Advanced Statistical Mechanics: Assignment #1

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Problem 1

Part (a)
Given that

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

Part (d)
In our case, in time interval dt, the walker can go left with probability αdt, right with probability αdt and can stay at the same position with probability $1 - 2\alpha dt$. So then, at position i and time $t + dt$,

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

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,

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

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,

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