Theo. 4. Statistical Physics.

Lecture 21.

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Last time: Two-level system + ideal gas in canonical ensemble
Single vs. multiparticle partition fcn.

Today: Gibbs canonical ensemble
Grand canonical ensemble.

From last time, we discussed the canonical ensemble, where a system is thermally coupled to a reservoir at constant T. By analyzing the Helmholtz free energy via the partition fcn. expression

$$F(T, \vec{x}) = -k_B T \ln Z(T, \vec{x}),$$

we can calculate (any) desired thermodynamic property of the system, such as avg. energy, heat capacity, pressure, chemical potential, etc.

Now, we construct a new stat. mech system, where a system is allowed to change internal energy via heat and work. Macrostates $M \equiv (T, \vec{J})$ specifies ext. temperature and forces. System maintained at constant force via external elements (pistons or magnets). Energy of the combined system is $\mathcal{H} - \vec{J} \cdot \vec{x}$ including work done against the forces. Work done on the system is $+\vec{J} \cdot \vec{x}$.

Microstates of combined system has canonical prob.

$$p(\mu_s, \vec{x}) = \exp\left[-\beta \mathcal{H}(\mu_s) + \beta \vec{J} \cdot \vec{x}\right] / \mathcal{Z}(T, N, \vec{J})$$

with Gibbs partition fcn $\mathcal{Z}(N, T, \vec{J}) = \sum_{\mu_s, \vec{x}} \exp\left[\beta \vec{J} \cdot \vec{x} - \beta \mathcal{H}(\mu_s)\right]$

Note RHS has no N dependence: there is no chemical potential (will be considered for grand canonical ensemble ~~potential~~).

It is easy to calculate the equilibrium exp. values of the displacements $\vec{x}_i$

$$\langle \vec{x}_i \rangle = k_B T \frac{\partial \ln Z}{\partial J_i}$$

Since $\vec{x} = -\frac{\partial G}{\partial \vec{J}} \Rightarrow$ identify $G(N,T,\vec{J}) = -k_B T \ln Z$,

where $G = E - TS - \vec{x} \cdot \vec{J}$. Can also derive by maximizing probability wrt. $\vec{x}$.

Enthalpy $H \equiv E - \vec{x} \cdot \vec{J}$ obtained by

$$-\frac{\partial \ln Z}{\partial \beta} = \langle \mathcal{H} - \vec{x} \cdot \vec{J} \rangle = H.$$

Heat capacities at const. force (including work done against ext. forces) arise from enthalpy as $C_J = \frac{\partial H}{\partial T}$.

Example 1. Ideal gas in isobaric ensemble.

$$M \equiv (N, T, P) \quad \text{macrostate.}$$

Microstate $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$ with volume V.

$$p(\{\vec{p}_i, \vec{q}_i\}, V) = \frac{1}{Z} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta P V\right] \cdot \begin{cases} 1 & \text{for } \{q_i\} \text{ in box } V \\ 0 & \text{otherwise.} \end{cases}$$

Note, again, not uniform prob. distribution, but instead weighted by Boltzmann factor $\exp\left(\frac{-\epsilon}{k_B T}\right)$ and $\exp\left(\frac{-PV}{k_B T}\right)$.

Normalization factor: as usual, total # of ~~[illegible]~~ probabilities.

$$\mathcal{Z}(N,T,P) = \int_0^\infty dV \, e^{-\beta PV} \int \frac{1}{N!} \prod_{i=1}^{N} \frac{d^3\vec{p}_i \, d^3\vec{q}_i}{h^3} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right]$$

$$= \int_0^\infty dV \, V^N e^{-\beta PV} \frac{1}{N! \, \lambda(T)^{3N}}$$

$$= \frac{1}{(\beta P)^{N+1} \lambda(T)^{3N}}$$

where $\lambda(T) = \dfrac{h}{\sqrt{2\pi m k_B T}}$ is the thermal wavelength from before.

$$G = -k_B T \ln \mathcal{Z}$$

Ignore non-extensive contributions

$$\simeq N k_B T \left[\ln P - \frac{5}{2} \ln(k_B T) + \frac{3}{2} \ln\left(\frac{h^2}{2\pi m}\right) \right]$$

Given $dG = -S\,dT + \cancel{P\,dV}\; V\,dP + \mu\,dN$,

volume is $V = \left.\dfrac{\partial G}{\partial P}\right|_{T,N} = \dfrac{N k_B T}{P} \Rightarrow PV = N k_B T.$

Enthalpy is $H = \langle E + PV \rangle$

$$H = -\frac{\partial \ln \mathcal{Z}}{\partial \beta} = \frac{5}{2} N k_B T,$$

$$C_P = \frac{dH}{dT} = \frac{5}{2} N k_B.$$

Example 2.

Spins in ext. magnetic field $\vec{B}$.

