STATISTICAL-MECHANICS MASTER REVISION GUIDE

Compiled by Ansh Thukral

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1. Core Statistical Mechanics Logic

1.1 Microstates, Macrostates, Multiplicity

A **microstate** specifies every microscopic detail. A **macrostate** specifies only coarse information, such as the number of heads, energy quanta in a solid, or number of mutated DNA sites.

If all accessible microstates are equally likely,

$$P(\text{macrostate}) = \frac{\Omega_{\text{macro}}}{\Omega_{\text{total}}}.$$

For coin flips,

$$\Omega(n_H) = \binom{N}{n_H}, \qquad P(n_H) = \frac{\binom{N}{n_H}}{2^N}.$$

Example:

$$P(25 \text{ heads out of } 50) = \frac{\binom{50}{25}}{2^{50}}.$$

Large systems are dominated by the macrostate with overwhelmingly largest multiplicity. This is why equilibrium entropy is essentially the entropy of the most likely macrostate.

2. Entropy

2.1 Boltzmann Entropy

$$\boxed{S = k_B \ln \Omega.}$$

Often entropy is written in units of k_B, so

$$S = \ln \Omega.$$

2.2 Shannon/Gibbs Entropy

For a general probability distribution $\{p_i\}$,

$$\boxed{S = -k_B \sum_i p_i \ln p_i.}$$

If all Ω states are equally likely, $p_i = 1/\Omega$, then

$$S = -k_B \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = k_B \ln \Omega.$$

2.3 Statistical Meaning of the Second Law

For an isolated macroscopic system, equilibrium corresponds to the macrostate of largest multiplicity:

$$\Omega \uparrow \qquad \Longleftrightarrow \qquad S \uparrow .$$

Lower-entropy macrostates are not impossible; they are just fantastically unlikely for large systems.

3. Stirling Approximation and Large-N Tools

3.1 Stirling Approximation

Basic form:

$$\boxed{\ln n! \approx n \ln n - n.}$$

More accurate form:

$$n! \sim \sqrt{2\pi n} \left(\frac{n}{e}\right)^n.$$

Use this whenever factorials appear in multiplicities.

3.2 Binomial Distribution and Gaussian Approximation

For

$$P_N(n) = \binom{N}{n} p^n (1-p)^{N-n},$$

large N gives

$$P_N(n) \approx \frac{1}{\sqrt{2\pi N p(1-p)}} \exp\left[-\frac{(n-Np)^2}{2Np(1-p)}\right].$$

For fair coins, $p = 1/2$:

$$P_N(n) \approx \sqrt{\frac{2}{\pi N}} \exp\left[-\frac{2(n-N/2)^2}{N}\right].$$

4. Einstein Solids

4.1 Multiplicity

For an Einstein solid with N oscillators and q energy units,

$$\boxed{\Omega(N,q) = \binom{q+N-1}{q}.}$$

For large N, q,

$$\Omega(N,q) \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N.$$

Entropy:

$$S(N,q) = k_B \ln \Omega.$$

Using the approximation,

$$S(N,q) = k_B \left[q \ln\left(\frac{q+N}{q}\right) + N \ln\left(\frac{q+N}{N}\right)\right].$$

The omitted prefactors only give logarithmic corrections to $\ln \Omega$, negligible compared with extensive $O(N)$ entropy terms.

4.2 Temperature of an Einstein Solid

With

$$U = q\epsilon,$$
$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_N = \frac{1}{\epsilon}\left(\frac{\partial S}{\partial q}\right)_N.$$

Using the entropy above,

$$\frac{\partial S}{\partial q} = k_B \ln\left(\frac{q+N}{q}\right),$$

so

$$\boxed{T = \frac{\epsilon}{k_B \ln\left(\frac{q+N}{q}\right)}.}$$

4.3 Energy and Heat Capacity

Exponentiating,

$$e^{\epsilon/k_BT} = 1 + \frac{N}{q},$$

so

$$q = \frac{N}{e^{\epsilon/k_BT} - 1},$$

and

$$\boxed{U(T) = \frac{N\epsilon}{e^{\epsilon/k_BT} - 1}.}$$

Heat capacity:

$$\boxed{C = \frac{dU}{dT} = Nk_B\left(\frac{\epsilon}{k_BT}\right)^2 \frac{e^{\epsilon/k_BT}}{\left(e^{\epsilon/k_BT} - 1\right)^2}.}$$

High-temperature limit:

$$T \to \infty \qquad \Rightarrow \qquad C \to Nk_B.$$

More accurate high-temperature expansion:

$$\boxed{C = Nk_B\left[1 - \frac{1}{12}\left(\frac{\epsilon}{k_BT}\right)^2\right].}$$

4.4 Two Interacting Einstein Solids

For solids A and B,

$$q_{\text{tot}} = q_A + q_B,$$
$$\Omega_{\text{tot}}(q_A) = \Omega_A(N_A, q_A)\Omega_B(N_B, q_{\text{tot}} - q_A).$$

Equilibrium maximizes

$$S_{\text{tot}} = S_A + S_B.$$

Condition:

$$\frac{\partial S_A}{\partial q_A} = \frac{\partial S_B}{\partial q_B}.$$

Using the high-temperature form,

$$\ln\left(\frac{q_A + N_A}{q_A}\right) = \ln\left(\frac{q_B + N_B}{q_B}\right),$$

so

$$\boxed{\frac{q_A}{N_A} = \frac{q_B}{N_B}.}$$

The most probable macrostate has equal energy quanta per oscillator, not necessarily equal total energies.

