4 Statistical Ensembles : Summary

• *Distributions*: Let $\varrho(\boldsymbol{\varphi})$ be a normalized distribution on phase space. Then

$$\big\langle f(\boldsymbol{\varphi})\big\rangle = \mathsf{Tr}\,\big[\varrho(\boldsymbol{\varphi})\,f(\boldsymbol{\varphi})\big] = \int\! d\mu\;\varrho(\boldsymbol{\varphi})\,f(\boldsymbol{\varphi}) \quad ,$$

where $d\mu = W(\boldsymbol{\varphi})\prod_i d\varphi_i$ is the phase space measure. For a Hamiltonian system of N identical indistinguishable point particles in d space dimensions, we have

$$d\mu = \frac{1}{N!}\prod_{i=1}^N \frac{d^d\!p_i\, d^d\!q_i}{(2\pi\hbar)^d} \quad .$$

The $\frac{1}{N!}$ prefactor accounts for indistinguishability. Normalization means $\mathsf{Tr}\,\varrho = 1$.

• *Microcanonical ensemble* (μCE): $\varrho(\boldsymbol{\varphi}) = \delta\big(E - \hat{H}(\boldsymbol{\varphi})\big)/D(E)$, where $D(E) = \mathsf{Tr}\,\delta\big(E - \hat{H}(\boldsymbol{\varphi})\big)$ is the density of states and $\hat{H}(\boldsymbol{\varphi}) = \hat{H}(\boldsymbol{q},\boldsymbol{p})$ is the Hamiltonian. The energy E, volume V, and particle number N are held fixed. Thus, the density of states $D(E,V,N)$ is a function of all three variables. The statistical entropy is $S(E,V,N) = k_{\rm B}\ln D(E,V,N)$, where $k_{\rm B}$ is Boltzmann's constant. Since D has dimensions of E^{-1}, an arbitrary energy scale is necessary to convert D to a dimensionless quantity before taking the log. In the thermodynamic limit, one has

$$S(E,V,N) = Nk_{\rm B}\,\phi\bigg(\frac{E}{N},\frac{V}{N}\bigg) \quad .$$

The differential of E is defined to be $dE = T\,dS - p\,dV + \mu\,dN$, thus $T = \big(\frac{\partial E}{\partial S}\big)_{V,N}$ is the temperature, $p = -\big(\frac{\partial E}{\partial V}\big)_{S,N}$ is the pressure, and $\mu = \big(\frac{\partial E}{\partial N}\big)_{S,V}$ is the chemical potential. Note that E, S, V, and N are all extensive quantities, *i.e.* they are halved when the system itself is halved.

• *Ordinary canonical ensemble* (OCE): In the OCE, energy fluctuates, while V, N, and the temperature T are fixed. The distribution is $\varrho = Z^{-1}\,e^{-\beta\hat{H}}$, where $\beta = 1/k_{\rm B}T$ and $Z = \mathsf{Tr}\;e^{-\beta\hat{H}}$ is the partition function. Note that Z is the Laplace transform of the density of states: $Z = \int\! dE\;D(E)\,e^{-\beta E}$. The Boltzmann entropy is $S = -k_{\rm B}\,\mathsf{Tr}\,(\varrho\ln\varrho)$. This entails $F = E - TS$, where $F = -k_{\rm B}T\ln Z$ is the Helmholtz free energy, a Legendre transform of the energy E. From this we derive $dF = -S\,dT - p\,dV + \mu\,dN$.

• *Grand canonical ensemble* (GCE): In the GCE, both E and N fluctuate, while T, V, and chemical potential μ remain fixed. Then $\varrho = \Xi^{-1}\,e^{-\beta(\hat{H}-\mu\hat{N})}$, where $\Xi = \mathsf{Tr}\;e^{-\beta(\hat{H}-\mu\hat{N})}$ is the grand partition function and $\Omega = -k_{\rm B}T\ln\Xi$ is the grand potential. Assuming $[\hat{H},\hat{N}] = 0$, we can label states $|\,n\,\rangle$ by both energy and particle number. Then $P_n = \Xi^{-1}\,e^{-\beta(E_n-\mu N_n)}$. We also have $\Omega = E - TS - \mu N$, hence $d\Omega = -S\,dT - p\,dV - N\,d\mu$.

• *Thermodynamics*: From $E = \mathsf{Tr}\,(\varrho\,\hat{H})$, we have $dE = \mathsf{Tr}\,(\hat{H}\,d\varrho) + \mathsf{Tr}\,(\varrho\,d\hat{H}) = đQ - đW$, where $đQ = T\,dS$ and

$$đW = -\,\mathsf{Tr}\,(\varrho\,d\hat{H}) = -\sum_n P_n \sum_i \frac{\partial E_n}{\partial X_i}\,dX_i = \sum_i F_i\,dX_i \quad ,$$

with $P_n = Z^{-1} e^{-E_n/k_\mathrm{B}T}$. Here $F_i = -\big\langle \frac{\partial \hat{H}}{\partial X_i} \big\rangle$ is the generalized force conjugate to the generalized displacement X_i.

