

Canonical and Grand Canonical Ensembles:

Applications

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- * here: concentrate on situations where effects of quantum statistics are negligible
 - straightforward for non-interacting systems
- * examples: ideal gas, paramagnetism, Ising model
- * for ideal gas: semi-classical approximation,
 - derive Maxwell-Boltzmann velocity distribution, equipartition theorem
- * specific heat of diatomic molecules ⇒ translational, rotational, vibrational motion
- * subsequently ⇒ treat classical interacting systems ⇒ pair correlation function
- * chemical potential ⇒ useful in describing phase transitions / chemical reactions
- * grand-canonical formalism

NOTE: the microcanonical ensemble / ideal gas was worked out in Exercise 2.7.9 (at least the number of states from which everything can be derived!)

Simple Examples in the Canonical Ensemble (2)

* definition of canonical ensemble: equilibrium distribution when ~~the~~ average energy is fixed \rightarrow Lagrange multiplier $\approx -\beta$

$$D_B = \frac{1}{Z} e^{-\beta H} = \frac{1}{Z} \sum_r |r\rangle e^{-\beta E_r} \langle r|$$

$$Z = \text{Tr} e^{-\beta H} = \sum_r e^{-\beta E_r}$$

$$Z = \int dE g(E) e^{-\beta E} \quad g(E) - \text{density of states}$$

* we know with precision the values of a set of external parameters: examples; volume, electric or magnetic field, etc.

- Hamiltonian depends on these parameters

$$H = H(x_i) \quad (x_1, \dots, x_N)$$

- only the average value of the energy is known

(not the actual eigenstate of the Hamiltonian)

$$E(\beta, x) = - \left. \frac{\partial \ln Z}{\partial \beta} \right|_x$$

- can also obtain the average value of

generalised force

$$X_i = - \frac{1}{\beta} \frac{\partial \ln Z}{\partial x_i} = \left\langle \frac{\partial H}{\partial x_i} \right\rangle$$

* note: $\ln Z$ is the relevant variable

- $\ln Z$ is extensive (Z is not)

(3)

$$\frac{S}{k} = -\text{Tr} \rho \ln \rho = -\text{Tr} \hat{\rho} [-\beta \hat{H} - \ln Z]$$

$$\frac{S}{k} = \beta \bar{E} + \ln Z \Rightarrow \ln Z = \frac{S}{k} - \beta \bar{E}$$

$$\frac{dS}{k} = d \ln Z + d(\beta \bar{E}) = d \ln Z + \beta d\bar{E} + \bar{E} d\beta$$

since $\ln Z = \ln Z(\beta, x_i)$ (x_i - generalised displacements)

$$d \ln Z = \frac{\partial \ln Z}{\partial \beta} d\beta + \sum_i \frac{\partial \ln Z}{\partial x_i} dx_i$$

$$= -\bar{E} d\beta - \beta \sum_i X_i dx_i$$

$$\frac{dS}{k} = \beta d\bar{E} - \beta \sum_i X_i dx_i$$

$$\boxed{T dS = dE - \sum_i X_i dx_i} \rightarrow T dS \text{ equation}$$

thermodynamic potential: $F = -\frac{1}{\beta} \ln Z$

$$F = -kT \ln Z$$

$$dF = -k \ln Z dT - kT \frac{\partial \ln Z}{\partial T} dT - kT \sum_i \frac{\partial \ln Z}{\partial x_i} dx_i$$

$$dF = -S dT + \sum_i X_i dx_i$$

example: pressure

$$P = \frac{1}{\beta} \left. \frac{\partial \ln Z}{\partial V} \right|_{\beta, N} = - \left. \frac{\partial F}{\partial V} \right|_{T, N}$$

(4)

chemical potential

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{T, V} = - \frac{1}{\beta} \left. \frac{\partial \ln Z}{\partial N} \right|_{\beta, V}$$

fluctuations in canonical ensemble

$$\left. \frac{\partial^2 \ln Z}{\partial \beta^2} \right|_x = \langle E^2 \rangle - \langle E \rangle^2 = - \left. \frac{\partial E}{\partial \beta} \right|_x = kT^2 C_x \geq 0$$

verification of stability

consider the relative fluctuation:

$$\frac{\delta E}{E} = \frac{\sqrt{\langle E^2 \rangle - \langle E \rangle^2}}{E} = \frac{\sqrt{kT^2 C_x}}{E}$$

C_x - extensive

E - extensive

as size goes to infinity $\frac{\delta E}{E} \rightarrow 0$

\Rightarrow argument for the equivalence of the canonical/
microcanonical ensembles

Partition function and thermodynamics of an ideal gas (8)

* mono-atomic ideal gas \rightarrow energy levels determined by quantum numbers n_x, n_y, n_z $\vec{n} = \frac{2\pi}{L} (n_x, n_y, n_z)$

ideal gas approximation: energy of atom on average given by $\bar{\epsilon} \sim \frac{E}{N}$

average occupation number $n_r \sim \frac{N}{\Phi(E)}$

$\Phi(E) \sim$ number of states with energies less than or equal to E
(this is a rough approximation!!!)

