

Discrete random variables...

**Frequentist probability:**  $p = \lim_{N \rightarrow \infty} \frac{N_s}{N}$

**Elementary events:**  $A = \{a_j | j = 1, N_A\}$

**Normalization of Probability:**  $\sum_{j=1}^{N_A} P(a_j) = 1, \quad 0 \leq P(a_j) \leq 1$

**Joint probability:**  $P(a, b)$

**Marginal probability:**  $P_A(a) = \sum_b P(a, b)$

**Conditional probability:**  $P(a|b) = \frac{P(a, b)}{P_B(b)}, \quad P_B(b) \neq 0$

**Normalization of joint probability:**  $\sum_a \sum_b P(a, b) = 1, \quad 0 \leq P(a, b) \leq 1$

**Independent variables:**  $P(a, b) = P_A(a)P_B(b)$

**Conditional probability for independent variables:**  $P(a|b) = P_A(a)$

**Kronecker delta:**  $\delta_{x,y} = \begin{cases} 1 & x = y \\ 0 & x \neq y \end{cases}$

**Probability distribution:**  $P_F(f) = \sum_a \delta_{f,F(a)} P_A(a)$

**Mean:**  $\langle F \rangle \equiv \sum_a F(a) P_A(a)$

**Moment:**  $\langle F^n \rangle \equiv \sum_a F(a)^n P_A(a)$

**Central moment:**  $\langle (F - \langle F \rangle)^n \rangle \equiv \sum_a (F(a) - \langle F \rangle)^n P_A(a)$

**Variance:**  $\sigma^2 = \langle (F - \langle F \rangle)^2 \rangle = \sum_a (F(a) - \langle F \rangle)^2 P_A(a) = \langle F^2 \rangle - \langle F \rangle^2$

**Standard deviation:**  $\sigma \equiv \sqrt{\langle F^2 \rangle - \langle F \rangle^2}$

**Correlation function:**  $f_{FG} = \langle FG \rangle - \langle F \rangle \langle G \rangle$

**Mean of a sum:**  $\langle S \rangle = \langle F \rangle N$

**Variance of sum:**  $\sigma_S^2 = \sigma^2 N$

**Standard deviation of a sum:**  $\sigma_S = \sigma \sqrt{N}$

**Binomial coefficient:**  $\binom{N}{n} = \frac{N!}{n!(N-n)!}$

**Binomial distribution:**  $P(n|N) = \binom{N}{n} p^n (1-p)^{N-n}$

**Binomial theorem:**  $(p+q)^N = \sum_{n=0}^N \binom{N}{n} p^n q^{N-n}$

**Binomial identities:**  $\binom{N}{0} = \binom{N}{N} = 1, \quad \binom{N-1}{n} + \binom{N-1}{n-1} = \binom{N}{n}, \quad \binom{N}{n+1} = \frac{N-n}{n+1} \binom{N}{n}$

**Gaussian function:**  $g(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x-x_0)^2}{2\sigma^2}\right], \quad \langle x \rangle = x_0 = x_{max}, \quad \langle (x-x_0)^2 \rangle = \sigma^2$

**Gaussian approximation to binomial distribution:**  $P(n|N) \approx \frac{1}{\sqrt{2\pi p(1-p)N}} \exp\left[-\frac{(n-pN)^2}{2p(1-p)N}\right]$

Continuous random variables...