5. Entropy of Mixing

For two distinguishable components A, B,

$$N_A = (1-x)N, \qquad N_B = xN.$$

Thermodynamic free-expansion derivation:

$$\Delta S_A = N_A k_B \ln\frac{V}{V_A}, \qquad \Delta S_B = N_B k_B \ln\frac{V}{V_B}.$$

With

$$V_A = (1-x)V, \qquad V_B = xV,$$

$$\boxed{\Delta S_{\text{mix}} = -Nk_B\left[(1-x)\ln(1-x) + x\ln x\right].}$$

For $x = 1/2$,

$$\boxed{\Delta S_{\text{mix}} = Nk_B \ln 2.}$$

Combinatorial derivation:

$$\Omega_{\text{mix}} = \binom{N}{N_B} = \frac{N!}{N_A! N_B!}, \qquad \Delta S_{\text{mix}} = k_B \ln \Omega_{\text{mix}}.$$

Using Stirling gives the same result.

6. DNA Sequence Entropy and Mutation Model

Each DNA site has four bases. Relative to a reference sequence, treat each site as either "same" or "different." Mutation probability per generation is μ.

Transition probabilities:

$$P(\text{same} \to \text{different}) = \mu,$$

$$P(\text{different} \to \text{same}) = \frac{\mu}{3},$$

$$P(\text{different} \to \text{different}) = 1 - \frac{\mu}{3}.$$

Let p_t be the probability a site differs from the reference after t generations. Then

$$p_{t+1} = (1-p_t)\mu + p_t\left(1 - \frac{\mu}{3}\right),$$

so

$$\boxed{p_{t+1} = \mu + \left(1 - \frac{4\mu}{3}\right)p_t.}$$

Given $p_0 = 0$,

$$p_t = \frac{3}{4}\left[1 - \left(1 - \frac{4\mu}{3}\right)^t\right].$$

Long-time limit:

$$\boxed{p_t \to \frac{3}{4}.}$$

If q of L sites differ,

$$P_t(q) = \binom{L}{q} p_t^q (1-p_t)^{L-q}.$$

Mean:

$$\langle q(t) \rangle = L p_t \to \frac{3L}{4}.$$

Number of sequences differing at exactly q sites:

$$\Omega(q) = \binom{L}{q} 3^q.$$

Entropy:

$$S(q) = \ln \Omega(q) = \ln \binom{L}{q} + q \ln 3.$$

Let

$$x = \frac{q}{L}.$$

Using Stirling,

$$S(x) \approx L\left[-x \ln x - (1-x)\ln(1-x) + x \ln 3\right].$$

Maximize:

$$\frac{1}{L}\frac{dS}{dx} = -\ln x + \ln(1-x) + \ln 3 = \ln\left(\frac{3(1-x)}{x}\right).$$

Set equal to zero:

$$\frac{3(1-x)}{x} = 1,$$

so

$$\boxed{x_{\max} = \frac{3}{4}.}$$

This matches the mutation long-time limit.

7. Random Walks, Delta Functions, and Characteristic Functions

7.1 Delta Function

Useful properties:

$$\int_{-\infty}^{\infty} \delta(x - x_0)\mathrm{d}x = 1,$$

$$\int_{-\infty}^{\infty} f(x)\delta(x - x_0)\mathrm{d}x = f(x_0).$$

Fourier representation:

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{ikx}\mathrm{d}k.$$

For a constraint such as

$$x = \sum_{i=1}^{N} s_i,$$

insert

$$\delta\left(x - \sum_{i=1}^{N} s_i\right).$$

7.2 General N-Step Distribution

For independent steps with one-step density $w(s)$,

$$\rho_N(x) = \int \cdots \int \left[\prod_{i=1}^{N} w(s_i)\right] \delta\left(x - \sum_{i=1}^{N} s_i\right) \mathrm{d}s_1 \cdots \mathrm{d}s_N.$$

Define the characteristic function

$$Q(k) = \int_{-\infty}^{\infty} w(s) e^{-iks} \mathrm{d}s.$$

Then

$$\boxed{\rho_N(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{ikx} [Q(k)]^N \mathrm{d}k.}$$

7.3 Fixed-Step Biased Random Walk

For

$$w(s) = p\delta(s - \ell) + q\delta(s + \ell), \qquad p + q = 1,$$
$$Q(k) = pe^{-ik\ell} + qe^{ik\ell}.$$

Then

$$\boxed{\rho_N(x) = \sum_{n=0}^{N} \binom{N}{n} p^n q^{N-n} \delta\left(x - (2n - N)\ell\right).}$$

Thus

$$P\left(X_N = (2n - N)\ell\right) = \binom{N}{n} p^n q^{N-n}.$$

8. Thermodynamic Identity and Equilibrium Conditions

8.1 Fundamental Thermodynamic Identity

For a simple compressible system:

$$\boxed{dU = T\mathrm{d}S - P\mathrm{d}V + \mu \mathrm{d}N.}$$

Conjugate pairs:

$$T \leftrightarrow S, \qquad -P \leftrightarrow V, \qquad \mu \leftrightarrow N.$$

Equivalent entropy derivatives:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N},$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N},$$
$$-\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V}.$$

8.2 Equilibrium Conditions

If systems exchange energy,

$$\boxed{T_A = T_B.}$$

If systems exchange volume,

$$\boxed{P_A = P_B.}$$

If systems exchange particles,

$$\boxed{\mu_A = \mu_B.}$$

Particles flow from higher μ to lower μ. Heat flows from higher T to lower T.

9. Heat, Entropy, and Irreversibility

9.1 Reversible Heat Transfer

$$\boxed{dS = \frac{\delta Q_{\text{rev}}}{T}.}$$

For finite reversible transfer at constant temperature:

$$\Delta S = \frac{Q_{\text{rev}}}{T}.$$

9.2 Heat Flow from Hot to Cold

If heat Q flows from hot reservoir T_h to cold reservoir T_c,

$$\Delta S_{\text{hot}} = -\frac{Q}{T_h}, \qquad \Delta S_{\text{cold}} = +\frac{Q}{T_c}.$$

Total:

$$\boxed{\Delta S_{\text{univ}} = Q\left(\frac{1}{T_c} - \frac{1}{T_h}\right) > 0}$$

for $T_c < T_h$.

