CHM 421/621 Statistical Mechanics

Lecture 24 Fluctuations in Canonical Ensemble

Ensembles

Lecture Plan

Thermodynamic relations from canonical ensemble

Energy fluctuations in the canonical ensemble

A classical system at finite temperature

A quantum system at finite temperature

Ensembles

Canonical Ensemble

Summary of thermodynamic relations

$$U = \overline{E} = k_B T^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{V,N}$$

$$P = k_B T \left(\frac{\partial \ln Z}{\partial V} \right)_{N,T}$$

$$S = k_B T \left(\frac{\partial \ln Z}{\partial T} \right)_{V,N} + k_B \ln Z$$

$$F = -k_B T \ln Z(N,V,T)$$

Ensembles

Canonical Ensemble

Energy fluctuations in the canonical ensemble

What is the variance?

$$\implies \Delta^2 E = \overline{E^2} - \overline{E}^2 = ?$$

$$\overline{E^2} = \sum_k P(E_k) E_k^2$$

$$= \frac{1}{Z} \sum_k \exp\left(-\beta E_k\right) E_k^2$$

$$= \frac{1}{Z} \frac{\partial^2}{\partial \beta^2} \sum_k \exp\left(-\beta E_k\right) = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}$$

Ensembles

Canonical Ensemble

Energy fluctuations in the canonical ensemble

$$\Longrightarrow \quad \Delta^2 E = \overline{E^2} - \overline{E}^2$$

$$= \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)^2$$

$$= \frac{\partial}{\partial \beta}\left(\frac{\partial \ln Z}{\partial \beta}\right)$$

$$= k_B T^2 \left(\frac{\partial U}{\partial T}\right)_{V,N} = k_B T^2 C_V$$

$$\Longrightarrow \boxed{\sigma(E) = \left(k_B T^2 C_V\right)^{\frac{1}{2}}}$$

Ensembles

Canonical Ensemble

Energy fluctuations in the canonical ensemble: Ideal gas

$$\implies \sigma(E) = \left(k_B T^2 \frac{3}{2} N k_B\right)^{\frac{1}{2}}$$
$$= \left(\frac{3N}{2}\right)^{\frac{1}{2}} k_B T$$

$$\implies \frac{\sigma(E)}{\overline{E}} = \frac{1}{\left(\frac{3N}{2}\right)^{\frac{1}{2}}} \sim \frac{1}{\sqrt{N}}$$

Thus, the fluctuations from average go to zero as the size of the system becomes infinitely large. This justifies the equilibrium thermodynamics point of view.

Ensembles

Canonical Ensemble

A classical system at finite temperature: Dilute paramagnetic gas

Consider a system on *N* non-interacting magnetic point dipoles with mass *m* in a volume *V* at temperature *T.* An external magnetic field ***H*** is applied to the system.

$$
\begin{aligned}
H\left(\{\vec{r},\vec{p},\Omega\}\right) &= \sum_{i=1}^{N}\left\{\frac{p_i^2}{2m} - \vec{\mu}_i\cdot\vec{H}\right\} \\
&= \sum_{i=1}^{N}\left\{\frac{p_i^2}{2m} - \mu H\cos\theta_i\right\}
\end{aligned}
\qquad \Omega = (\theta,\phi)
$$

All dipoles are assumed to have the same magnitude of the moment and field is along *z* direction.

Ensembles

Canonical Ensemble

A classical system at finite temperature: Dilute paramagnetic gas

The classical canonical partition function is

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

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}

Ensembles

Canonical Ensemble

A classical system at finite temperature: Dilute paramagnetic gas

Helmholtz free energy
$$F = -k_B T \ln Z = -N k_B T \ln Z$$
$$= F_{trans} - N k_B T \ \ln\left(\frac{4\pi \sinh(\beta\mu H)}{\beta\mu H}\right)$$

