CHM 421/621 Statistical Mechanics

Lecture 25 A quantum system at finite temperature

Canonical Ensemble

Lecture Plan

Canonical Ensemble

A classical system at finite temperature: Dilute paramagnetic gas

The classical canonical partition function is

$$Z\left(\beta, V, N, \vec{H}\right) = \frac{1}{h^{3N}} \int d^{3N}p \int d^{3N}r \int d\Omega_1 d\Omega_2 \ldots d\Omega_N \exp\left(-\beta \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m} - \mu H \cos\theta_i \right\}\right)$$
$$\equiv z^N$$

Where the molecular partition function is given as

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}}$$

$$z = \left(\frac{V}{\Lambda^3}\right) \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin\theta \ \exp\left(\beta\mu H \cos\theta\right)$$

$$= \left(\frac{V}{\Lambda^3}\right) 2\pi \int_{-1}^{1} dx \ \exp\left(\beta\mu H x\right) = z_{trans} \times 4\pi \frac{\sinh\left(\beta\mu H\right)}{\beta\mu H}$$

z_{mag}

Canonical Ensemble

<u>A classical system at finite temperature: Dilute paramagnetic gas</u>

Helmholtz free energy

$$F = -k_B T \ln Z = -N k_B \ln z$$

$$= F_{trans} - N k_B T \; \ln\left(\frac{4\pi \sinh(\beta\mu H)}{\beta\mu H}\right)$$

Average magnetic moment
Per particle

$$\overline{\mu}_z = \frac{1}{N}\overline{\left(\sum_{i=1}^{N}\mu_{i,z}\right)}$$

$$= \frac{1}{z_{mag}}\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \; \sin\theta \; \mu \; \cos\theta \; \exp\left(\beta\mu H \cos\theta\right)$$

$$= \frac{1}{\beta}\left(\frac{\partial \ln z_{mag}}{\partial H}\right)_{V,N,\beta} = \mu\left[\coth\left(\beta\mu H\right) - \frac{1}{\beta\mu H}\right]$$

