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,

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

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,

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