**Probability density:**  $P([a, b]) = \int_a^b P(x)dx, \quad \int_{\Omega} P(x)dx = 1$

**Marginal probability:**  $P_x(x) = \int_{-\infty}^{\infty} P(x, y)dy$

**Conditional probability:**  $P(y|x) = \frac{P(x, y)}{P_x(x)}$

**Baye's theorem:**  $P(y|x) = \frac{P(x|y)P_y(y)}{P_x(x)}$

**Independence:**  $P(x, y) = P_x(x)P_y(y)$

**Conditional probability for independent variables:**  $P(x|y) = P_x(x)$

**Average of a function:**  $\langle F(x) \rangle = \int_{-\infty}^{\infty} F(x)P(x)dx$

**Mean:**  $\langle x \rangle = \int_{-\infty}^{\infty} xP(x)dx$

**Moment:**  $\langle x^n \rangle = \int_{-\infty}^{\infty} x^n P(x)dx$

**Central moment:**  $\langle (x - \langle x \rangle)^n \rangle = \int_{-\infty}^{\infty} (x - \langle x \rangle)^n P(x)dx$

**Variance:**  $\sigma^2 = \langle (x - \langle x \rangle)^2 \rangle = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 P(x)dx = \langle x \rangle^2 - \langle x^2 \rangle$

**Standard deviation:**  $\sigma = \sqrt{\langle x \rangle^2 - \langle x^2 \rangle}$

**Gaussian integral:**  $G = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

**Stirling's Approximation:**  $\ln N! \approx N \ln N - N + 1, \quad \text{or} \quad N! \approx N^N \exp(1 - N)$

Entropy...

**Total entropy:**  $S_{total}(E, V, N) = S_q(V, N) + S_p(E, N)$

**Number probability distribution:**  $P(N_j, N_k) = \frac{N_T!}{N_j!N_k!} \left( \frac{V_j}{V_T} \right)^{N_j} \left( \frac{V_k}{V_T} \right)^{N_k}, \quad \text{where } N_j + N_k = N_T$

$P(N_j, N_k) = \frac{\Omega_q(N_j, V_j)\Omega_q(N_k, V_k)}{\Omega_q(N_T, V_T)}, \quad \text{where } \Omega_q(N, V) = \frac{V^N}{N!}$

**Configurational entropy (Boltzmann):**  $S_q(N, V) = k \ln \Omega_q(N, V) + kXN$

**Additivity of configurational entropy:**  $S_q(N_j, V_j, N_k, V_k) = S_q(N_j, V_j) + S_q(N_k, V_k)$

**Analytic approximation:**  $S_q(N, V) \approx kN \left[ \ln \left( \frac{V}{N} \right) + X \right]$

**Energy in subsystem of classical ideal gas:**  $E_{\alpha} = \sum_{i=1}^{N_{\alpha}} \frac{|\vec{p}_{\alpha,i}|^2}{2m}$

**Integral over momenta of all particles:**  $\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} (\cdots) dp_{\alpha,1}^3 \cdots dp_{\alpha,N_j}^3 \equiv \int_{-\infty}^{\infty} (\cdots) dp_{\alpha}$

**Energy probability distribution:**  $P(E_j, E_k) = \frac{\int_{-\infty}^{\infty} \delta \left( E_j - \sum_{i=1}^{N_j} \frac{|\vec{p}_{j,i}|^2}{2m} \right) dp_j \int_{-\infty}^{\infty} \delta \left( E_k - \sum_{\ell=1}^{N_k} \frac{|\vec{p}_{k,\ell}|^2}{2m} \right) dp_k}{\int_{-\infty}^{\infty} \delta \left( E_T - \sum_{i=1}^{N_T} \frac{|\vec{p}_i|^2}{2m} \right) dp}$

$$P(E_j, E_k) = \frac{\Omega_p(E_j, N_j)\Omega_p(E_k, N_k)}{\Omega_p(E_T, N_T)} \quad \text{where } \Omega_p(E_\alpha, N_\alpha) = \int_{-\infty}^{\infty} \delta\left(E_\alpha - \sum_{i=1}^{N_\alpha} \frac{|\vec{p}_{\alpha,i}|^2}{2m}\right) dp_\alpha$$

$$\Omega_p(E, N) = S_n m (2mE)^{3N/2-1} \quad \text{where } S_n = n \frac{\pi^{n/2}}{(n/2)!}$$