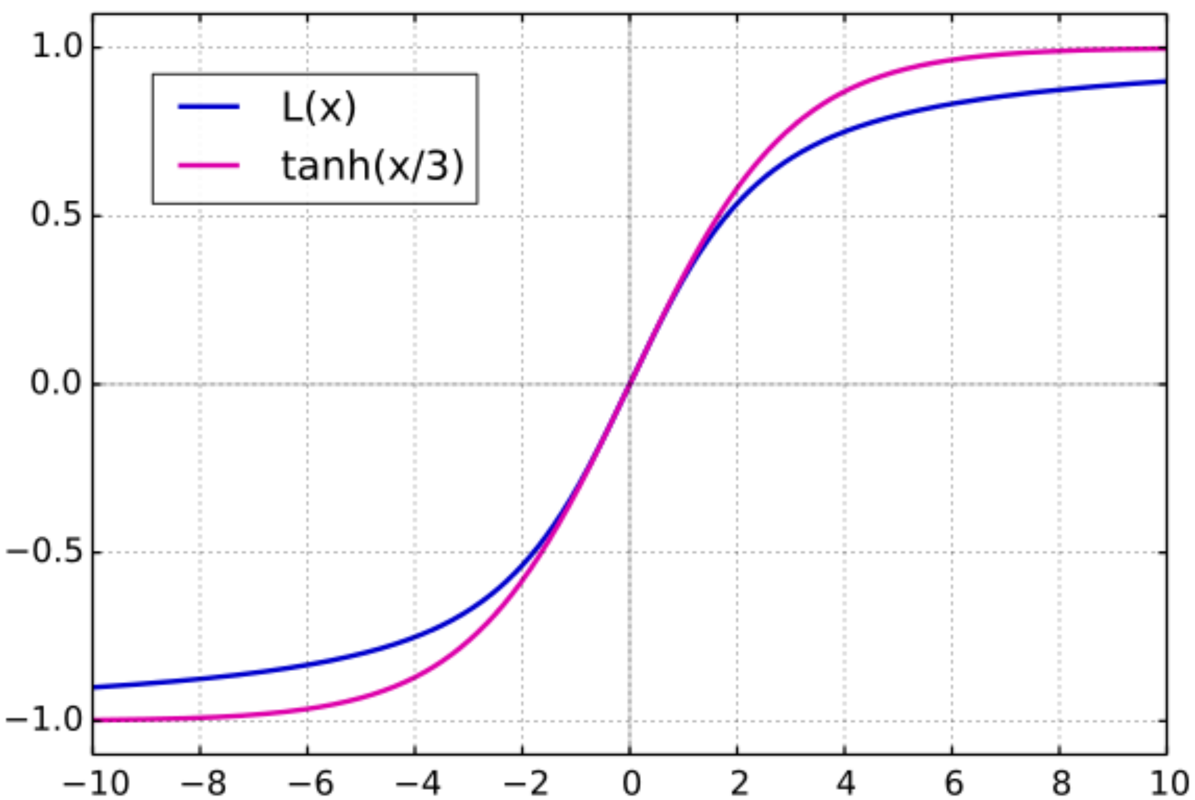
Canonical Ensemble

<u>A classical system at finite temperature: Dilute paramagnetic gas</u>

Average magnetic moment
Per particle

$$\frac{\overline{\mu}_z}{\mu} = \left[\coth(x) - \frac{1}{x}\right]_{x=\beta\mu H} \equiv L(x)$$

Langevin function



At a given temperature when the field is varied from 0 to large values, the magnetic dipoles continuously align with the field.

Their alignment is opposed by thermal motion.

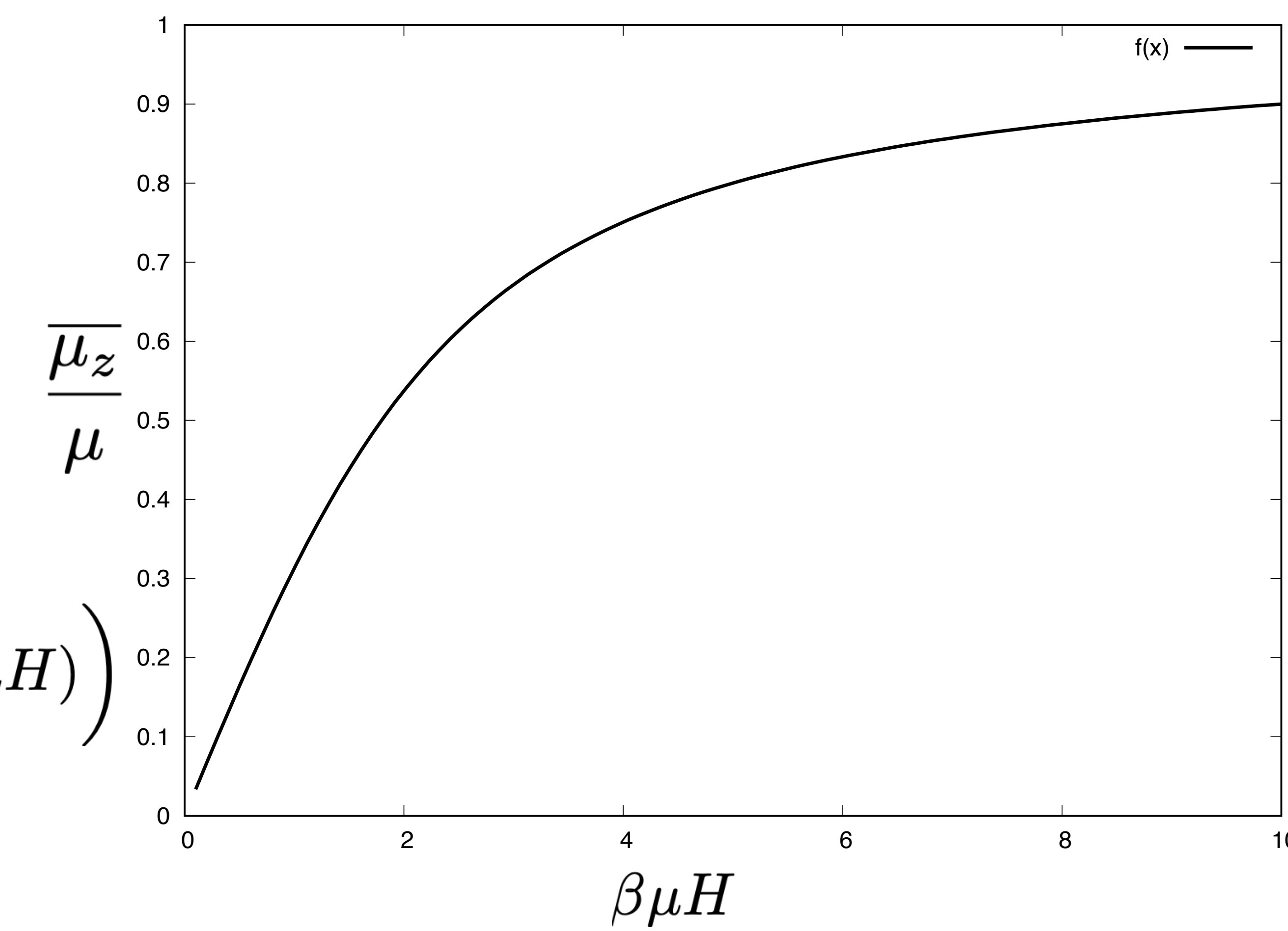
But at large enough fields the thermal opposition is overcome.