Average magnetic moment
Per particle
$$\overline{\mu}_z = \frac{1}{N}\overline{\left(\sum_{i=1}^{N}\mu_{i,z}\right)}$$
$$= \frac{1}{z_{mag}}\int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \ \sin\theta \ \mu \ \cos\theta \ \exp\left(\beta\mu H \cos\theta\right)$$
$$= \frac{1}{\beta}\left(\frac{\partial \ln z_{mag}}{\partial H}\right)_{V,N,\beta} = \mu\left[\coth\left(\beta\mu H\right) - \frac{1}{\beta\mu H}\right]$$

Ensembles

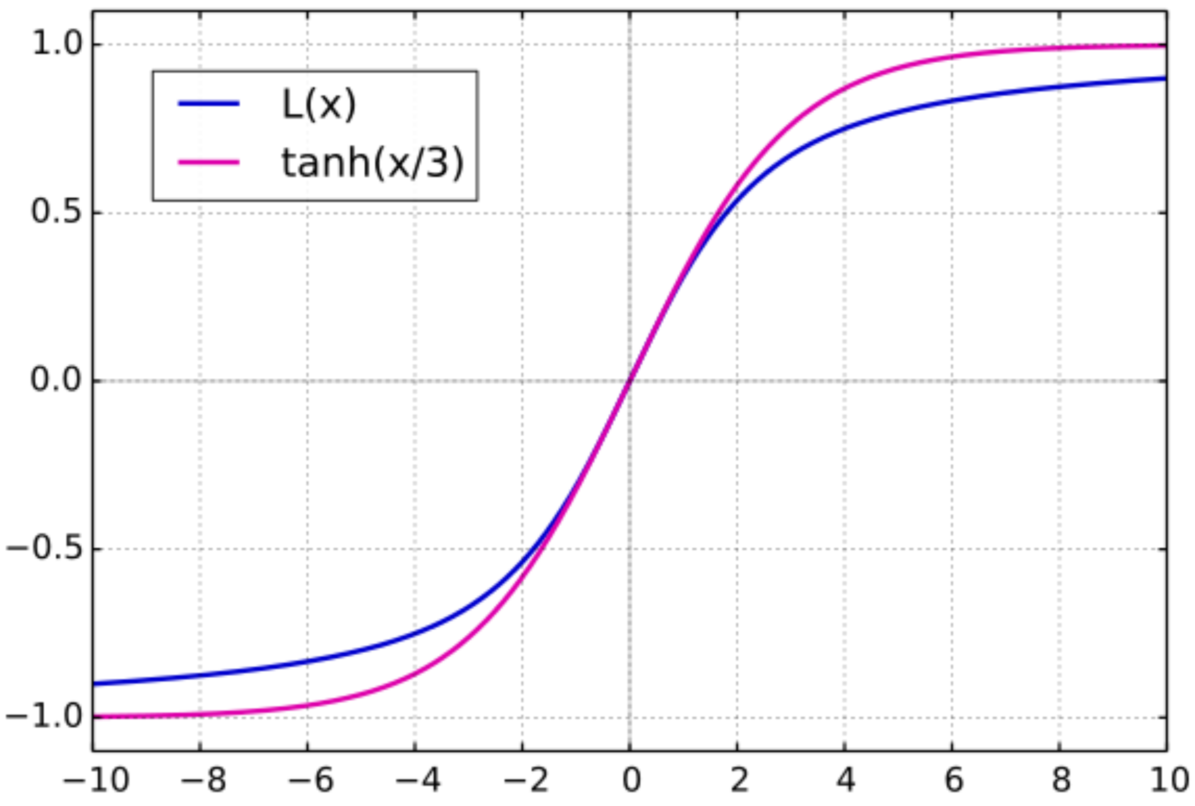
Canonical Ensemble

A classical system at finite temperature: Dilute paramagnetic gas

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.

