Today

I. Parametric Plot Exploration
II. Last Time
III. Computing Averages with the Partition Function
IV. Paramagnetism From a Canonical Perspective
V. Rotation of Diatomic Molecules and the Equipartition Theorem

I. Covered a derivation of the "canonical ensemble", which tells us the probabilities of states with energies E_s and describes equilibrium at constant temperature.

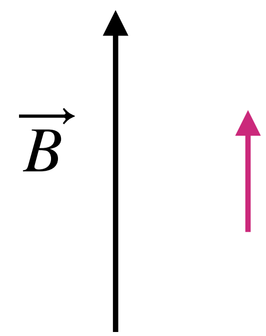
Boltzmann factor: $e^{-\frac{E_s}{kT}}$ (relative probability of state s)

Partition function: $Z = \sum_s e^{-\beta E_s}$

Probabilities of states: $P(s) = \frac{1}{Z} e^{-\beta E_s}$

I. We can also compute averages in this framework:

$$\overline{X} = \frac{1}{Z}\sum_s X_s e^{-\beta E_s}.$$



III. We need to be convinced that we should bother with whole additional formalism. Let's return to paramagnetism

Let's repeat all Andrew's calculations: we begin with the partition function

$$Z = e^{-\beta(-\mu B)} + e^{-\beta(\mu B)} = e^{\mu\beta B} + e^{-\mu\beta B} = 2\cosh(\mu\beta B).$$

The probability of finding a given spin in the up state is then

$P(\uparrow) = \dfrac{e^{\mu\beta B}}{2\cosh(\mu\beta B)}$. Then the average energy is

$$\overline{E} = (-\mu B)P(\uparrow) + (\mu B)P(\downarrow) = \mu B\frac{-e^{\mu\beta B} + e^{-\mu\beta B}}{2\cosh(\mu\beta B)} = -\mu B\tanh(\mu\beta B).$$

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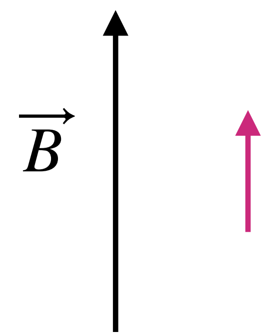

III. $Z = e^{-\beta(-\mu B)} + e^{-\beta(\mu B)} = e^{\mu\beta B} + e^{-\mu\beta B} = 2\cosh(\mu\beta B).$

The probability of finding a given spin in the up state is then

$P(\uparrow) = \dfrac{e^{\mu\beta B}}{2\cosh(\mu\beta B)}$. Let's also consider the average magnetic moment of the spin

$$\overline{\mu_z} = (+\mu)\frac{e^{\mu\beta B}}{2\cosh(\mu\beta B)} + (-\mu)\frac{e^{-\mu\beta B}}{2\cosh(\mu\beta B)} = \mu\tanh(\mu\beta B).$$

From this we can immediately compute the magnetization of N spins

$M = \mu N\tanh(\mu\beta B).$

There's one more technique that works particularly well for average energies…

I. We can also compute averages in this framework:

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There's one more technique that works particularly well for average energies…

$$\overline{E} = \frac{1}{Z} \sum_s E_s e^{-\beta E_s}.$$

Let's compute the β derivative of Z, $Z = \sum_s e^{-\beta E_s}$:

$$\frac{\partial Z}{\partial \beta} = \sum_s \left(-E_s\right) e^{-\beta E_s}.$$

We can easily fix this up

$$\overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln(Z).$$

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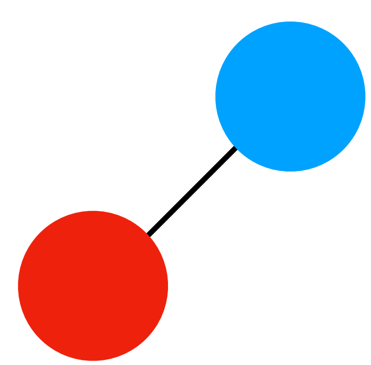
Then

$$\frac{\partial Z}{\partial \beta} = 2\mu B\sinh(\mu\beta B),$$

And so

$$\overline{E} = -\mu B\tanh(\mu\beta B), \quad U = -\mu BN\tanh(\mu\beta B).$$

IV. Applying these tools to a diatomic gas. We'll begin with cases like carbon monoxide or HCl, which have distinct molecules at each end.