Canonical Ensemble

<u>A classical system at finite temperature: Dilute paramagnetic gas</u>

Note that

$$N\overline{\mu_z} = -\left(\frac{\partial F}{\partial H}\right)_{T,N,V}$$



Contributions from magnetic interactions

Entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

$$= Nk_B\left(1 + \ln\left[\frac{4\pi\sinh(\beta\mu H)}{\beta\mu H}\right] - (\beta\mu H)\,\coth(\beta\mu H)\right)$$

Calculate *U* and C_H.

$$U = F + TS \;= Nk_B T\left[1 - (\beta\mu H)\,\coth(\beta\mu H)\right]$$

Canonical Ensemble

A classical system at finite temperature: Dilute paramagnetic gas

Contributions from magnetic interactions

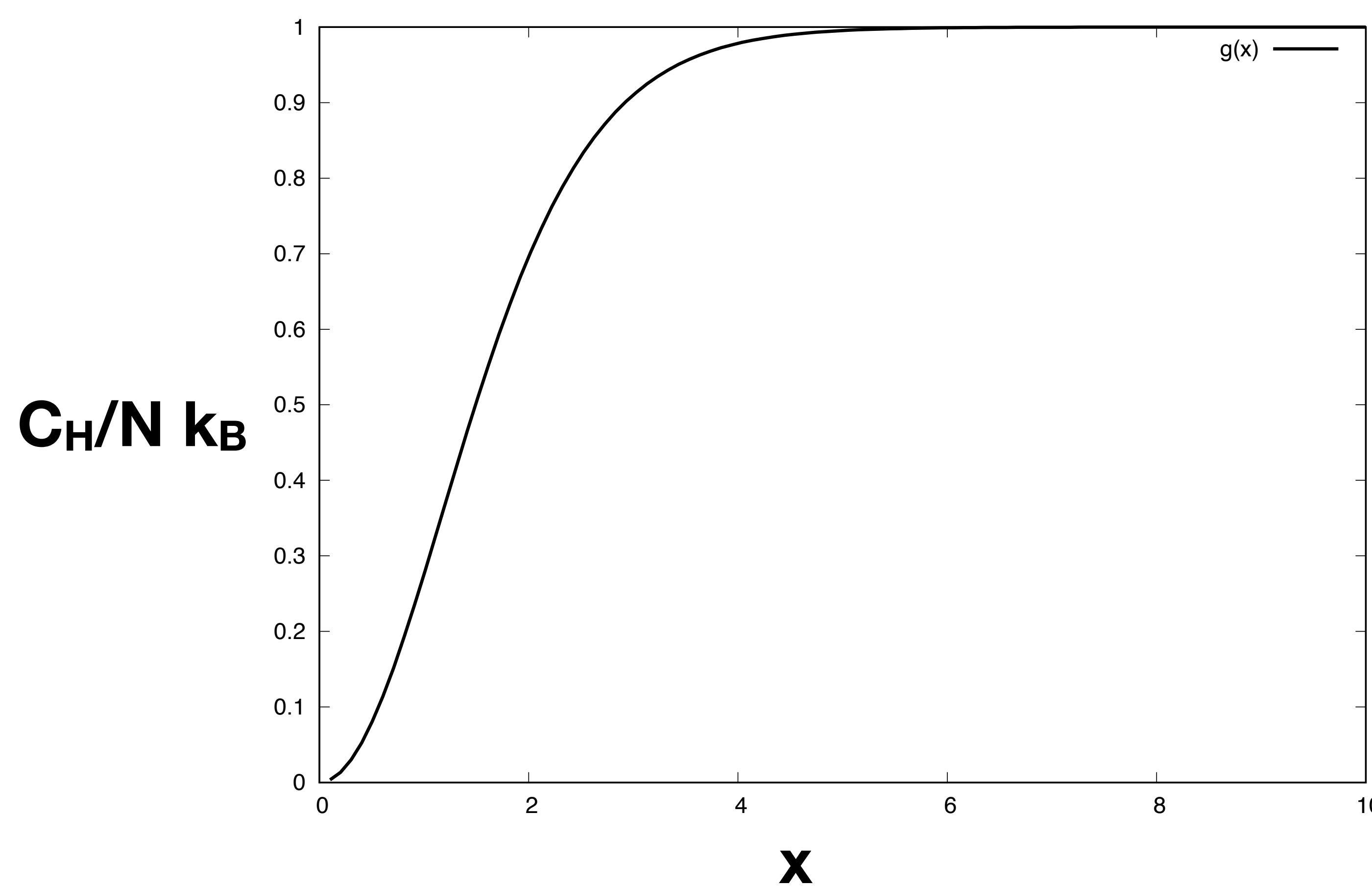
$$C_H = \left(\frac{\partial U}{\partial T}\right)_{H,V,N}$$

