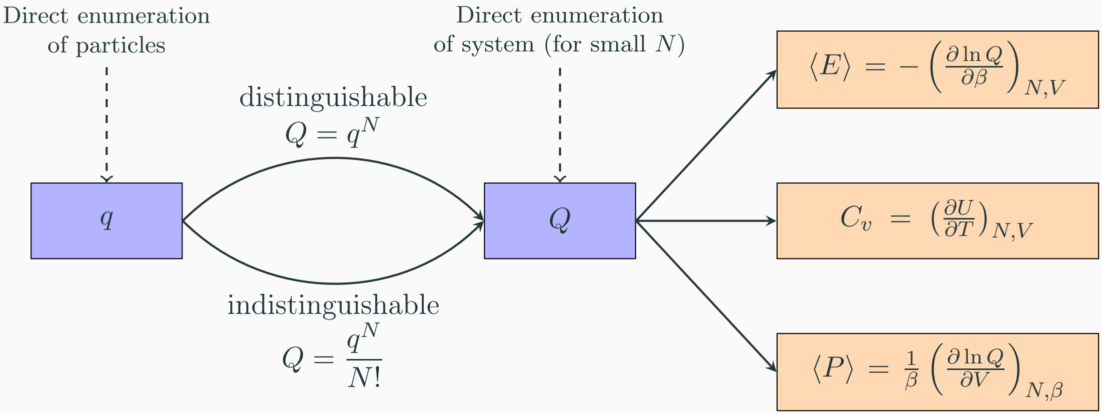
Lecture 4: Thermodynamic Properties

Average Energy, Heat Capacity, Pressure

Flow Chart



Direct enumeration of particles
Direct enumeration of system (for small N)
distinguishable
$Q = q^N$
indistinguishable
$Q = \frac{q^N}{N!}$
q
Q
$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$
$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V}$
$\langle P \rangle = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$

Average Energy

Probability of being in state i:

$$P_i = \frac{e^{-\beta E_i}}{Q}$$

Average value of $f(x)$:

$$\langle f(x) \rangle = \sum_i f(x_i) p_i$$

Write expression for average energy:

$$\langle E \rangle = \sum_i E_i P_i = \frac{1}{Q} \sum_i E_i e^{-\beta E_i}$$

Recall our definition of the partition function, and notice similarities:

$$Q = \sum_i e^{-\beta E_i}$$

Average Energy in Terms of Q

Consider taking the partial derivative of $\ln Q$ wrt to β, using chain rule:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = \left(\frac{\partial \ln Q}{\partial Q}\right)_{N,V} \left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = \frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$$

Evaluate $\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$:

$$Q = \sum_i e^{-\beta E_i}$$

$$\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = \frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i}$$

Derivative of sum = sum of derivatives:

$$= \sum_i \frac{\partial}{\partial \beta}\left(e^{-\beta E_i}\right)$$

$$\left(\frac{\partial Q}{\partial \beta}\right)_{N,V} = \sum_i \left(-E_i\right) e^{-\beta E_i}$$

Average Energy in Terms of Q

Substituting back in we get:

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = -\frac{1}{Q}\sum_i E_i e^{-\beta E_i} = -\langle E\rangle$$

Average Energy

$$\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$$

Choose the partial that makes math easier.

When to use T vs β?

Consider an arbitrary function f, how do we convert between $\frac{\partial}{\partial T}$ and $\frac{\partial}{\partial \beta}$?

$$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial \beta} \cdot \frac{\partial \beta}{\partial T}$$

$$= \frac{\partial f}{\partial \beta} \cdot \frac{\partial \left(\frac{1}{k_B T}\right)}{\partial T}$$

$$= -\frac{1}{k_B T^2} \frac{\partial f}{\partial \beta}$$

Example: Partition Function

$$f = \ln Q$$

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

Convert between $\frac{\partial}{\partial T} \longleftrightarrow \frac{\partial}{\partial \beta}$

$$\frac{\partial f}{\partial \beta} = -k_B T^2 \frac{\partial f}{\partial T}$$

Choose the partial that makes math easier.

