4 Statistical Ensembles: Summary

- **Distributions**: Let \( \varrho(\varphi) \) be a normalized distribution on phase space. Then
  \[
  \langle f(\varphi) \rangle = \text{Tr} \left[ \varrho(\varphi) f(\varphi) \right] = \int d\mu \, \varrho(\varphi) \, f(\varphi),
  \]
  where \( d\mu = W(\varphi) \prod_i d\varphi_i \) is the phase space measure. For a Hamiltonian system of \( N \) identical indistinguishable point particles in \( d \) space dimensions, we have
  \[
  d\mu = \frac{1}{N!} \prod_{i=1}^{N} \frac{d^4p_i \, d^4q_i}{(2\pi\hbar)^d}.
  \]
  The \( \frac{1}{N!} \) prefactor accounts for indistinguishability. Normalization means \( \text{Tr} \varrho = 1 \).

- **Microcanonical ensemble** (\( \mu \)CE): \( \varrho(\varphi) = \delta(E - \hat{H}(\varphi)) / \Omega(E) \), where \( \Omega(E) = \text{Tr} \delta(E - \hat{H}(\varphi)) \) is the density of states and \( \hat{H}(\varphi) = \hat{H}(q, p) \) is the Hamiltonian. The energy \( E \), volume \( V \), and particle number \( N \) are held fixed. Thus, the density of states \( \Omega(E,V,N) \) is a function of all three variables. The statistical entropy is \( S(E,V,N) = k_B \ln \Omega(E,V,N) \), where \( k_B \) is Boltzmann’s constant. Since \( \Omega \) has dimensions of \( E^{-1} \), an arbitrary energy scale is necessary to convert \( \Omega \) to a dimensionless quantity before taking the log. In the thermodynamic limit, one has
  \[
  S(E,V,N) = Nk_B \phi \left( \frac{E}{N}, \frac{V}{N} \right).
  \]
  The differential of \( E \) is defined to be \( dE = T \, dS - p \, dV + \mu \, dN \), thus \( T = (\partial E / \partial S)_{V,N} \) is the temperature, \( p = - (\partial E / \partial V)_{S,N} \) is the pressure, and \( \mu = (\partial E / \partial N)_{S,V} \) is the chemical potential. Note that \( E, S, V, \text{and } N \) 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 \( \beta = 1/k_BT \) and \( Z = \text{Tr} e^{-\beta \hat{H}} \) 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 \( S = -k_B \text{Tr} (\varrho \ln \varrho) \). This entails \( F = E - TS \), where \( F = -k_B T \ln Z \) 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 \( \mu \) remain fixed. Then \( \varrho = \Xi^{-1} e^{-\beta (\hat{H} - \mu N)} \), where \( \Xi = \text{Tr} e^{-\beta (\hat{H} - \mu N)} \) is the grand partition function and \( \Omega = -k_BT \ln \Xi \) 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 \( E = \text{Tr} (\varrho \, \hat{H}) \), we have \( dE = \text{Tr} (\hat{H} \, d\varrho) + \text{Tr} (\varrho \, d\hat{H}) = dQ - dW \), where \( dQ = T \, dS \) and
  \[
  dW = - \text{Tr} (\varrho \, d\hat{H}) = - \sum_n P_n \sum_i \frac{\partial E_n}{\partial X_i} dX_i = \sum_i F_i \, dX_i,
  \]
with \( P_n = Z^{-1}e^{-E_n/k_B T} \). Here \( F_i = -\langle \partial H/\partial X_i \rangle \) 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 \( \mu \).

- **Generalized susceptibilities:** Within the OCE\(^1\), let \( \dot{H}(\lambda) = \dot{H}_0 - \sum_i \lambda_i \dot{Q}_i \), where \( \dot{Q}_i \) are observables with \( [\dot{Q}_i; \dot{\dot{Q}}_j] = 0 \). Then
  \[
  Q_k(T, V, N; \lambda) = \langle \dot{Q}_k \rangle = -\frac{\partial F}{\partial \lambda_k}, \quad \chi_{kl}(T, V, N; \lambda) = \frac{1}{V} \frac{\partial Q_k}{\partial \lambda_l} = -\frac{1}{V} \frac{\partial^2 F}{\partial \lambda_k \partial \lambda_l}.
  \]
  The quantities \( \chi_{kl} \) are the generalized susceptibilities.

- **Ideal gases:** For \( \dot{H} = \sum_{i=1}^N \frac{k_i^2}{2m_i} \), one finds \( Z(T, V, N) = \frac{1}{N!} \left( \frac{V}{N \lambda_T} \right)^N \), where \( \lambda_T = \sqrt{\frac{2\pi k_B T}{m}} \) is the thermal wavelength. Thus \( F = Nk_B T \ln(N/V) - \frac{1}{2}dNk_B T \ln T + Na \), where \( a \) is a constant. From this one finds \( p = -\left( \frac{\partial F}{\partial \mu} \right)_{T,N} = nk_BT \), 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
  \[
  f(v) = \left( \frac{1}{N} \sum_{i=1}^N \delta(v - v_i) \right) = \left( \frac{m}{2\pi k_B T} \right)^{3/2} e^{-mv^2/2k_BT},
  \]
  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 \( \dot{H} = -\mu_0 H \sum_{i=1}^N \sigma_i \), where \( \sigma_i = \pm 1 \). The spins, if on a lattice, are regarded as distinguishable. Then \( Z = \zeta^N \), where \( \zeta = \sum_{\sigma=\pm 1} e^{i\mu_0 H \sigma} = 2 \cosh(\beta \mu_0 H) \). The magnetization and magnetic susceptibility are then
  \[
  M = -\left( \frac{\partial F}{\partial H} \right)_{T,N} = N\mu_0 \tanh \left( \frac{\mu_0 H}{k_B T} \right), \quad \chi = \frac{\partial M}{\partial H} = \frac{N\mu_0^2}{k_B T} \text{sech}^2 \left( \frac{\mu_0 H}{k_B T} \right).
  \]

- **Example:** For noninteracting particles with kinetic energy \( \frac{p^2}{2m} \) and internal degrees of freedom, \( Z_N = \frac{1}{N!} \left( \frac{V}{N \lambda_T} \right)^N \xi^N(T) \), where \( \xi(T) = \text{Tr} e^{-\beta \dot{H}_{\text{int}}} \) is the partition function for the internal degrees of freedom, which include rotational, vibrational, and electronic excitations. One still has \( pV = Nk_B T \), but the heat capacities at constant \( V \) and \( p \) are
  \[
  C_V = T \left( \frac{\partial S}{\partial T} \right)_{V,N} = \frac{1}{2}dNk_B - NT \frac{\partial^2}{\partial T^2} \varphi''(T), \quad C_p = T \left( \frac{\partial S}{\partial T} \right)_{p,N} = C_V + Nk_B,
  \]
  where \( \varphi(T) = -k_B T \ln \xi(T) \).

\(^1\)The generalization to the GCE is straightforward.