$$\textbf{Energy-dependent entropy: } S_p(E, N) = k \ln \Omega_p(E, N), \quad \text{where } \ln \Omega_p(E, N) \approx N \left[ \frac{3}{2} \ln \left( \frac{E}{N} \right) + X \right]$$

$$\text{Note the exact expression } \Omega_P(E, N) = \frac{3N\pi^{3N/2}}{(3N/2)!} m (2mE)^{3N/2-1}$$

$$\textbf{Entropy of a subsystem of a classical ideal gas: } S_j(E_j, V_j, N_j) = kN_j \left[ \frac{3}{2} \ln \left( \frac{E_j}{N_j} \right) + \ln \left( \frac{V_j}{N_j} \right) + X \right]$$

$$\text{Note that traditionally } X = \frac{3}{2} \ln \left( \frac{4\pi m}{3h^2} \right) + \frac{5}{2}$$

$$\textbf{Hamiltonian for Ideal gas: } H_\alpha(q_\alpha, p_\alpha) = \sum_{i=1}^{3N_\alpha} \frac{|\vec{p}_{\alpha,i}|^2}{2m}$$

$$\textbf{Hamiltonian for interacting particles: } H_\alpha(q_\alpha, p_\alpha) = \sum_{i=1}^{3N_\alpha} \frac{|\vec{p}_{\alpha,i}|^2}{2m} + \sum_{i=1}^{N_\alpha} \sum_{i'=1}^{N_\alpha} \phi(\vec{r}_{\alpha,i}, \vec{r}_{\alpha,i'})$$

$$\textbf{Entropy for interacting particles: } S_\alpha(E_\alpha, V_\alpha, N_\alpha) = k \ln \Omega_\alpha(E_\alpha, V_\alpha, N_\alpha)$$

$$\text{where } \Omega_\alpha(E_\alpha, V_\alpha, N_\alpha) = \frac{1}{h^{3N_\alpha} N_\alpha!} \int dq_\alpha \int dp_\alpha \delta(E_\alpha - H_\alpha) \quad \text{and } H_\alpha \text{ is the Hamiltonian for the subsystem } \alpha$$

Thermodynamic quantities...

$$\textbf{Maxwell-Boltzmann distribution for momentum of a single particle: } P(\vec{p}_1) = \left( \frac{\beta}{2\pi m} \right)^{3/2} \exp \left( -\beta \frac{|\vec{p}_1|^2}{2m} \right)$$

$$\textbf{Ideal gas law: } PV = \frac{N}{\beta} \quad \text{where } \beta = \frac{1}{k_B T} \quad \text{or } PV = Nk_B T$$

$$\textbf{Celsius to Kelvin conversion: } T [\text{K}] = T [^\circ\text{C}] + 273.15$$

$$\textbf{Equipartition theorem: } \frac{E}{N} = \frac{3}{2} k_B T$$

$$\textbf{Equations of state: } \left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{1}{T}, \quad \left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{P}{T}, \quad \left( \frac{\partial S}{\partial N} \right)_{E,V} = -\frac{\mu}{T}$$

Laws and postulates of thermodynamics...

**0<sup>th</sup> Law:** If two systems are in thermal equilibrium with a third system, they are in equilibrium with each other.

**1<sup>st</sup> Law:** Heat is a form of energy, and energy is conserved.

**2<sup>nd</sup> Law:** If a system is constrained, its entropy cannot decrease after the constraints are removed.

**3<sup>rd</sup> Law:** The entropy of any quantum mechanical system goes to constant as temperature goes to zero.

**1<sup>st</sup> Postulate:** There exist equilibrium states characterized by a small number of extensive parameters.

**2<sup>nd</sup> Postulate:** Without internal constraints, values of extensive parameters are those that maximize entropy.

**3<sup>rd</sup> Postulate:** Entropy of a composite system is additive.

**4<sup>th</sup> Postulate:** Entropy is a continuous and differentiable function of extensive parameters.

“Sometimes true” postulates:

**5<sup>th</sup> Postulate:** Entropy is an extensive function of extensive variables.

**6<sup>th</sup> Postulate:** The entropy is a monotonically increasing function of energy for equilibrium values of energy.