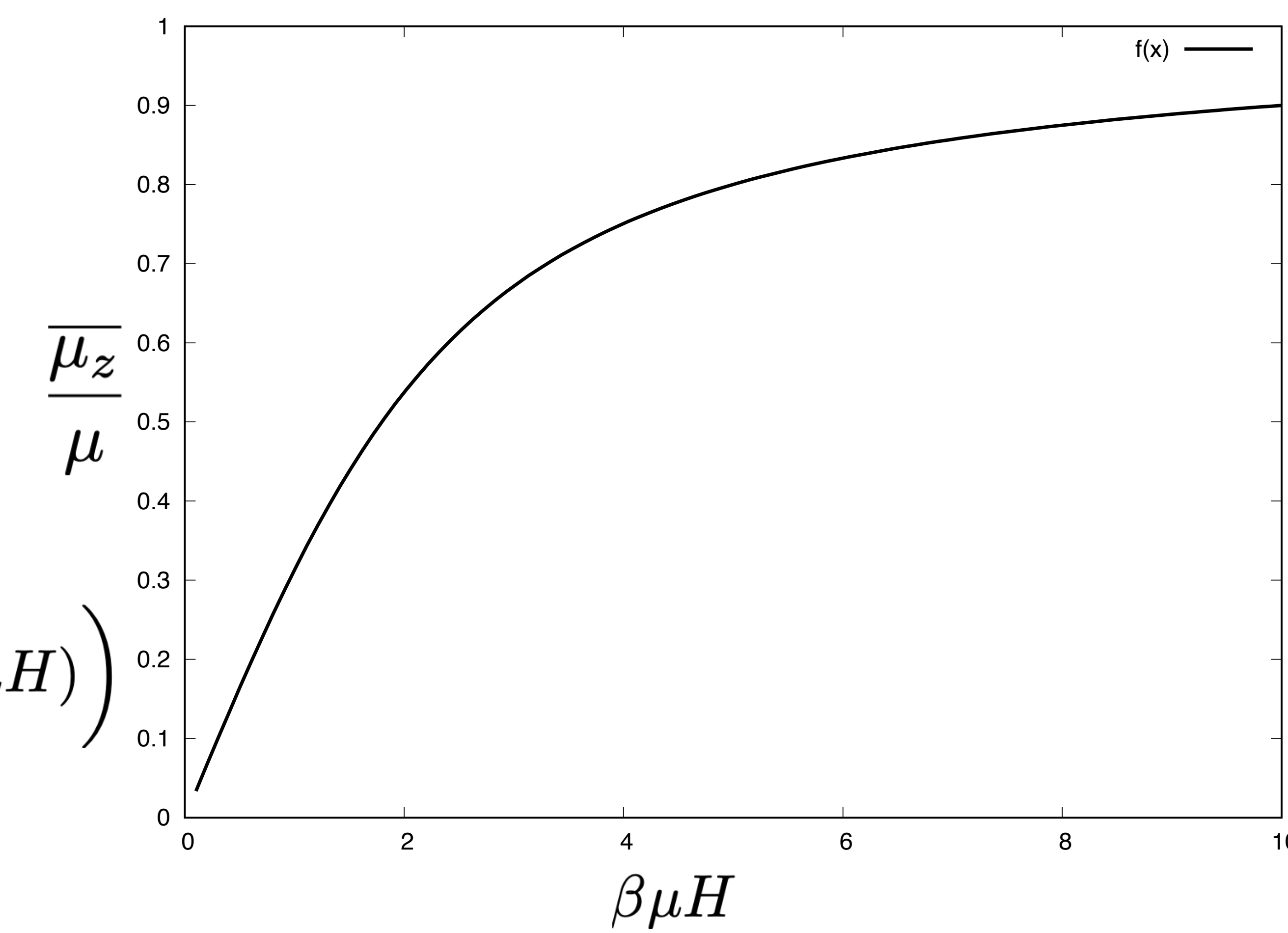
Ensembles

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.

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

Ensembles

Canonical Ensemble

A classical system at finite temperature: Dilute paramagnetic gas

Contributions from magnetic interactions

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

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

$$x = \beta \mu H$$

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

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