9.3 Melting Ice Example

For ice of mass m at 0°C melting in a room at T_r:

$$Q_{\text{melt}} = mL_f, \qquad \Delta S_{\text{melt}} = \frac{mL_f}{T_0}.$$

Warming water from T_0 to T_r:

$$\Delta S_{\text{warm}} = \int_{T_0}^{T_r} \frac{mc\mathrm{d}T}{T} = mc\ln\frac{T_r}{T_0}.$$

Room entropy:

$$\Delta S_{\text{room}} = -\frac{Q_{\text{melt}} + mc(T_r - T_0)}{T_r}.$$

Universe:

$$\Delta S_{\text{univ}} = \Delta S_{\text{ice/water}} + \Delta S_{\text{room}} > 0.$$

9.4 Landauer Erasure

One bit initially has $\Omega_i = 2$, after erasure $\Omega_f = 1$.

$$\Delta S_{\text{memory}} = -k_B \ln 2.$$

The environment must gain at least

$$\Delta S_{\text{env,min}} = k_B \ln 2.$$

For N_{bits},

$$\Delta S_{\text{min}} = N_{\text{bits}} k_B \ln 2.$$

Minimum heat dumped into reservoir at temperature T:

$$\boxed{Q_{\text{min}} = T N_{\text{bits}} k_B \ln 2.}$$

For 1 GB:

$$N_{\text{bits}} = 8 \cdot 2^{30} = 2^{33}.$$

10. Thermodynamic Potentials

10.1 Internal Energy

$$U = U(S, V, N),$$

$$\boxed{dU = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N.}$$

Minimized at fixed S, V, N.

10.2 Enthalpy

$$H = U + PV.$$

$$dH = dU + P\mathrm{d}V + V\mathrm{d}P.$$

Using $dU = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$,

$$\boxed{dH = T\mathrm{d}S + V\mathrm{d}P + \mu\mathrm{d}N.}$$

Natural variables:

$$H = H(S, P, N).$$

Minimized at fixed S, P, N.

10.3 Helmholtz Free Energy

$$F = U - TS.$$

$$dF = dU - T\mathrm{d}S - S\mathrm{d}T.$$

Thus

$$\boxed{dF = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N.}$$

Natural variables:

$$F = F(T, V, N).$$

Minimized at fixed T, V, N.

Derivatives:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N},$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N},$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

10.4 Gibbs Free Energy

$$G = U - TS + PV = F + PV = H - TS.$$

$$\boxed{dG = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N.}$$

Natural variables:

$$G = G(T, P, N).$$

Minimized at fixed T, P, N. For a pure phase,

$$G = N\mu.$$

Molar form:

$$g = \mu.$$

Derivatives:

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N},$$

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,N},$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}.$$

At fixed pressure,

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_{P} = -S.}$$

So the phase with larger entropy has a more steeply decreasing $G(T)$ curve.

10.5 Grand Potential

$$\Phi = U - TS - \mu N.$$

$$d\Phi = dU - T\mathrm{d}S - S\mathrm{d}T - \mu\mathrm{d}N - N\mathrm{d}\mu.$$

Using $dU = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$,

$$\boxed{d\Phi = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu.}$$

Natural variables:

$$\Phi = \Phi(T, V, \mu).$$

Derivatives:

$$S = -\left(\frac{\partial\Phi}{\partial T}\right)_{V,\mu},$$

$$P = -\left(\frac{\partial\Phi}{\partial V}\right)_{T,\mu},$$

$$N = -\left(\frac{\partial\Phi}{\partial \mu}\right)_{T,V}.$$

Minimized at fixed T, V, μ. For a macroscopic homogeneous system,

$$\boxed{\Phi = -PV.}$$

11. Maxwell Relations

Use equality of mixed partial derivatives.

11.1 From $U(S, V)$

$$dU = T\mathrm{d}S - P\mathrm{d}V.$$

So

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \qquad -P = \left(\frac{\partial U}{\partial V}\right)_S.$$

Maxwell relation:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V.}$$

11.2 From $H(S, P)$

$$dH = T\mathrm{d}S + V\mathrm{d}P.$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \qquad V = \left(\frac{\partial H}{\partial P}\right)_S.$$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P.}$$

11.3 From $F(T, V)$

$$dF = -S\mathrm{d}T - P\mathrm{d}V.$$

$$-S = \left(\frac{\partial F}{\partial T}\right)_V, \qquad -P = \left(\frac{\partial F}{\partial V}\right)_T.$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V.}$$

11.4 From $G(T, P)$

$$dG = -S\mathrm{d}T + V\mathrm{d}P.$$

$$-S = \left(\frac{\partial G}{\partial T}\right)_P, \qquad V = \left(\frac{\partial G}{\partial P}\right)_T.$$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P.}$$