**7<sup>th</sup> Postulate (The Nernst Postulate):** The entropy of any system is non-negative.

Thermodynamic processes...

**Energy:**  $U = \langle E \rangle$

**First law in differential form:**  $dU = dQ + dW$ , for fixed  $N$

**Condition for exact differential:**  $\frac{\partial f}{\partial y} = \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial^2 F}{\partial x \partial y} = \frac{\partial g}{\partial x}$ , for  $dF = f(x, y)dx + g(x, y)dy$

**Integrating factor:**  $dG = r(x, y) dF$

**Fundamental relation:**  $dU = TdS - PdV + \mu dN$

Note that  $dQ = TdS$ ,  $dW = PdV$  for fixed number of particles.

**Entropy in heat cycle:**  $dS = \frac{dQ_H}{T_H} + \frac{dQ_L}{T_L} = 0$

**Work in heat cycle:**  $dW = \left(1 - \frac{T_L}{T_H}\right) dQ_H$

**Efficiency of heat engine:**  $\eta = \frac{dW}{dQ_H} = 1 - \frac{T_L}{T_H}$

**Coefficient of performance for refrigerator:**  $\epsilon_R = \frac{dQ_L}{-dW} = \frac{T_L}{T_H - T_L}$

**Coefficient of performance for heat pump:**  $\epsilon_{HP} = \frac{-dQ_H}{-dW} = \frac{T_H}{T_H - T_L}$

Thermodynamic potentials...

**Helmholtz free energy:**  $F(T, V, N) \equiv U[T] = U - TS$ ,  $dF = -SdT - PdV + \mu dN$

**Enthalpy:**  $H(S, P, N) \equiv U[P] = U + PV$ ,  $dH = TdS + VdP + \mu dN$

**Gibbs free energy:**  $G(T, P, N) \equiv U[T, P] = U - TS + PV$ ,  $dG = -SdT + VdP + \mu dN$

Extensivity...

**Condition for extensivity:**  $S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N)$

**Euler equation:**  $U = TS - PV + \mu N$

**Gibbs-Duhem relation:**  $d\mu = -\left(\frac{S}{N}\right)dT + \left(\frac{V}{N}\right)dP$

**Thermodynamic potentials for extensive systems:**

$F = U - TS = -PV + \mu N$ ,  $H = U + PV = TS + \mu N$ ,  $G = U - TS + PV = \mu N$

Thermodynamic identities...

**Coefficient of thermal expansion:**  $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_{P,N}$

**Isothermal compressibility:**  $\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{T,N}$

**Specific heat per particle at constant pressure:**  $c_P = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_{P,N}$

**Specific heat per particle at constant volume:**  $c_V = \frac{T}{N} \left( \frac{\partial S}{\partial T} \right)_{V,N}$

**Heat capacity:**  $C_P = Nc_P, \quad C_V = Nc_V$

**Jacobians:**  $\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial v}{\partial x}$

**Symmetry of Jacobians:**  $\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)} = \frac{\partial(v,u)}{\partial(y,x)} = -\frac{\partial(u,v)}{\partial(y,x)}$

**Jacobians as partial derivatives:**  $\frac{\partial(u,v)}{\partial(x,y)} = \left( \frac{\partial u}{\partial x} \right)_y$

**Chain rule for Jacobians:**  $\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(r,s)} \frac{\partial(r,s)}{\partial(x,y)}$

**Reciprocals of partial derivatives:**  $\left( \frac{\partial u}{\partial x} \right)_y = 1 / \left( \frac{\partial x}{\partial u} \right)_y$

**Specific heat identity:**  $c_P = c_V + \frac{\alpha^2 TV}{N\kappa_T}$

Extremum principles, Stability conditions, Phase transitions...