• *Thermal contact*: In equilibrium, two systems which can exchange energy satisfy $T_1 = T_2$. Two systems which can exchange volume satisfy $p_1/T_1 = p_2/T_2$. Two systems which can exchange particle number satisfy $\mu_1/T_1 = \mu_2/T_2$.

• *Gibbs-Duhem relation*: Since $E(S,V,N)$ is extensive, Euler's theorem for homogeneous functions guarantees that $E = TS - pV + \mu N$. Taking the differential, we obtain the equation $S\,dT - V\,dp + N\,d\mu = 0$, so there must be a relation among any two of the intensive quantities T, p, and μ.

• *Generalized susceptibilities*: Within the OCE[1], let $\hat{H}(\boldsymbol{\lambda}) = \hat{H}_0 - \sum_i \lambda_i\,\hat{Q}_i$, where $\hat{Q}_i$ are observables with $[\hat{Q}_i, \hat{Q}_j] = 0$. Then

$$Q_k(T,V,N;\boldsymbol{\lambda}) = \langle \hat{Q}_k \rangle = -\frac{\partial F}{\partial \lambda_k} \qquad , \qquad \chi_{kl}(T,V,N;\boldsymbol{\lambda}) = \frac{1}{V}\,\frac{\partial Q_k}{\partial \lambda_l} = -\frac{1}{V}\,\frac{\partial^2 F}{\partial \lambda_k\,\partial \lambda_l} \quad .$$

The quantities χ_{kl} are the generalized susceptibilities.

• *Ideal gases*: For $\hat{H} = \sum_{i=1}^N \frac{\boldsymbol{p}_i^2}{2m}$, one finds $Z(T,V,N) = \frac{1}{N!}\big(\frac{V}{\lambda_T^d}\big)^N$, where $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m k_\mathrm{B} T}}$ is the thermal wavelength. Thus $F = N k_\mathrm{B} T \ln(N/V) - \frac{1}{2} d N k_\mathrm{B} T \ln T + N a$, where a is a constant. From this one finds $p = -\big(\frac{\partial F}{\partial V}\big)_{T,N} = n k_\mathrm{B} T$, which is the ideal gas law, with $n = \frac{N}{V}$ the number density. The distribution of velocities in $d = 3$ dimensions is given by

$$f(\boldsymbol{v}) = \Big\langle \frac{1}{N} \sum_{i=1}^N \delta(\boldsymbol{v} - \boldsymbol{v}_i) \Big\rangle = \left(\frac{m}{2\pi k_\mathrm{B} T} \right)^{3/2} e^{-m\boldsymbol{v}^2/2k_\mathrm{B}T} \quad ,$$

and this leads to a speed distribution $\bar{f}(v) = 4\pi v^2 f(v)$.

• *Example*: For N noninteracting spins in an external magnetic field H, the Hamiltonian is $\hat{H} = -\mu_0 H \sum_{i=1}^N \sigma_i$, where $\sigma_i = \pm 1$. The spins, if on a lattice, are regarded as distinguishable. Then $Z = \zeta^N$, where $\zeta = \sum_{\sigma=\pm 1} e^{\beta\mu_0 H \sigma} = 2\cosh(\beta\mu_0 H)$. The magnetization and magnetic susceptibility are then

$$M = -\left(\frac{\partial F}{\partial H}\right)_{T,N} = N\mu_0 \tanh\!\left(\frac{\mu_0 H}{k_\mathrm{B} T}\right) \qquad , \qquad \chi = \frac{\partial M}{\partial H} = \frac{N\mu_0^2}{k_\mathrm{B} T}\,\mathrm{sech}^2\!\left(\frac{\mu_0 H}{k_\mathrm{B} T}\right) \quad .$$

• *Example*: For noninteracting particles with kinetic energy $\frac{\boldsymbol{p}^2}{2m}$ and internal degrees of freedom, $Z_N = \frac{1}{N!}\big(\frac{V}{\lambda_T^d}\big)^N \xi^N(T)$, where $\xi(T) = \mathsf{Tr}\; e^{-\beta \hat{h}_\mathrm{int}}$ is the partition function for the internal degrees of freedom, which include rotational, vibrational, and electronic excitations. One still has $pV = N k_\mathrm{B} T$, but the heat capacities at constant V and p are

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{V,N} = \tfrac{1}{2} d N k_\mathrm{B} - N T \varphi''(T) \qquad , \qquad C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = C_V + N k_\mathrm{B} \quad ,$$

where $\varphi(T) = -k_\mathrm{B} T \ln \xi(T)$.

[1] The generalization to the GCE is straightforward.