12. Heat Capacities and Response Functions

12.1 Heat Capacities

At constant volume:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V.$$

From $dU = T\mathrm{d}S - P\mathrm{d}V$, at fixed V,

$$dU = T\mathrm{d}S.$$

Therefore

$$\boxed{C_V = T\left(\frac{\partial S}{\partial T}\right)_V.}$$

At constant pressure:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

From $dH = T\mathrm{d}S + V\mathrm{d}P$, at fixed P,

$$dH = T\mathrm{d}S.$$

Therefore

$$\boxed{C_P = T\left(\frac{\partial S}{\partial T}\right)_P.}$$

12.2 Response Functions

Thermal expansion coefficient:

$$\boxed{\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P.}$$

Isothermal compressibility:

$$\boxed{\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.}$$

Isentropic compressibility:

$$\boxed{\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S.}$$

12.3 General Identity for $C_P - C_V$

$$\boxed{C_P = C_V + \frac{TV\beta^2}{\kappa_T}.}$$

For ordinary stable matter,

$$T > 0, \qquad V > 0, \qquad \beta^2 \geq 0, \qquad \kappa_T > 0,$$

so

$$\boxed{C_P \geq C_V.}$$

For an ideal gas,

$$PV = Nk_BT, \qquad \beta = \frac{1}{T}, \qquad \kappa_T = \frac{1}{P}.$$

Then

$$C_P - C_V = \frac{TV(1/T^2)}{1/P} = \frac{PV}{T} = Nk_B.$$

For n moles,

$$C_P - C_V = nR.$$

12.4 Compressibility Identity

$$\boxed{\kappa_T = \kappa_S + \frac{TV\beta^2}{C_P}.}$$

For an ideal gas,

$$\kappa_S = \frac{1}{\gamma P}, \qquad \kappa_T = \frac{1}{P}, \qquad \gamma = \frac{C_P}{C_V}.$$

12.5 Third Law Consequence

Third law statement:

$$S(T = 0, P) = \text{constant independent of } P.$$

Then

$$\left(\frac{\partial S}{\partial P}\right)_T \to 0 \qquad \text{as } T \to 0.$$

Using the Maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P,$$

we get

$$\left(\frac{\partial V}{\partial T}\right)_P \to 0.$$

Thus

$$\boxed{\beta \to 0 \qquad \text{as } T \to 0.}$$

13. Ideal Gas Thermodynamics

13.1 Ideal Gas Law

$$\boxed{PV = Nk_BT = nRT.}$$

13.2 Monatomic Ideal Gas Internal Energy

Equipartition:

$$\boxed{U = \frac{3}{2}Nk_BT.}$$

Using the ideal gas law:

$$\boxed{U = \frac{3}{2}PV.}$$

13.3 Diatomic Ideal Gas at Room Temperature

For a rigid diatomic molecule at room temperature:

- 3 translational degrees of freedom,
- 2 rotational degrees of freedom,
- vibrations approximately frozen out.

So

$$f = 5.$$

Internal energy:

$$\boxed{U = \frac{5}{2}nRT.}$$

Enthalpy:

$$H = U + PV = \frac{5}{2}nRT + nRT,$$

so

$$\boxed{H = \frac{7}{2}nRT.}$$

For one mole:

$$U = \frac{5}{2}RT, \qquad H = \frac{7}{2}RT.$$

13.4 General Equipartition

Each quadratic degree of freedom contributes

$$\frac{1}{2}k_BT$$

to the average energy. Thus

$$\boxed{U = \frac{f}{2}Nk_BT.}$$

Heat capacity:

$$\boxed{C_V = \frac{f}{2} N k_B.}$$

For one mole:

$$C_V = \frac{f}{2} R.$$

For an ideal gas:

$$C_P = C_V + N k_B,$$

or per mole

$$C_P = C_V + R.$$

14. Sackur–Tetrode Equation and Ideal Gas Entropy

For a monatomic ideal gas,

$$\boxed{S = N k_B \left[\ln \left(\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) + \frac{5}{2} \right].}$$

In terms of number density $n = N/V$,

$$\frac{S}{N k_B} = \ln \left[\frac{1}{n} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] + \frac{5}{2}.$$

Equivalent energy form:

$$S(E, V, N) \simeq N k_B \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right) + \frac{5}{2} \right].$$

Temperature from entropy:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{3 N k_B}{2E},$$

so

$$E = \frac{3}{2} N k_B T.$$

Pressure:

$$P = T \left(\frac{\partial S}{\partial V} \right)_{E,N} = T \frac{N k_B}{V},$$

so

$$PV = N k_B T.$$

14.1 Low-Temperature Failure of Sackur–Tetrode

Set $S = 0$:

$$\ln \left[\frac{1}{n} \left(\frac{2\pi m k_B T_*}{h^2} \right)^{3/2} \right] + \frac{5}{2} = 0.$$

Then

$$\frac{1}{n} \left(\frac{2\pi m k_B T_*}{h^2} \right)^{3/2} = e^{-5/2}.$$

Solving:

$$\boxed{T_* = \frac{h^2}{2\pi m k_B} n^{2/3} e^{-5/3}.}$$

For helium at room-temperature density and atmospheric pressure,

$$T_* \approx 1.2 \times 10^{-2}\,\mathrm{K}.$$

Below this, the Sackur–Tetrode equation would predict negative entropy, showing classical ideal-gas theory has broken down.

15. Chemical Potential

15.1 General Definition

$$\boxed{\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}.}$$

Entropy form:

$$\boxed{\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}.}$$

For a pure phase:

$$G = N\mu.$$

15.2 Monatomic Ideal Gas Chemical Potential

$$\boxed{\mu = -k_B T \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right].}$$

Using $P = Nk_BT/V$,

$$\boxed{\mu = -k_B T \ln\left[\frac{k_B T}{P}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right].}$$

15.3 Ideal Gas Mixture and Partial Pressure

For species i,

$$P_i = x_i P, \qquad x_i = \frac{N_i}{N_{\text{total}}}.$$

The chemical potential is the same as if species i were alone at partial pressure P_i:

$$\boxed{\mu_i(T, P_i) = -k_B T \ln\left[\frac{k_B T}{P_i}\left(\frac{2\pi m_i k_B T}{h^2}\right)^{3/2}\right].}$$

15.4 Gas in a Gravitational Field

Potential energy:

$$U_{\text{grav}} = mgz.$$

Chemical potential at height z:

$$\boxed{\mu(z) = \mu_{\text{ideal}} + mgz.}$$

For ideal gas:

$$\mu(z) = -k_B T \ln\left[\frac{V}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right] + mgz.$$

Diffusive equilibrium requires

$$\mu(z) = \mu(0).$$

Then

$$\boxed{N(z) = N(0)e^{-mgz/k_B T}.}$$

This is the Boltzmann factor in gravity.