**Energy minimum principle:**  $dU = dW$ , for constant entropy and constant number of particles

**Stability with respect to volume changes:**  $\kappa_S \geq 0$

**Stability with respect to heat transfer:**  $c_V \geq 0$

**All stability conditions:**

$$U(S, V, N) \quad \left( \frac{\partial^2 U}{\partial S^2} \right)_{V,N} \geq 0 \quad \left( \frac{\partial^2 U}{\partial V^2} \right)_{S,N} \geq 0$$

$$F(T, V, N) \quad \left( \frac{\partial^2 F}{\partial T^2} \right)_{V,N} \leq 0 \quad \left( \frac{\partial^2 F}{\partial V^2} \right)_{S,N} \geq 0$$

$$H(S, P, N) \quad \left( \frac{\partial^2 H}{\partial S^2} \right)_{P,N} \geq 0 \quad \left( \frac{\partial^2 H}{\partial P^2} \right)_{S,N} \leq 0$$

$$G(T, P, N) \quad \left( \frac{\partial^2 G}{\partial T^2} \right)_{P,N} \leq 0 \quad \left( \frac{\partial^2 G}{\partial P^2} \right)_{T,N} \leq 0$$

**Helmholtz free energy of van der Waals fluid:**  $F_{vdW} = -Nk_B T \left[ \ln \left( \frac{V - bN}{N} \right) + \frac{3}{2} \ln(k_B T) + X \right] - a \left( \frac{N^2}{V} \right)$

**Equations of state for van der Waals fluid:**  $P = \frac{Nk_B T}{V - bN} - \frac{aN^2}{V^2}, \quad U = \frac{3}{2}Nk_B T - a \left( \frac{N^2}{V} \right)$

**Latent heat:**  $\ell = \frac{T\Delta S}{N} = \frac{L}{N}$

**Clausius-Clapeyron equation:**  $\frac{dP}{dT} = \frac{\ell N}{T\Delta V} = \frac{L}{T\Delta V}$

The Nernst postulate...

**Specific heat at low temperatures:**  $\lim_{T \rightarrow 0} c_X(T) = 0$

**Coefficient of thermal expansion at low temperatures:**  $\lim_{T \rightarrow 0} \alpha(T) = 0$

Canonical ensemble...

**Partition function for canonical ensemble:**  $Z = \frac{1}{h^{3N} N!} \int dq \int dp \exp[-\beta H(q, p)]$

**Canonical distribution:**  $P(p, q) = \frac{1}{h^{3N} N! Z} \exp[-\beta H(p, q)]$

**Liouville theorem:**  $\frac{dP}{dt} = 0$

**Helmholtz free energy of canonical ensemble:**  $F(T, V, N) = -k_B T \ln Z(T, V, N)$

**Specific heat in statistical mechanics:**  $\frac{1}{N k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2)$

**Forces independent of momentum:**  $Z = \frac{1}{h^{3N} N!} (2\pi m k_B T)^{3N/2} \int dq \exp \left[ -\beta \sum_{j=1}^N \sum_{i>j}^N \phi(\vec{r}_i, \vec{r}_j) \right]$

**Classical ideal gas (no forces):**  $Z = \frac{1}{h^{3N} N!} (2\pi m k_B T)^{3N/2} V^N$

**Hamiltonian for SHO:**  $H = \frac{1}{2} K x^2 + \frac{p^2}{2m}$

**Partition function for SHO:**  $Z = \frac{1}{\beta \hbar \omega}, \quad \omega = \sqrt{\frac{K}{m}}$

**Hamiltonian for N SHOs:**  $H = \sum_{j=1}^N \left( \frac{1}{2} K_j x_j^2 + \frac{p_j^2}{2m_j} \right)$

**Partition function for N SHOs:**  $Z = \prod_{j=1}^N \left( \frac{1}{\beta \hbar \omega_j} \right), \quad \omega_j = \sqrt{\frac{K_j}{m_j}}$