$$= N k_B \left(1 - \frac{x^2}{\sinh^2 x}\right)$$

$$x = \beta \mu H$$

$$C_H(T \to 0) = N k_B$$

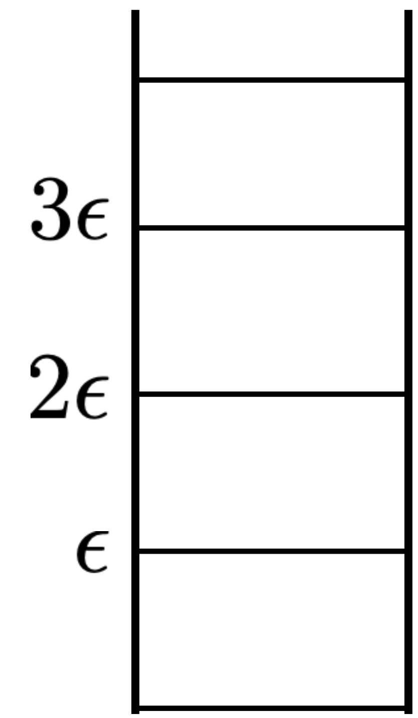
$$C_H(T \to \infty) = 0$$



Canonical Ensemble

A quantum system at finite temperature: Atoms with ladder levels

Consider a system of *N* non-interacting atoms each with a ladder like spectrum of energy levels $0, \epsilon, 2\epsilon, \ldots$



What is the microstate?

(a) Atom *j* in level with energy ϵ_j $\quad \Longrightarrow \quad E_k = \sum_{j=1}^{N} \epsilon_j^{(k)}$

Microstate is specified by $(\epsilon_1^{(k)}, \epsilon_2^{(k)}, \epsilon_3^{(k)}, \ldots)$

(b) n_j atoms in j^{th} energy level $\quad \Longrightarrow \quad E_k = \sum_{j=0}^{\infty} n_j^k (j\epsilon)$