$$n_r \sim \frac{N}{\Phi(E)} \sim \frac{N}{\cancel{V} \frac{6\pi^2}{h^3}} \sim \frac{N 6\pi^2 \frac{h^3}{3}}{V (2m\epsilon)^{3/2}}$$

$N \approx \frac{V}{d^3}$ $d^3 \rightarrow$ average volume associated with one atom

$d \sim$ average distance between atoms \rightarrow

$$n_r \sim \frac{V}{d^3} \frac{6\pi^2 \frac{h^3}{3}}{V (2m\epsilon)^{3/2}} \quad \epsilon \sim kT \text{ (verified later)}$$

$$n_r \sim \frac{h^3}{d^3 (2m\epsilon)^{3/2}} \quad (\text{neglect numerical factors})$$

$$n_r \sim \frac{\lambda^3}{d^3} \quad \lambda = \frac{h}{\sqrt{2\pi m kT}} \quad \lambda - \text{de Broglie wavelength}$$

as $T \rightarrow \infty$, $\lambda \rightarrow 0$, $n_r \rightarrow 0 \Rightarrow$ the probability (6)
 that a state is doubly occupied is negligible

\Downarrow
 so are a priori quantum effects

$\lambda \rightarrow$ measure of the 'quantum size' of an atom

λ large \Rightarrow system is very quantum

λ small \Rightarrow system is classical

\Downarrow
 classical methods are applicable

\Downarrow
 $\lambda \ll d$

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

can be derived by other means $-\beta \epsilon = \frac{p_i R}{Tm}$

$$Z_N = \frac{1}{N! h^{3N}} \int d\mathbf{r}_1 \dots d\mathbf{r}_N \int d\mathbf{p}_1 \dots d\mathbf{p}_N e^{-\beta \sum \frac{p_i^2}{2m}}$$

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

- this expression allows a probabilistic interpretation of the partition function

(7)

* N atoms M boxes

size of boxes λ^3

~~volume~~ number of boxes $M = \frac{V}{\lambda^3}$

$$\langle n_r \rangle = \frac{N}{M}$$

- "fermions": 1 particle in each box

how many ways can we do that?

$$\frac{M!}{N! (M-N)!} \stackrel{N \ll M}{\approx} \frac{M(M-1)\dots(M-N+1)}{N!} \approx \frac{M^N}{N!} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

- "bosons": any number of particles in a given box

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$$\Rightarrow \frac{(M+N+1)!}{N! (M+1)!} = \frac{(M+N+1)(M+N)\dots(M+2)}{N!}$$

$$\text{if } N \ll M \Rightarrow \frac{(M+N+1)!}{N! (M+1)!} \approx \frac{M^N}{N!} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$

- can calculate thermodynamic properties using Stirling approximation:

(8)

$$\ln N! = N \ln N - N$$

$$\ln Z_N = N \ln \frac{V}{\lambda^3} - N \ln N + N$$

$$= N \left(\ln \frac{V}{\lambda^3} + 1 \right)$$

$v = \frac{V}{N} \Rightarrow$ specific volume

$$= N \left[\ln \frac{V}{N} - 3 \ln \lambda + 1 \right]$$

$$E = - \frac{\partial \ln Z}{\partial \beta} = -3 \left(\frac{N}{\lambda} \right) \frac{\partial \lambda}{\partial \beta} = \frac{3N k_B T}{2}$$

$$C_V = \frac{3N k_B}{2} \quad (\text{violates third law} \Rightarrow \text{of course it does!} \Rightarrow \text{classical approximation})$$

free energy: $F = -kT \ln Z$

$$F = -NkT \left[\ln \frac{V}{N \lambda^3} + 1 \right]$$

$$S = - \frac{\partial F}{\partial T} \Big|_{V,N} = kN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2 \pi m k T}{h^2} \right) + \frac{5}{2} \right]$$

$$P = - \frac{\partial F}{\partial V} \Big|_T = \frac{N}{V} kT \Rightarrow \text{ideal gas law}$$

$$PV = \frac{2}{3} E \quad (\text{we derived this before by other means})$$

chemical potential of an ideal gas

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{T, V} = kT \ln(n \lambda^3) = kT \ln \frac{\lambda^3}{v}$$

(9)

if $v > \lambda^3 \Rightarrow \mu < 0 \rightarrow$ case for ideal gas \Rightarrow does this make sense?

$$\frac{\mu}{T} = - \left. \frac{\partial S}{\partial N} \right|_{E, V}$$

$$\frac{\mu}{T} = - [S(N+1) - S(N)]$$

indeed adding ~~part~~ a particle to the system increases the entropy (number of states)

- for interacting systems (also for non-interacting fermions) chemical potential can become ~~negative~~ positive

- at energy

$$\frac{1}{2} m \langle v^2 \rangle = \frac{E}{N} = \frac{3}{2} kT$$