Work done against magnetic field + internal Hamiltonian gives Gibbs partition fcn.

$$\mathcal{Z}(N,T,B) = \operatorname{tr}\left[\exp\left(-\beta \mathcal{H} + \beta \vec{B} \cdot \vec{M}\right)\right]$$

"sum over all dofs"

Here, the dofs. can be taken as spin ½ particles with two possible projections of spin along magnetic field.

Microstate of N spins is a set of Ising variables $\{\sigma_i = \pm 1\}$.

Corresponding magnetization along field direction

$$M = \mu_0 \sum_{i=1}^{N} \sigma_i \,, \quad \mu_0 \text{ is microscopic mag. moment.}$$

If $\mathcal{H} = 0$ (no interactions among spins),

$$p(\{\sigma_i\}) = \frac{1}{Z}\left[\beta B \mu_0 \sum_{i=1}^{N} \sigma_i\right]$$

(cf. two-level system from earlier)

Gibbs partition fcn.

Recall: $\cosh(x) = \frac{1}{2}(e^{x} + e^{-x})$

$$Z(N,T,B) = \left[2\cosh(\beta\mu_0 B)\right]^N$$

Gibbs free energy $G = -k_B T \ln Z = -N k_B T \ln\left[2\cosh(\beta\mu_0 B)\right]$

Avg. magnetization

Recall: $\frac{d}{dx}\cosh x = \sinh x$

$$M = -\frac{\partial G}{\partial B} = N\mu_0 \tanh(\beta\mu_0 B)$$

Can expand for small B & obtain well-known Curie Law of magnetic susceptibility

$$\chi(T) = \left.\frac{\partial M}{\partial B}\right|_{B=0} = \frac{N\mu_0^2}{k_B T}$$

Enthalpy $H = \langle \mathcal{H} - BM \rangle$

$$= -BM$$

$$C_B = -B\frac{\partial M}{\partial T}.$$

The final ensemble to consider is the grand canonical ensemble, which allows chemical work but not mechanical work. Hence, system macrostate fixed by chemical potential μ, $M \equiv (T, \mu, \vec{x})$. Microstates μ_S contain indefinite # of particles.

$$p(\mu_S) = \frac{\exp[\beta \mu N(\mu_S) - \beta \mathcal{H}(\mu_S)]}{Q}$$

Grand partition fcn. $\mathcal{Q}(T, \mu, \vec{x}) = \sum_{\mu_S} \exp[\beta \mu N(\mu_S) - \beta \mathcal{H}(\mu_S)]$

Easier to analyze by separating a sum over # of given particles,

$$\mathcal{Q}(T, \mu, \vec{x}) = \sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{(\mu_S | N)} e^{-\beta \mathcal{H}_N(\mu_S)}$$

Can recognize that restricted sums $\sum_{(\mu_S | N)}$ are regular N-particle partition fcns. Each term in $\mathcal{Q}$ is total weight of all microstates of N particles.

Unconditional prob. of finding N particles is

$$p(N) = \frac{e^{\beta \mu N} Z(T, N, \vec{x})}{\mathcal{Q}(T, \mu, \vec{x})}$$

$$\langle N \rangle = \frac{1}{\mathcal{Q}} \frac{\partial}{\partial(\beta\mu)} \mathcal{Q} = \frac{\partial \ln \mathcal{Q}}{\partial(\beta\mu)}$$

Can check number fluctuations are related to variance

$$\langle N^2 \rangle_c = \frac{\partial \langle N \rangle}{\partial(\beta\mu)}$$

$\Rightarrow$ Relative number fluct. vanish in thermodynamic limit.

Sharpness for $N \Rightarrow$ approx. sum by largest term at $N = N^* \simeq \langle N \rangle$.

$$\mathcal{Q}(T,\mu,\vec{x}) = \lim_{N\to\infty} \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,N,\vec{x})$$
$$= e^{\beta\mu N^*} Z(T,N^*,\vec{x})$$
$$= e^{\beta\mu N^* - \beta F} \equiv e^{-\beta \mathcal{G}}$$

where $\mathcal{G}(T,\mu,\vec{x}) = E - TS - \mu N = F - \mu N$
$$= -k_B T \ln \mathcal{Q}$$

is grand potential.

We know $d\mathcal{G} = -SdT - N d\mu + \vec{J}\cdot d\vec{x}$.

Again, example in Kardar for ideal gas, p.119-120.

Get $\mathcal{Q}(T,\mu,V) = \exp\left[\beta\mu \frac{V}{\lambda^3}\right]$,

$$\mathcal{G}(T,\mu,V) = -k_B T (e^{\beta\mu}) \frac{V}{\lambda^3}$$

$$\mu = k_B T \ln\left(\frac{P\lambda^3}{k_B T}\right)$$

Next time: Legendre transforms.

Comments about interacting systems.