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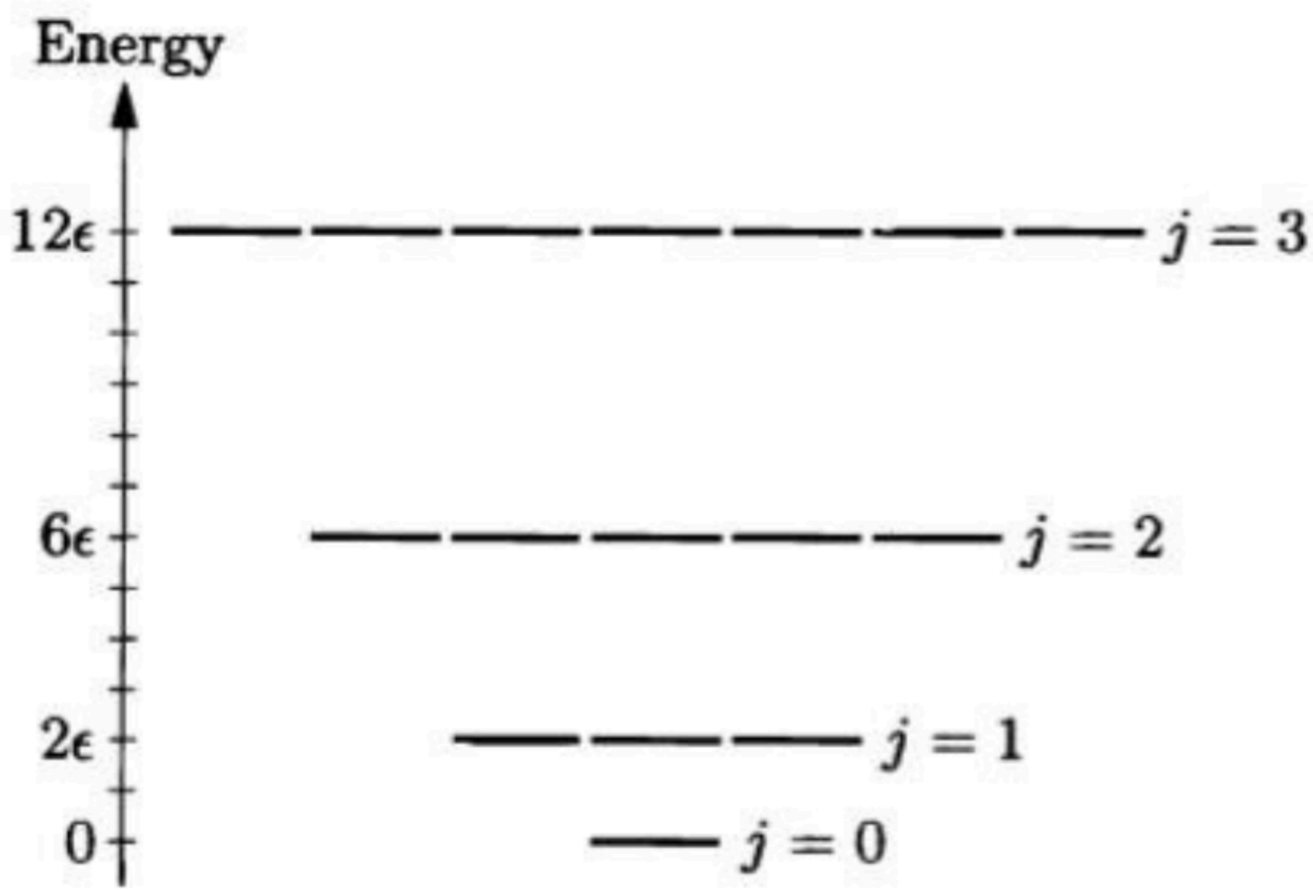
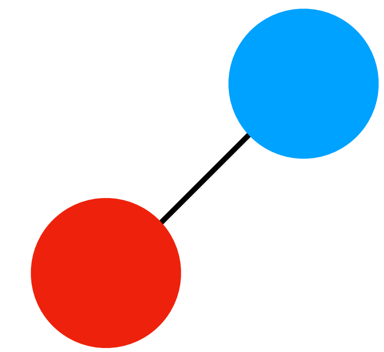
$$E(j) = j(j+1)\epsilon, \qquad j = 0,1,2,\ldots.$$





These states are degenerate with degeneracy $(2j+1)$.