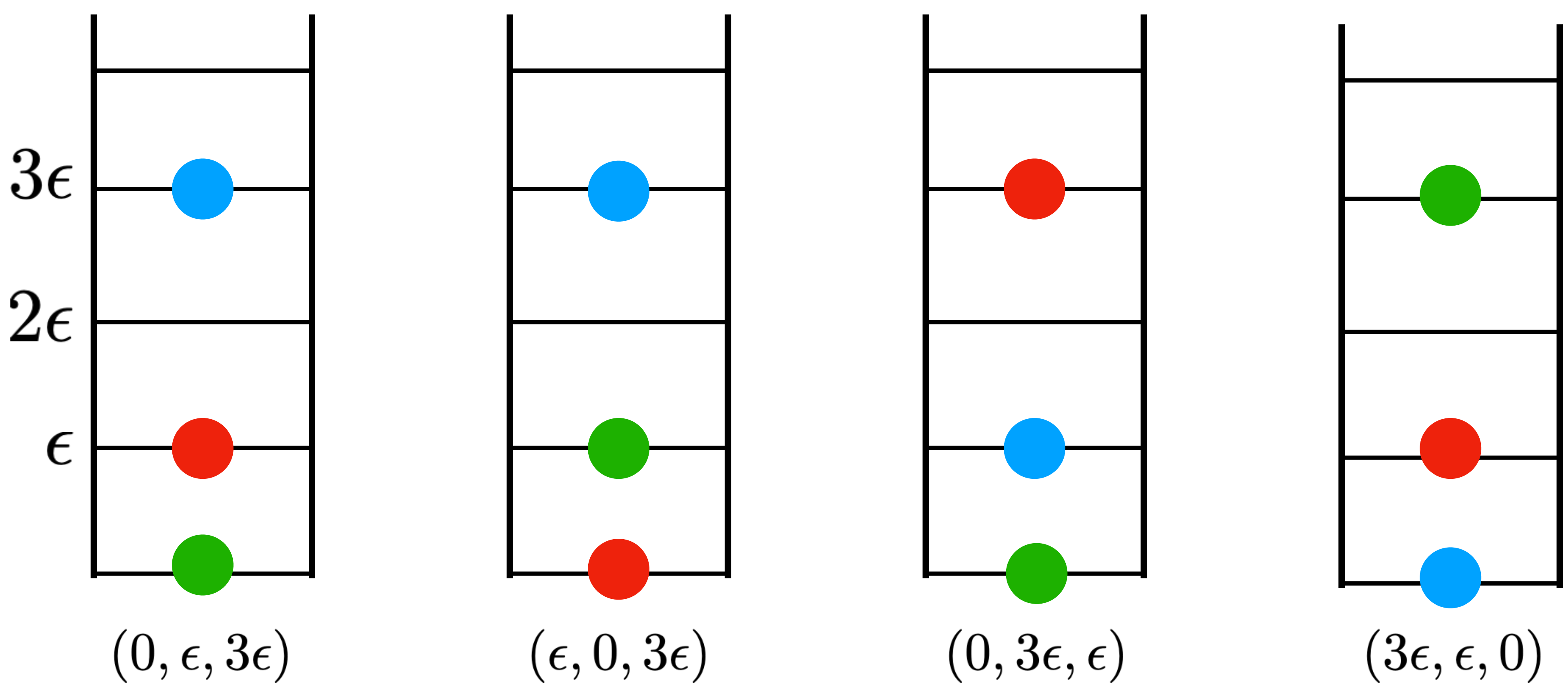
Microstate is specified by $(n_1^{(k)}, n_2^{(k)}, n_3^{(k)}, \ldots)$

