Grand canonical ensemble: ideal gas and simple harmonics

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1. Approach from the grand canonical ensemble: ideal gas

The partition function of the grand canonical ensemble for the ideal gas is

$$\begin{aligned} Z_G &= \sum_{N=0} z^N Z_C(N,\beta) \\ &= \sum_{N=0} \frac{(zZ_{C1})^N}{N!} \\ &= \exp(zZ_{C1}) \end{aligned}$$

or

$$\ln Z_G = zZ_{C1} = zVn_Q$$

The average number

$$\langle N \rangle_G = z\frac{\partial \ln Z_G}{\partial z} = zVn_Q$$

$$n = \frac{\langle N \rangle_G}{V} = zn_Q$$

or

$$z = \frac{n}{n_Q} \qquad \text{(the fugacity, or the absolute activity)}$$

and

$$n_Q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \left(\frac{m k_B T}{2\pi \hbar^2}\right)^{3/2} \qquad \text{(quantum concentration)}$$

The chemical potential:

$$z = \frac{n}{n_Q} = e^{\beta\mu}$$

$$\mu = k_B T \ln\left(\frac{n}{n_Q}\right).$$

The variance of number:

$$\begin{aligned}(\Delta N)^2 &= (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2} \\ &= V n_Q z\end{aligned}$$

Thus we have

$$(\Delta N)^2 = \langle N \rangle_G$$

and

$$\frac{\Delta N}{\langle N \rangle_G} = \frac{1}{\sqrt{\langle N \rangle_G}}; \qquad \text{(uncertainty)}$$

The grand potential

$$\Phi_G = -k_B T \ln Z_G = -k_B T (z V n_Q)$$

The equation of state:

$$PV = -\Phi_G = k_B T (z V n_Q) = \langle N \rangle_G k_B T \qquad \text{(Boyle's law)}$$

or

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

Using this expression, the chemical potential can be rewritten as

$$\mu = k_B T \ln\left(\frac{P}{n_Q k_B T}\right) = k_B T \ln\left[\frac{P}{P_0(T)}\right]$$

where

$$P_0(T) = n_Q k_B T = k_B T \left(\frac{m k_B T}{2\pi\hbar^2}\right)^{3/2}$$

The entropy:

$$\begin{aligned} S &= k_B \ln Z_G + k_B \beta U - \langle N \rangle_G k_B \beta\mu \\ &= k_B (\ln Z_G - \beta \frac{\partial}{\partial\beta} \ln Z_G) - \langle N \rangle_G k_B \beta\mu \end{aligned}$$

$$\ln Z_G = z Z_{C1} = z V n_Q = e^{\beta\mu} V (\frac{2\pi m}{\beta h^2})^{3/2} = \alpha e^{\beta\mu} \beta^{-3/2}$$

with

$$\alpha = V(\frac{2\pi m}{h^2})^{3/2}, \qquad n_Q V = \alpha \beta^{-3/2}$$

We get

$$\begin{aligned} S &= k_B (\ln Z_G - \beta \frac{\partial}{\partial\beta} \ln Z_G) \\ &= k_B [\alpha e^{\beta\mu} \beta^{-3/2} - \beta \frac{\partial}{\partial\beta} (\alpha e^{\beta\mu} \beta^{-3/2})] \\ &= k_B [\alpha e^{\beta\mu} \beta^{-3/2} - \beta (\alpha\mu e^{\beta\mu} \beta^{-3/2} - \frac{3}{2} \alpha e^{\beta\mu} \beta^{-5/2})] \\ &= \alpha k_B e^{\beta\mu} (\beta^{-3/2} - \mu\beta^{-1/2} + \frac{3}{2} \beta^{-3/2}) \\ &= \alpha k_B e^{\beta\mu} (-\mu\beta^{-1/2} + \frac{5}{2} \beta^{-3/2}) \\ &= k_B V e^{\beta\mu} (-\mu\beta n_Q + \frac{5}{2} n_Q) \end{aligned}$$

$$\beta\mu = \ln(\frac{n}{n_Q}), \qquad e^{\beta\mu} = \frac{n}{n_Q}, \qquad nV = \langle N \rangle .$$

Therefore we have

$$\begin{aligned} S &= k_B \langle N \rangle_G [-\ln\left(\frac{n}{n_Q}\right) + \frac{5}{2}] \\ &= k_B \langle N \rangle_G [-\ln\left(\frac{n}{n_Q}\right) + \frac{5}{2}] \end{aligned}$$

(Sacker-Tetrode equation)

The internal energy:

$$U = -\left(\frac{\partial \ln Z_G}{\partial \beta}\right) + \mu \langle N \rangle_G = \frac{3}{2} \langle N \rangle_G k_B T$$

where

$$\begin{aligned} -\left(\frac{\partial \ln Z_G}{\partial \beta}\right) &= -(\alpha\mu e^{\beta\mu}\beta^{-3/2} - \frac{3}{2}\alpha e^{\beta\mu}\beta^{-5/2}) + \\ &= \alpha e^{\beta\mu}\beta^{-3/2}(-\mu + \frac{3}{2\beta}) \\ &= n_Q V e^{\beta\mu}(\frac{3}{2}k_B T - \mu) \\ &= nV(\frac{3}{2}k_B T - \mu) \\ &= \langle N \rangle_G (\frac{3}{2}k_B T - \mu) \end{aligned}$$