With these results in hand we can compute the partition function

$$Z_{\text{tot}} = \sum_s e^{-\beta E_s} = \sum_{j=0}^{\infty} (2j+1) e^{-\beta E(j)} = \sum_{j=0}^{\infty} (2j+1) e^{-\beta j(j+1)\epsilon}$$

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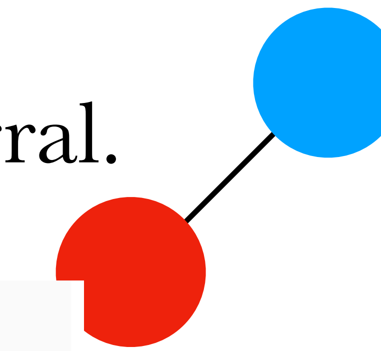
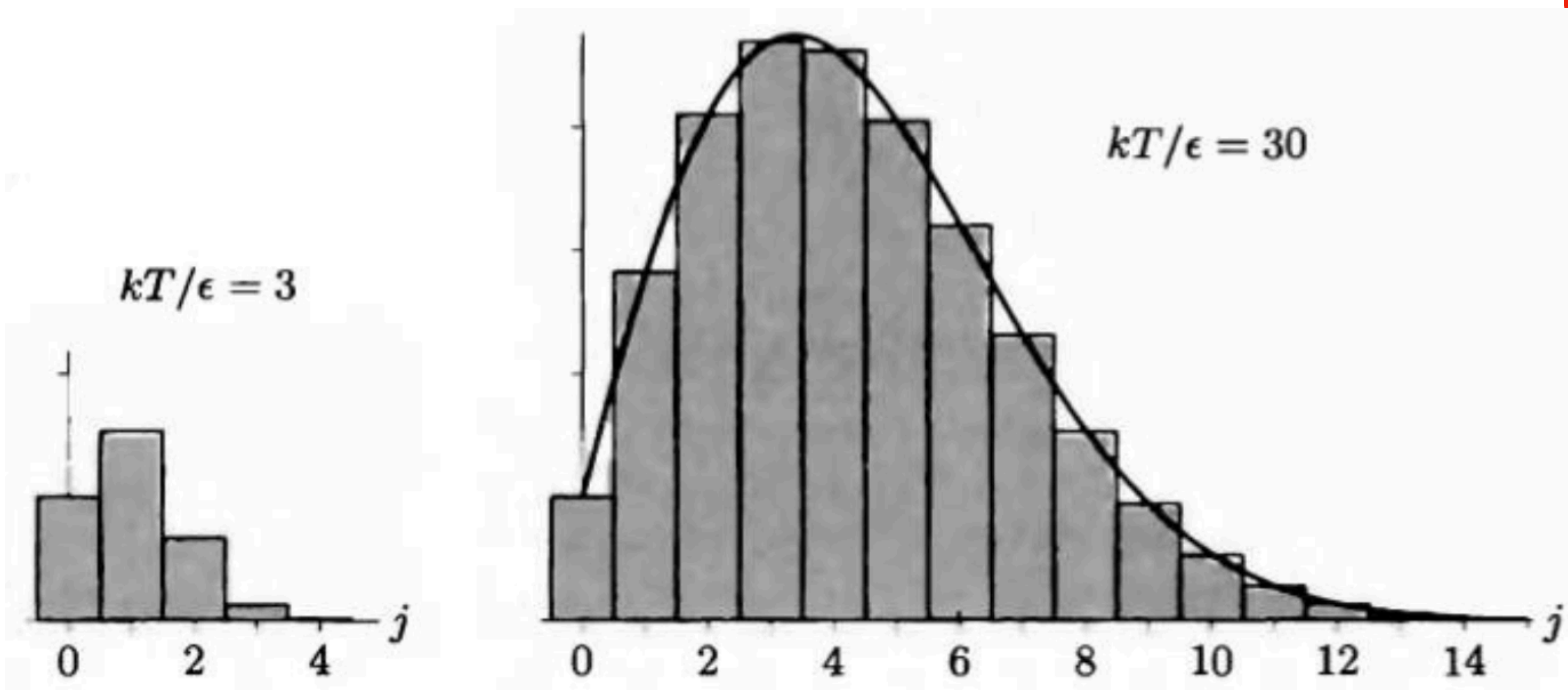
To do this sum we're going to have to convert it to an integral.





For carbon monoxide we have $\epsilon = 0.00024$ eV. To convert to an integral we introduce a *dj* and multiply by the summand to get…

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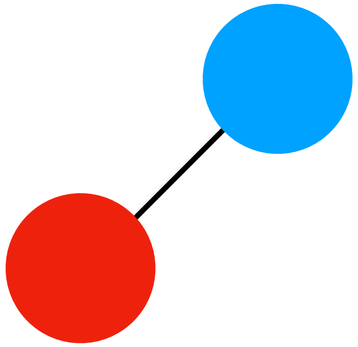

$$Z_{\text{tot}} \approx \int_0^{\infty} (2j+1) e^{-\beta j(j+1)\epsilon} dj = \frac{kT}{\epsilon} = \frac{1}{\epsilon\beta}.$$

With the partition, we can compute average energy:

$$\overline{E}_{\text{rot}} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -(\epsilon\beta)\left(-\frac{1}{\epsilon\beta^2}\right) = \frac{1}{\beta} = kT$$