Canonical Ensemble

<u>A quantum system at finite temperature: Atoms with ladder levels</u>

What's the difference? Take for e.g. 3 atoms

Case (a)
Consider 4 microstates with the same energy

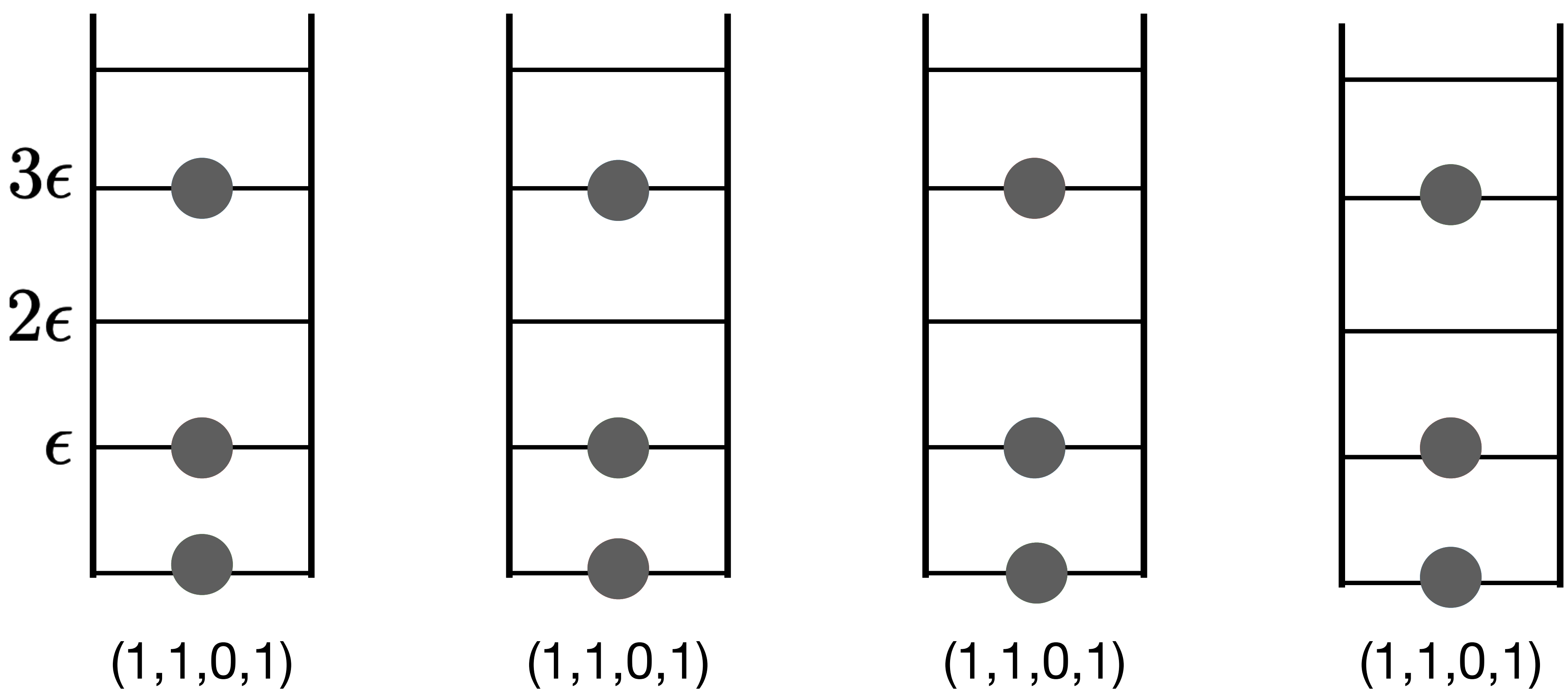


These are distinguishable because the atoms are **distinguishable** (by colour here).

Canonical Ensemble

<u>A quantum system at finite temperature: Atoms with ladder levels</u>

Case (b)
Consider again 4 microstates with the same energy. This time lets count the number of particles in each level instead.



The atoms might as well be colourless.

These are indistinguishable because the atoms are **indistinguishable** (by colour here).

Canonical Ensemble

<u>A quantum system at finite temperature: Atoms with ladder levels</u>

Let us first assume that the atoms are distinguishable.
Canonical partition function for the system is given by

$$Z = \sum_k \exp\left(-\beta E_k\right)$$

Since, each atom will ultimately occupy any of the levels over all the micro states

$$= \sum_k \exp\left(-\beta \sum_{j=1}^{N} \epsilon_j^{(k)}\right) = \sum_{j_1, j_2, j_3, \ldots} \exp\left(-\beta \sum_{i=1}^{N} j_i \epsilon\right)$$

$$= \left(\sum_{j=0}^{\infty} \exp(-\beta(j\epsilon))\right)^N = z^N$$

$$z = \sum_{j=0}^{\infty} \exp(-\beta(j\epsilon)) = \frac{1}{1 - \exp(-\beta\epsilon)}$$

$$Z = \left(\frac{1}{1 - \exp(-\beta\epsilon)}\right)^N$$

Canonical Ensemble

A quantum system at finite temperature: Atoms with ladder levels

Now let us consider indistinguishable atoms.

$$
\begin{aligned}
Z &= \sum_k \exp(-\beta E_k) \\
&= \sum_k \exp\left(-\beta \sum_{j=0}^{\infty} n_j^{(k)} (j\epsilon)\right)
\end{aligned}
$$