16. Ideal Gas in a Finite Gravitational Box

Gas in a box $0 \le z \le L$ at temperature T. Kinetic energy is unaffected by gravity:

$$\boxed{\langle K\rangle = \frac{3}{2}k_B T.}$$

Potential energy:

$$U(z) = mgz.$$

Boltzmann distribution:

$$p(z) \propto e^{-\beta mgz}.$$

Average height:

$$\langle z\rangle = \frac{\int_0^L z e^{-\beta mgz}\mathrm{d}z}{\int_0^L e^{-\beta mgz}\mathrm{d}z}.$$

Let

$$a = \beta mg.$$

Then

$$\langle z\rangle = \frac{1}{a} - \frac{L}{e^{aL}-1}.$$

Thus

$$\boxed{\langle U\rangle = mg\langle z\rangle = k_B T - \frac{mgL}{e^{mgL/k_B T}-1}.}$$

Limits:

$$mgL \ll k_B T \qquad \Rightarrow \qquad \langle z\rangle \to \frac{L}{2}, \qquad \langle U\rangle \to \frac{mgL}{2}.$$

Large gravity or low temperature:

$$\langle U\rangle \to k_B T.$$

17. Canonical Ensemble

17.1 Canonical Probability

For states s with energies E_s,

$$\boxed{P_s = \frac{e^{-\beta E_s}}{Z}, \qquad Z = \sum_s e^{-\beta E_s}, \qquad \beta = \frac{1}{k_B T}.}$$

17.2 Average Energy

$$\boxed{U = \langle E \rangle = \sum_s P_s E_s.}$$

Equivalent partition-function formula:

$$\boxed{U = -\frac{\partial}{\partial \beta} \ln Z.}$$

17.3 Helmholtz Free Energy and Entropy

$$\boxed{F = -k_B T \ln Z.}$$

Since

$$F = U - TS,$$

$$\boxed{S = \frac{U - F}{T}.}$$

Also,

$$S = -k_B \sum_s P_s \ln P_s.$$

17.4 Shifting All Energy Levels

If

$$E'_s = E_s + \epsilon,$$

then

$$Z' = \sum_s e^{-\beta(E_s+\epsilon)} = e^{-\beta\epsilon} Z.$$

Probabilities:

$$P'_s = \frac{e^{-\beta(E_s+\epsilon)}}{Z'} = P_s.$$

Energy:

$$U' = U + \epsilon.$$

Free energy:

$$F' = -k_B T \ln Z' = F + \epsilon.$$

Entropy:

$$S' = \frac{U' - F'}{T} = \frac{U - F}{T} = S.$$

So shifting the zero of energy changes Z, U, and F, but not probabilities or entropy.

18. Maximum Entropy and the Canonical Distribution

Given arbitrary probabilities P_s,

$$S = -k_B \sum_s P_s \ln P_s.$$

Canonical probabilities:

$$P_s^{(0)} = \frac{e^{-\beta E_s}}{Z}.$$

Assume both distributions have the same mean energy:

$$\sum_s E_s P_s = \sum_s E_s P_s^{(0)} = E.$$

Then

$$S - S_0 = k_B \sum_s P_s \ln \frac{P_s^{(0)}}{P_s}.$$

Using

$$\ln x < x - 1,$$

with equality only at $x = 1$,

$$\ln \frac{P_s^{(0)}}{P_s} \leq \frac{P_s^{(0)}}{P_s} - 1.$$

Therefore

$$S - S_0 \leq k_B \sum_s P_s \left(\frac{P_s^{(0)}}{P_s} - 1 \right) = k_B \left(\sum_s P_s^{(0)} - \sum_s P_s \right) = 0.$$

Thus

$$\boxed{S_0 \geq S.}$$

Equality only if

$$P_s = P_s^{(0)}$$

for every state. Therefore, for fixed mean energy, the canonical distribution maximizes entropy.

19. Two-Level and Three-Level Systems

19.1 Two-Level System

Energies:

$$E_0 = 0, \qquad E_1 = \epsilon.$$

Partition function:

$$Z = 1 + e^{-\beta\epsilon}.$$

Free energy:

$$\boxed{F = -k_B T \ln\left(1 + e^{-\beta\epsilon}\right).}$$

Probabilities:

$$P_0 = \frac{1}{1 + e^{-\beta\epsilon}}, \qquad P_1 = \frac{e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}.$$

Average energy:

$$U = \epsilon P_1 = \frac{\epsilon e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}} = \frac{\epsilon}{e^{\beta\epsilon} + 1}.$$

19.2 Three-Level Example

Energies:

$$E_i = -0.05\,\text{eV}, \quad 0, \quad +0.05\,\text{eV}.$$

Partition function:

$$Z = e^{+\beta 0.05} + 1 + e^{-\beta 0.05}.$$

Probabilities:

$$P_i = \frac{e^{-\beta E_i}}{Z}.$$

If all energies shift by constant C, probabilities do not change.