Example: Average Energy of Monoatomic Ideal Gas

Partition Function of Monoatomic Ideal Gas:

$$Q(N, V, \beta) = \frac{\left(\frac{2\pi m}{h^2 \beta}\right)^{3N/2} V^N}{N!}$$

Take the natural log of Q:

$$\ln Q = \frac{3N}{2} \ln\left(\frac{2\pi m}{h^2 \beta}\right) + N \ln V - \ln N!$$

$$= \frac{3N}{2} \ln\left(\frac{2\pi m}{h^2}\right) - \frac{3N}{2} \ln \beta + N \ln V - \ln N!$$

When take the partial $\frac{\partial}{\partial \beta}$:

$$= \cancel{\frac{3N}{2} \ln\left(\frac{2\pi m}{h^2}\right)} - \frac{3N}{2} \ln \beta + \cancel{N \ln V} - \cancel{\ln N!}$$

Example: Average Energy of Monoatomic Ideal Gas

Take the partial to find average energy:

$$\begin{aligned}\langle E\rangle &= -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} \\ &= -\left(\frac{\partial}{\partial \beta}\left(-\frac{3N}{2}\ln\beta\right)\right)_{N,V} \\ &= \frac{3N}{2}\frac{1}{\beta} = \boxed{\frac{3N}{2}k_B T}\end{aligned}$$

Simplify:

$$\begin{aligned}\langle E\rangle &= \frac{3N}{2}k_B T \\ &= \frac{3(nN_A)}{2}\cdot\frac{R}{N_A}T \\ &= \boxed{\frac{3}{2}nRT}\end{aligned}$$

Recall definitions:

$$N = nN_A \qquad k_B = \frac{R}{N_A}$$

Heat Capacity

Constant Volume Heat Capacity

Amount of energy required to raise temperature by one degree

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

where U is the internal energy. $U = \langle E \rangle$

Example: Molar heat capacity of Monoatomic Ideal Gas

$$C_V = \left(\frac{\partial \langle E \rangle}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{3}{2}nRT\right) = \frac{3}{2}nR$$

$$\overline{C}_V = \frac{C_V}{n} = \frac{3}{2}R$$

Note: Line over variable means molar quantity

Average Pressure

Write expression for average pressure:

$$\langle P \rangle = \sum_i p_i \, P_i = \sum_i \left(\frac{e^{-\beta E_i}}{Q} \right) \left(-\frac{\partial E_i}{\partial V} \right)_N$$

Where P_i comes from the first law of thermodynamics:

$$\Delta U = q + w$$
$$dU = dq + dw = dq - P \, dV$$

Assume no heat transfer, $dq = 0$:

$$dE = -P \, dV$$
$$P = -\frac{dE}{dV}$$

Average Pressure

This expression contains $\frac{\partial}{\partial V}$, so consider $\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$:

$$Q = \sum_i e^{-\beta E_i}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{1}{Q}\frac{\partial Q}{\partial V}$$

$$= \frac{1}{Q}\frac{\partial}{\partial V}\sum_i e^{-\beta E_i}$$

$$= \frac{1}{Q}\sum_i \frac{\partial}{\partial V} e^{-\beta E_i(N,V)}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{1}{Q}\sum_i \left(-\beta\frac{\partial E_i}{\partial V}\right)_N e^{-\beta E_i}$$

Compare to average pressure:

$$\langle P\rangle = \sum_i \left(\frac{e^{-\beta E_i}}{Q}\right)\left(-\frac{\partial E_i}{\partial V}\right)_N$$

Average Pressure

$$\langle P\rangle = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Example: Average Pressure of Monoatomic Ideal Gas

Partition Function of Monoatomic Ideal Gas:

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2} V^N$$

Evaluate natural log:

$$\ln Q = \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N\ln V - \ln N!$$

When take the partial $\frac{\partial}{\partial V}$:

$$\ln Q = \cancel{\frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right)} + N\ln V - \cancel{\ln N!}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V}$$

Example: Average Pressure of a Monoatomic Ideal Gas

Plug in for $\langle P \rangle$:

$$\begin{aligned}
\langle P \rangle &= \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} \\
&= \frac{1}{\beta}\frac{N}{V} = k_B T \frac{N}{V} \\
&= \frac{R}{N_A} \cdot T \cdot \frac{nN_A}{V} \\
\langle P \rangle &= \frac{nRT}{V} \implies \boxed{PV = nRT}
\end{aligned}$$

Recall definitions:

$$N = nN_A \qquad k_B = \frac{R}{N_A}$$

For an ideal gas: $\langle P \rangle = P$