PHYS 301: Thermodynamics and Statistical Mechanics
Problem #8 Solution

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(a) The Grand Canonical Partition Function $\mathcal{Z}$

The grand canonical partition function is defined as the sum over all possible particle numbers N of the canonical partition function weighted by the chemical potential factor:

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N$$

Substitute the given expression for the N-particle canonical partition function Z_N:

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{(Z_1)^N}{N!}$$

We can group the terms raised to the power of N:

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{\left(Z_1 e^{\beta\mu}\right)^N}{N!}$$

Using the hint for the exponential series expansion ($\sum_{N=0}^{\infty} \frac{x^N}{N!} = e^x$) where $x = Z_1 e^{\beta\mu}$:

$$\boxed{\mathcal{Z} = \exp\left(Z_1 e^{\beta\mu}\right)}$$

(b) The Grand Canonical Potential Φ

The grand canonical potential is defined via its relation to the grand partition function:

$$\Phi = -k_B T \ln \mathcal{Z}$$

Substituting our result from part (a):

$$\begin{aligned}\Phi &= -k_B T \ln\left[\exp\left(Z_1 e^{\beta\mu}\right)\right] \\ &= -k_B T \left(Z_1 e^{\beta\mu}\right)\end{aligned}$$

Substituting $Z_1 = V/\lambda_Q^3$ to show the explicit volume dependence:

$$\boxed{\Phi(T, V, \mu) = -k_B T \frac{V}{\lambda_Q^3} e^{\beta\mu}}$$

(c) The Average Number of Particles $\langle N \rangle$

We can find the average number of particles by taking the negative partial derivative of the grand canonical potential with respect to the chemical potential μ, holding T and V constant:

$$\langle N \rangle = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

Using our expression for Φ from part (b):

$$\begin{aligned}
\langle N \rangle &= -\frac{\partial}{\partial \mu}\left(-k_B T Z_1 e^{\beta\mu}\right) \\
&= k_B T Z_1 \frac{\partial}{\partial \mu}\left(e^{\beta\mu}\right) \\
&= k_B T Z_1 (\beta e^{\beta\mu})
\end{aligned}$$

Since $\beta = 1/(k_B T)$, the terms cancel perfectly:

$$\boxed{\langle N \rangle = Z_1 e^{\beta\mu}}$$

(d) Deriving the Equation of State (Pressure)

We are given the extensive thermodynamic relation:

$$\Phi = -PV \implies P = -\frac{\Phi}{V}$$

Substitute the expression for Φ from part (b):

$$\begin{aligned}
P &= -\frac{1}{V}\left(-k_B T Z_1 e^{\beta\mu}\right) \\
&= \frac{k_B T}{V}\left(Z_1 e^{\beta\mu}\right)
\end{aligned}$$

Now, notice from part (c) that the term in the parentheses is exactly the average number of particles: $Z_1 e^{\beta\mu} = \langle N \rangle$.

Substituting $\langle N \rangle$ into the pressure equation:

$$P = \frac{k_B T}{V}\langle N \rangle$$

Rearranging this equation yields:

$$\boxed{PV = \langle N \rangle k_B T}$$

This is precisely the ideal gas law. It demonstrates that the grand canonical ensemble perfectly reproduces the classical thermodynamics of an ideal gas, substituting the strictly fixed particle number N with the ensemble average $\langle N \rangle$.

(e) Including rotational and vibrational degrees of freedom

We saw in parts (b) and (c) that $\Phi = -k_B T Z_1 e^{\beta\mu}$ and $\langle N \rangle = Z_1 e^{\beta\mu}$. These results are true even if Z_1 also contains vibrational and rotational degrees of freedom. Thus, the equation of state is still $PV = \langle N \rangle k_B T$ when these other degrees of freedom are taken into account.