20. Quantum Harmonic Oscillator / Einstein Oscillator

Energy levels with zero-point omitted:

$$E_n = n\epsilon, \qquad n = 0, 1, 2, \ldots$$

Partition function:

$$Z = \sum_{n=0}^{\infty} e^{-\beta n\epsilon}.$$

Let

$$x = e^{-\beta\epsilon}.$$

Then

$$Z = 1 + x + x^2 + \cdots,$$

so

$$\boxed{Z = \frac{1}{1 - e^{-\beta\epsilon}}.}$$

Average energy:

$$U = -\frac{\partial}{\partial\beta} \ln Z.$$

Since

$$\ln Z = -\ln\left(1 - e^{-\beta\epsilon}\right),$$

$$\boxed{U = \frac{\epsilon}{e^{\beta\epsilon} - 1}.}$$

Low-temperature limit:

$$k_B T \ll \epsilon \qquad \Rightarrow \qquad U \approx 0.$$

High-temperature limit:

$$k_B T \gg \epsilon \qquad \Rightarrow \qquad e^{\beta\epsilon} - 1 \approx \beta\epsilon,$$

so

$$U \approx \frac{1}{\beta} = k_B T.$$

For N independent oscillators:

$$Z_N = Z^N = \left(\frac{1}{1 - e^{-\beta\epsilon}}\right)^N.$$

Free energy:

$$F = -k_B T \ln Z_N = N k_B T \ln\left(1 - e^{-\beta\epsilon}\right).$$

Entropy: let

$$x = \frac{\epsilon}{k_B T}.$$

Then

$$\boxed{S = N k_B \left[\frac{x}{e^x - 1} - \ln\!\left(1 - e^{-x}\right) \right].}$$

21. Translational Partition Function

For one particle in volume V,

$$Z_{\mathrm{tr}} = \frac{1}{h^3} \int_V \mathrm{d}^3 r \int \mathrm{d}^3 p \exp\left[-\frac{p^2}{2 m k_B T} \right].$$

Position integral:

$$\int_V \mathrm{d}^3 r = V.$$

Momentum integral factors:

$$\int \mathrm{d}^3 p \, e^{-p^2/(2mk_BT)} = \left[\int_{-\infty}^{\infty} e^{-p_x^2/(2mk_BT)} \mathrm{d}p_x \right]^3.$$

Using

$$\int_{-\infty}^{\infty} e^{-a x^2} \mathrm{d}x = \sqrt{\frac{\pi}{a}},$$

$$\int_{-\infty}^{\infty} e^{-p_x^2/(2mk_BT)} \mathrm{d}p_x = \sqrt{2\pi m k_B T}.$$

Thus

$$\boxed{Z_{\mathrm{tr}} = \frac{V (2\pi m k_B T)^{3/2}}{h^3}.}$$

Thermal de Broglie volume:

$$v_Q = \left(\frac{h}{\sqrt{2\pi m k_B T}} \right)^3.$$

Then

$$Z_{\mathrm{tr}} = \frac{V}{v_Q}.$$

For N indistinguishable ideal-gas particles,

$$Z_N = \frac{Z_1^N}{N!}.$$

22. Rigid Diatomic Rotor

Rotational partition function:

$$Z_{\mathrm{rot}}(\tau) = \sum_{j=0}^{\infty} (2j+1) \exp\left[-\frac{j(j+1)}{\tau} \right],$$

where

$$\tau = \frac{k_B T}{\epsilon}.$$

High-temperature approximation:

$$\boxed{Z_{\mathrm{rot}} \approx \tau.}$$

More accurately, at large τ,

$$Z_{\text{rot}}(\tau) = \tau + \frac{1}{3} + O\left(\frac{1}{\tau}\right).$$

So $Z_{\text{rot}} \approx \tau$ is slightly low by about $1/3$ at large τ.

For N_2, if symmetry factor 2 is included:

$$Z_{\text{rot}} \approx \frac{k_B T}{2\epsilon}.$$

23. Maxwell Velocity and Speed Distributions

23.1 Velocity Components

In equilibrium, v_x, v_y, v_z are independent Gaussians:

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0.$$

Equipartition:

$$\frac{1}{2} m \left\langle v_x^2 \right\rangle = \frac{1}{2} k_B T,$$

so

$$\boxed{\left\langle v_x^2 \right\rangle = \left\langle v_y^2 \right\rangle = \left\langle v_z^2 \right\rangle = \frac{k_B T}{m}.}$$

Thus

$$\boxed{\left\langle v^2 \right\rangle = \left\langle v_x^2 + v_y^2 + v_z^2 \right\rangle = \frac{3 k_B T}{m}.}$$

Odd averages vanish by symmetry:

$$\langle v_x \rangle = 0, \qquad \left\langle v^2 v_x \right\rangle = 0, \qquad \left\langle v^3 v_y \right\rangle = 0.$$

For constant b,

$$\left\langle (v_x + b v_y)^2 \right\rangle = \left\langle v_x^2 \right\rangle + 2b \left\langle v_x v_y \right\rangle + b^2 \left\langle v_y^2 \right\rangle.$$

Since components are independent and zero mean,

$$\langle v_x v_y \rangle = 0,$$

so

$$\boxed{\left\langle (v_x + b v_y)^2 \right\rangle = \frac{k_B T}{m}(1 + b^2).}$$

Also,

$$\boxed{\left\langle v_x^2 v_y^2 \right\rangle = \left\langle v_x^2 \right\rangle \left\langle v_y^2 \right\rangle = \left(\frac{k_B T}{m}\right)^2.}$$

23.2 3D Maxwell Speed Distribution

$$D_3(v) \propto v^2 e^{-mv^2/(2k_B T)}.$$

Normalized:

$$D_3(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/(2k_B T)}.$$

Most probable speed:

$$\boxed{v_{\mathrm{mp}} = \sqrt{\frac{2k_BT}{m}}.}$$

Mean speed:

$$\boxed{\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}}.}$$

Root-mean-square speed:

$$\boxed{v_{\mathrm{rms}} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3k_BT}{m}}.}$$

Ordering:

$$\boxed{v_{\mathrm{mp}} < \langle v\rangle < v_{\mathrm{rms}}.}$$

23.3 2D Maxwell Distribution

Velocity-vector probability density:

$$f(v_x, v_y) = C\exp\left[-\frac{m(v_x^2+v_y^2)}{2k_BT}\right].$$

Normalization gives

$$\boxed{f(v_x, v_y) = \frac{m}{2\pi k_BT}\exp\left[-\frac{m(v_x^2+v_y^2)}{2k_BT}\right].}$$