((**Note-1**)) H.S. Robert, Statistical Thermodynamics (P T R Prentice Hall, 1993)

$$p_j(N) = \frac{1}{Z_G} z^N e^{-\beta E_j(N)}$$

$$\ln p_j(N) = N \ln z - \beta E_j(N) - \ln Z_G$$

The entropy *S*:

$$
\begin{aligned}
S &= -k_B \sum_{N,j} p_j(N) \ln p_j(N) \\
&= -k_B \sum_{N,j} p_j(N)[N \ln z - \beta E_j(N) - \ln Z_G] \\
&= -\langle N \rangle_G k_B \beta\mu + k_B \beta U + k_B \ln Z_G \\
&= k_B \beta [U - \langle N \rangle_G \mu] + k_B \ln Z_G \\
&= k_B (-\beta \frac{\partial}{\partial \beta} \ln Z_G + \ln Z_G)
\end{aligned}
$$

where

$$
U - \mu \langle N \rangle_G = -\frac{\partial \ln Z_G}{\partial \beta}
$$

((**Note-2**))

In the above example, we can find the most probable case; $N = \overline{N}$, where the probability takes maximum. This can be proved as follows.

$$
\begin{aligned}
f(N) &= \ln \frac{(zZ_1)^N}{N!} \\
&= N(\ln z + \ln Z_{C1}) - \ln N! \\
&= N(\ln z + \ln Z_{C1}) - N \ln N + N
\end{aligned}
$$

$$
f'(N) = (\ln z + \ln Z_{C1}) - \ln N = 0
$$

$$
\mu = -k_B T \ln(\frac{V n_Q}{N}) = -k_B T \ln(\frac{n_Q}{n})
$$

which agrees with the result derived from the grand canonical ensemble.

2. Approach from the grand canonical ensemble: simple harmonics

The partition function of the grand canonical ensemble for the simple harmonics is

$$
Z_G = \sum_{N=0} z^N Z_C(N, \beta)
$$

with

$$Z_C(N,\beta) = (Z_{C1})^N$$

and

$$\begin{aligned} Z_{C1} &= \sum_{n=0}^{\infty} \exp[-\beta\hbar\omega(n+\frac{1}{2})] \\ &= \frac{\exp(-\frac{\beta\hbar\omega}{2})}{1-\exp(-\beta\hbar\omega)} \\ &= \frac{\exp(\frac{\beta\hbar\omega}{2})}{\exp(\beta\hbar\omega)-1} \end{aligned}$$

Note that each simple harmonics is localized around the origin (so-called crystal-type symmetry, like a position of atoms in a crystal), unlike free particles (identical particles). So we do not have to put the factor $1/N!$.

Here we neglect the zero-point energy. For $\beta\hbar\omega << 1$

$$Z_{C1} = \frac{1}{\beta\hbar\omega}$$

The partition function is

$$Z_G = \sum_{N=0} \left(\frac{z}{\beta\hbar\omega}\right)^N = \frac{1}{1-\frac{z}{\beta\hbar\omega}}$$

for $z << \beta\hbar\omega$.

$$\begin{aligned}
\langle N\rangle_G &= z\frac{\partial \ln Z_G}{\partial z} \\
&= -z\frac{\partial}{\partial z}\ln\left(1-\frac{z}{\beta\hbar\omega}\right) \\
&= \frac{\dfrac{z}{\beta\hbar\omega}}{1-\dfrac{z}{\beta\hbar\omega}} \\
&= \frac{1}{\dfrac{\beta\hbar\omega}{z}-1}
\end{aligned}$$

or

$$\frac{\beta\hbar\omega}{z} = \frac{\langle N\rangle_G + 1}{\langle N\rangle_G}$$

or

$$z = e^{\beta\mu} = \frac{\langle N\rangle_G}{\langle N\rangle_G + 1}\beta\hbar\omega$$

The chemical potential:

$$\mu = k_B T\ln\left[\frac{\langle N\rangle_G}{\langle N\rangle_G + 1}\beta\hbar\omega\right]$$

In the limit of $\langle N\rangle_G \to \infty$

$$\mu = k_B T\ln(\beta\hbar\omega)\,.$$

which is the same as that derived for the canonical ensemble.

$$\begin{aligned}
\mu_C &= -k_B T\frac{\partial \ln Z_{CN}}{\partial N} \\
&= k_B T\frac{\partial}{\partial N}N\ln(\beta\hbar\omega) \\
&= k_B T\ln(\beta\hbar\omega)
\end{aligned}$$

((**Note**)) Is there any probable value of $N = \overline{N}$?

$$f(N) = \ln(zZ_{C1})^N$$
$$= N(\ln z + \ln Z_{C1})$$

$$f'(N) = (\ln z + \ln Z_{C1}) = 0$$

From this, the value of N cannot be determined. Nevertheless, we have the chemical potential

$$\mu = -k_B T \ln(\frac{Vn_Q}{N}) = -k_B T \ln(\frac{n_Q}{n})$$

which agrees with the result derived from the grand canonical ensemble.

REFERENCES

E. Fermi, Notes on Thermodynamics and Statistics (The University of Chicago, 1966).
H.S. Robertson, Statistical Thermodynamics (PRP Prentice Hall, 1993).

APPENDIX

$$\langle N \rangle_G = z\left(\frac{\partial \ln Z_G}{\partial z}\right)_{V,T}$$

$$\left(\Delta N\right)_G{}^2 = (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2}$$