial Z_N}{\partial L} \\ &= \frac{N k_B T}{L - Na} \\ &= \frac{n k_B T}{1 - na} \end{aligned}$$

where $n = \dfrac{N}{L}$.

Problem 6

A s-particle density is defined as,

$$f_s(\forall \vec{\mathbf{p}}_i, \forall \vec{\mathbf{q}}_i, t) = \frac{N!}{(N-s)!} \int \prod_{i=x+1}^{N} \mathrm{d}V_i \rho(\vec{\mathbf{p}}, \vec{\mathbf{q}}, t$$

Now one needs to use the defined s-particle density with the Hamiltonian of the form,

$$\begin{aligned}
H &= \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + U(\vec{\mathbf{q}}_\mathbf{i}) \right] + \sum_{i,j=1}^{N} \frac{1}{2} V(\vec{\mathbf{q}}_i - \vec{\mathbf{q}}_j) \\
&= \left[\sum_{i=1}^{s} \left[\frac{p_i^2}{2m} + U(\vec{\mathbf{q}}_\mathbf{i}) \right] + \sum_{i,j=1}^{s} \frac{1}{2} V(\vec{\mathbf{q}}_i - \vec{\mathbf{q}}_j) \right] + \left[\sum_{i=s+1}^{N} \left[\frac{p_i^2}{2m} + U(\vec{\mathbf{q}}_\mathbf{i}) \right] + \sum_{i,j=s+1}^{N} \frac{1}{2} V(\vec{\mathbf{q}}_i - \vec{\mathbf{q}}_j) \right] \\
&\quad + \left[\sum_{i=1}^{s} \sum_{j=s+1}^{N} V(\vec{\mathbf{q}}_i - \vec{\mathbf{q}}_j) \right] \\
&= H_s + H_{N-s} + H'
\end{aligned}$$

We know from Liouville Theorem that,

$$\begin{aligned}
\frac{\partial \rho_s}{\partial t} &= \int \prod_{i=s+1}^{N} \mathrm{d}V_i \frac{\partial \rho}{\partial t} \\
&= - \int \prod_{i=s+1}^{N} \mathrm{d}V_i \{\rho, H_s + H_{N-s} + H'\}
\end{aligned}$$

We now note the following,

$$\begin{aligned}
\int \prod_{i=s+1}^{N} \mathrm{d}V_i \{\rho, H_s\} &= \left\{ \left(\prod_{i=s+1}^{N} \mathrm{d}V_i \rho \right), H_s \right\} = \{\rho_s, H_s\} \\
- \int \prod_{i=s+1}^{N} \mathrm{d}V_i \{\rho, H_{N-s}\} &= \int \prod_{i=s+1}^{N} \mathrm{d}V_i \sum_{i=s+1}^{N} \left[\frac{\partial \rho}{\partial \vec{\mathbf{p}}_j} \frac{\partial H_{N-s}}{\partial \vec{\mathbf{q}}_j} - \frac{\partial \rho}{\partial \vec{\mathbf{q}}_j} \frac{\partial H_{N-s}}{\partial \vec{\mathbf{p}}_j} \right] \\
&= \int \prod_{i=s+1}^{N} \mathrm{d}V_i \sum_{i=s+1}^{N} \left[\frac{\partial \rho}{\partial \vec{\mathbf{p}}_j} \left(\frac{\partial U}{\partial \vec{\mathbf{q}}_j} + \sum_{j=s+1}^{N} \frac{\partial V}{\partial \vec{\mathbf{q}}_j} \right) - \frac{\partial \rho}{\partial \vec{\mathbf{q}}_j} \frac{\vec{\mathbf{p}}_j}{m} \right] \\
\int \prod_{i=s+1}^{N} \mathrm{d}V_i \{\rho, H_{N-s}\} &= \int \prod_{i=s+1}^{N} \mathrm{d}V_i \sum_{n=1}^{s} \left[\frac{\partial \rho}{\partial \vec{\mathbf{p}}_n} \left(\sum_{j=s+1}^{N} \frac{\partial V}{\partial \vec{\mathbf{q}}_j} \right) \right] - \left[\sum_{n=1}^{s} \frac{\partial \rho}{\partial \vec{\mathbf{p}}_j} \sum_{n=1}^{s} \frac{\partial V}{\partial \vec{\mathbf{q}}_j} \right]
\end{aligned}$$

In the last expression, we can integrate out the second term. The first term has $N-s$ equal terms (by symmetry),

$$(N-s) \int \prod_{i=s+1}^{N} \mathrm{d}V_i \sum_{n=1}^{s} \frac{\partial V}{\partial \vec{\mathbf{q}}_n} \frac{\partial \rho}{\partial \vec{\mathbf{p}}_n} = (N-s) \sum_{n=1}^{s} \mathrm{d}V_{s+1} \frac{\partial V}{\partial \vec{\mathbf{q}}_n} \cdot \frac{\partial}{\partial \vec{\mathbf{p}}_n} \left[\int \prod_{i=s+2}^{N} \mathrm{d}V_i \rho \right]$$

Adding up the three terms above, we get,

$$\frac{\partial f_s}{\partial t} - \{H_s, f_s\} = \sum_{n=1}^{s} \int \mathrm{d}V_{s+1} \frac{\partial V(q_n - q_{s+1})}{\partial \vec{\mathbf{q}}_n} \cdot \frac{\partial}{\partial \vec{\mathbf{p}}_n} \left[\int \prod_{i=s+2}^{N} \mathrm{d}V_i \rho \right]$$

Problem 6 continued on next page...

Part (b)

$$\frac{f_{s+1}}{f_s} = \frac{(N-s)!}{(N-s-1)!}\rho_1(x_{s+1})$$

We then have, from the BBGKY hierarchy,

$$\begin{aligned}
\left[\frac{\partial}{\partial t} + \sum_{n=1}^{s}\left(\frac{\vec{\mathbf{p}}_n}{m}\frac{\partial}{\partial \vec{\mathbf{q}}_n} - \frac{\partial U}{\partial \vec{\mathbf{q}}_n}\frac{\partial}{\partial \vec{\mathbf{p}}_n}\right)\right] f_s &\approx \sum_{n=1}^{s}\int \mathrm{d}V_{s+1}\frac{\partial V}{\partial \vec{\mathbf{q}}_\mathbf{n}}\frac{\partial}{\partial \vec{\mathbf{p}}_n}(N-s)f_s\rho_1(x_{s+1}) \\
&\approx \sum_{n=1}^{s}\frac{\partial}{\partial \vec{\mathbf{q}}_\mathbf{n}}\left[\int \mathrm{d}V_{s+1}\rho_1(x_{s+1})VN\right]\frac{\partial}{\partial \vec{\mathbf{p}}_n} f_s \\
\implies \left[\frac{\partial}{\partial t} + \sum_{n=1}^{s}\left(\frac{\vec{\mathbf{p}}_n}{m}\frac{\partial}{\partial \vec{\mathbf{q}}_n} - \frac{\partial U_{eff}}{\partial \vec{\mathbf{q}}_n}\frac{\partial}{\partial \vec{\mathbf{p}}_n}\right)\right] &= 0
\end{aligned}$$

where $U_{eff} = U(\vec{\mathbf{q}}) + N\int \mathrm{d}V' V(\vec{\mathbf{q}} - \vec{\mathbf{q}}')f_1(\vec{\mathbf{x}'}, t)$.