Convert to polar velocity coordinates:

$$\mathrm{d}v_x\mathrm{d}v_y = v\mathrm{d}v\mathrm{d}\theta.$$

Thus

$$D_2(v) = \int_0^{2\pi} f(v_x, v_y)v\mathrm{d}\theta.$$

$$\boxed{D_2(v) = \frac{m}{k_BT}v\exp\left[-\frac{mv^2}{2k_BT}\right], \qquad v \geq 0.}$$

Most probable speed maximizes

$$ve^{-av^2}, \qquad a = \frac{m}{2k_BT}.$$

$$\frac{d}{dv}\ln D_2(v) = \frac{1}{v} - 2av = 0.$$

So

$$v^2 = \frac{1}{2a} = \frac{k_BT}{m}.$$

$$\boxed{v_{\mathrm{mp}}^{(2D)} = \sqrt{\frac{k_BT}{m}} = \frac{1}{\sqrt{2}}v_{\mathrm{mp}}^{(3D)}.}$$

24. Energy Fluctuations

For energies E_i, average:

$$\langle E \rangle = \frac{1}{N} \sum_i E_i.$$

Deviation:

$$\Delta E_i = E_i - \langle E \rangle .$$

Variance:

$$\sigma_E^2 = \left\langle (\Delta E)^2 \right\rangle .$$

Identity:

$$\boxed{\sigma_E^2 = \left\langle E^2 \right\rangle - \langle E \rangle^2 .}$$

Proof:

$$\left\langle (E - \langle E \rangle)^2 \right\rangle = \left\langle E^2 - 2E \langle E \rangle + \langle E \rangle^2 \right\rangle = \left\langle E^2 \right\rangle - \langle E \rangle^2 .$$

In the canonical ensemble,

$$\sigma_E^2 = \left\langle E^2 \right\rangle - \langle E \rangle^2 = k_B T^2 C_V .$$

Equivalently,

$$\sigma_E^2 = \frac{\partial^2}{\partial \beta^2} \ln Z.$$

25. Engines and Thermodynamic Cycles

25.1 First Law Convention

The course uses W as work done by the gas:

$$\boxed{\Delta U = Q - W.}$$

So

$$Q = \Delta U + W.$$

If $\Delta U = 0$,

$$Q = W.$$

For an ideal gas, $\Delta U = 0$ whenever T is unchanged, equivalently PV is unchanged.

25.2 Work on a P-V Diagram

Work done by gas:

$$W = \int P \mathrm{d}V.$$

Net work over a cycle:

$$W_{\text{net}} = \oint P \mathrm{d}V.$$

For a clockwise cycle,

$$W_{\text{net}} > 0.$$

For a counterclockwise cycle,

$$W_{\text{net}} < 0.$$

Area enclosed equals net work.

25.3 Carnot Efficiency

For a reversible engine operating between T_h and T_c,

$$\boxed{\eta_{\text{Carnot}} = 1 - \frac{T_c}{T_h}.}$$

Always use kelvin.

25.4 Stirling Engine

Idealized cycle:

1. isothermal expansion at T_h,
2. constant-volume cooling,
3. isothermal compression at T_c,
4. constant-volume heating.

Let

$$r = \frac{V_{\max}}{V_{\min}}, \qquad \tau = \frac{T_c}{T_h}.$$

Isothermal work:

$$W_{\text{iso}} = nRT \ln \frac{V_f}{V_i}.$$

Hot isothermal expansion:

$$W_{AB} = Q_{AB} = nRT_h \ln r.$$

Cold isothermal compression:

$$W_{CD} = Q_{CD} = -nRT_c \ln r.$$

Net work:

$$W_{\text{net}} = nR(T_h - T_c) \ln r.$$

Without regenerator:

$$Q_h = nRT_h \ln r + nC_V(T_h - T_c).$$

Efficiency:

$$\boxed{\eta = \frac{(1-\tau)\ln r}{\ln r + (C_V/R)(1-\tau)}.}$$

Since denominator is bigger than $\ln r$,

$$\eta < 1 - \tau = \eta_{\text{Carnot}}.$$

With perfect regenerator:

$$Q_h = nRT_h \ln r, \qquad Q_c = nRT_c \ln r,$$

so

$$\boxed{\eta = 1 - \frac{T_c}{T_h}.}$$

26. Thermodynamic Cycle Diagrams

26.1 Ideal Gas Isotherms

For an ideal gas,

$$PV = Nk_BT.$$

Thus points with same PV lie on the same isotherm. On a P-V diagram,

$$P = \frac{Nk_BT}{V}.$$

Higher T means higher isotherm.

26.2 Ideal Gas Entropy

For monatomic ideal gas:

$$S = nC_V \ln T + nR \ln V + \text{constant}, \qquad C_V = \frac{3}{2}R.$$

So

$$S = nR\left(\frac{3}{2}\ln T + \ln V\right) + \text{constant}.$$

Same T, larger V means larger S. Same V, larger T means larger S.