Subject to the condition

$$\sum_{j=0}^{\infty} n_j^{(k)} = N$$

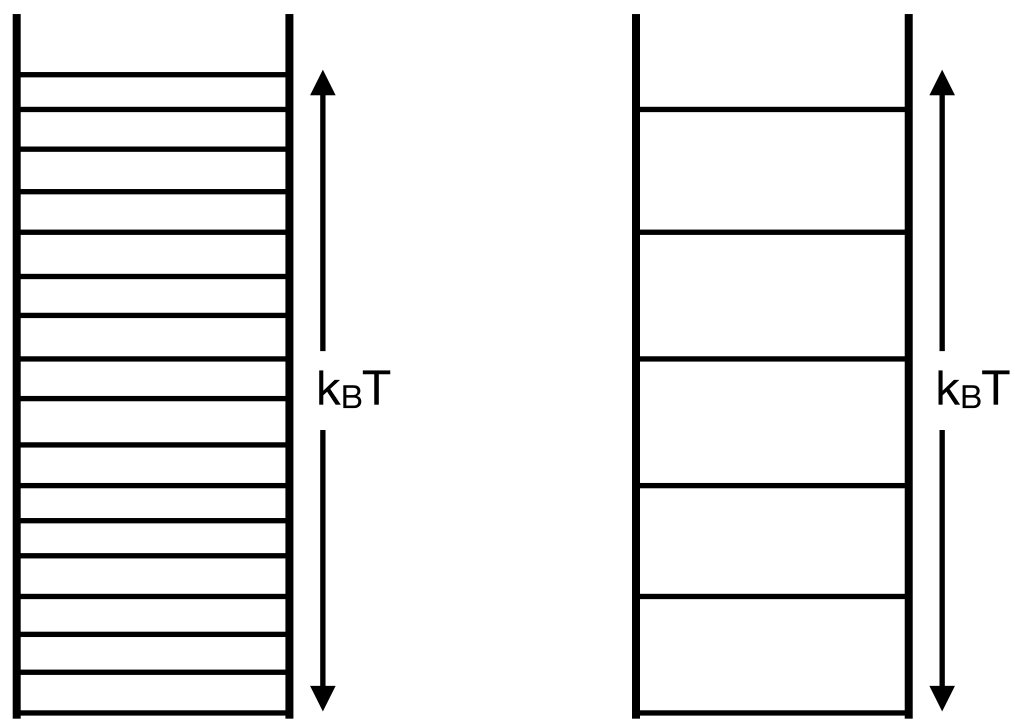
Difficult to simplify in the general case!

Canonical Ensemble

<u>A quantum system at finite temperature: Atoms with ladder levels</u>

Consider two situations:

Non-degenerate   Degenerate



$$\frac{k_B T}{\epsilon} >> N \qquad \frac{k_B T}{\epsilon} \leq N$$

In the non-degenerate case the likelihood of two atoms occupying the same level is very low and can be ignored.

If the atoms are occupying distinct levels then the number of ways of obtaining the same total energy is N!

Canonical Ensemble

<u>A quantum system at finite temperature: Atoms with ladder levels</u>

We can thus approximate the total partition function in the non-degenerate case as

$$Z \approx \frac{z^N}{N!}$$

For e.g. consider a 3-particle system $\quad Z(T,V,3) \approx \sum_{i \neq j \neq k} e^{-\beta(\epsilon_i + \epsilon_j + \epsilon_k)}$

$$z(T,V)^3 = \left(\sum_k e^{-\beta \epsilon_k} \right)^3$$

$$= \sum_k e^{-3\beta\epsilon_k} + \sum_{j \neq k} e^{-\beta(2\epsilon_j + \epsilon_k)} + 3! \times \sum_{i<j<k} e^{-\beta(\epsilon_i + \epsilon_j + \epsilon_k)}$$

$$\Rightarrow \quad \frac{z(T,V)^3}{3!} \approx \sum_{i<j<k} e^{-\beta(\epsilon_i + \epsilon_j + \epsilon_k)}$$

Approximation becomes better at larger *N*

Canonical Ensemble

Distinguishable and indistinguishable particles

Distinguishable

$$Z(N,V,T) = z(V,T)^N$$

Boltzmann statistics

Indistinguishable

$$Z \approx \frac{z^N}{N!}$$

Approximate and valid for non-degenerate systems