For the midterm points,

$$p_AV_A = 2, \qquad p_BV_B = 6, \qquad p_CV_C = 6, \qquad p_DV_D = 2.$$

So A, D are on low T, and B, C are on high T. Since D has same T as A but larger V, $S_D > S_A$. Since C has same T as B but larger V, $S_C > S_B$. Therefore

$$\boxed{S_A < S_D < S_B < S_C.}$$

27. Polymers, Rubber Bands, and Stretched Rods

27.1 One-Dimensional Polymer Model

Chain of N links, each length ℓ, pointing right or left. Let N_R point right and $N_L = N - N_R$ point left. Length:

$$L = (N_R - N_L)\ell = (2N_R - N)\ell.$$

So

$$N_R = \frac{1}{2}\left(N + \frac{L}{\ell}\right).$$

Multiplicity:

$$\Omega = \binom{N}{N_R}.$$

Entropy:

$$S = k_B \ln \Omega.$$

Using Stirling:

$$S \approx k_B \left[N \ln N - N_R \ln N_R - (N - N_R)\ln(N - N_R)\right].$$

27.2 Thermodynamic Identity for a Stretched System

For length L and tensile force f,

$$\boxed{dU = T\mathrm{d}S + f\mathrm{d}L.}$$

This sign differs from $dU = T\mathrm{d}S - P\mathrm{d}V$ because stretching work increases length.

27.3 Entropic Tension Force

If internal energy is approximately independent of configuration,

$$F = -T\left(\frac{\partial S}{\partial L}\right)_U.$$

Compute:

$$\frac{\partial S}{\partial N_R} = k_B \ln\left(\frac{N - N_R}{N_R}\right), \qquad \frac{dN_R}{dL} = \frac{1}{2\ell}.$$

Thus

$$\left(\frac{\partial S}{\partial L}\right)_U = \frac{k_B}{2\ell}\ln\left(\frac{N - N_R}{N_R}\right).$$

So

$$F = \frac{k_B T}{2\ell}\ln\left(\frac{N_R}{N - N_R}\right).$$

Substitute N_R:

$$\boxed{F = \frac{k_B T}{2\ell}\ln\left(\frac{N + L/\ell}{N - L/\ell}\right).}$$

Small extension:

$$a = \frac{L}{N\ell} \ll 1.$$

Then

$$\ln\left(\frac{1+a}{1-a}\right) \approx 2a.$$

So

$$\boxed{F \approx \frac{k_B T}{N\ell^2} L.}$$

Effective spring constant:

$$\boxed{k_{\text{eff}} = \frac{k_B T}{N\ell^2}.}$$

At fixed L, tension increases with T. Heating a stretched rubber band tends to make it contract. Sudden stretching warms the band because configurational entropy decreases and, if nearly adiabatic, work becomes thermal energy.

27.4 Midterm Stretched Rod

Given

$$f = aT^2(L - L_0),$$
$$C_L(T, L_0) = bT.$$

Thermodynamic identity:

$$dU = T\mathrm{d}S + f\mathrm{d}L.$$

Helmholtz free energy:

$$F = U - TS.$$

Then

$$dF = -S\mathrm{d}T + f\mathrm{d}L.$$

Therefore

$$S = -\left(\frac{\partial F}{\partial T}\right)_L, \qquad f = \left(\frac{\partial F}{\partial L}\right)_T.$$

Maxwell relation:

$$\boxed{\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L.}$$

Since

$$f = aT^2(L - L_0),$$
$$\left(\frac{\partial f}{\partial T}\right)_L = 2aT(L - L_0).$$

Thus

$$\boxed{\left(\frac{\partial S}{\partial L}\right)_T = -2aT(L - L_0).}$$

At $L = L_0$,

$$C_L = T\left(\frac{\partial S}{\partial T}\right)_L = bT.$$

So

$$\left(\frac{\partial S}{\partial T}\right)_{L_0} = b.$$

Integrate from (T_0, L_0) to (T, L):

$$\boxed{S(T, L) = S(T_0, L_0) + b(T - T_0) - aT(L - L_0)^2.}$$

For quasistatic insulated stretching,

$$dS = 0.$$

Thus

$$S(T_i, L_i) = S(T_f, L_f).$$

So

$$bT_i - aT_i(L_i - L_0)^2 = bT_f - aT_f(L_f - L_0)^2.$$

Therefore

$$\boxed{T_f = T_i \frac{b - a(L_i - L_0)^2}{b - a(L_f - L_0)^2}.}$$

If stretched farther from natural length and the expression remains physical,

$$|L_f - L_0| > |L_i - L_0| \qquad \Rightarrow \qquad T_f > T_i.$$

So the insulated rod warms up.

28. Paramagnetism

Two-state paramagnet with N independent dipoles in magnetic field B. Each dipole:

$$\text{up: } E = -\mu B, \qquad \text{down: } E = +\mu B.$$

Let $N_\uparrow, N_\downarrow$:

$$N = N_\uparrow + N_\downarrow.$$

Total energy:

$$\boxed{U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow).}$$

Magnetization:

$$\boxed{M = \mu(N_\uparrow - N_\downarrow) = -\frac{U}{B}.}$$

Multiplicity:

$$\Omega = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!}.$$

Entropy:

$$S = k_B \ln \Omega.$$

Using Stirling:

$$\frac{S}{k_B} = N \ln N - N_\uparrow \ln N_\uparrow - (N - N_\uparrow) \ln(N - N_\uparrow).$$

Temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,B}.$$

Since

$$\frac{\partial N_\uparrow}{\partial U} = -\frac{1}{2\mu B},$$

$$\frac{1}{T} = -\frac{1}{2\mu B}\frac{\partial S}{\partial N_\uparrow}.$$

And

$$\frac{1}{k_B}\frac{\partial S}{\partial N_\uparrow} = \ln\left(\frac{N - N_\uparrow}{N_\uparrow}\right).$$

Thus

$$\boxed{\frac{1}{T} = -\frac{k_B}{2\mu B} \ln\left(\frac{N - N_\uparrow}{N_\uparrow}\right).}$$

In terms of U:

$$N_\uparrow = \frac{N - U/\mu B}{2}, \qquad N_\downarrow = \frac{N + U/\mu B}{2}.$$

So

$$\boxed{\frac{1}{T} = \frac{k_B}{2\mu B} \ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right).}$$

Energy as function of T:

$$\boxed{U = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right).}$$

Magnetization:

$$\boxed{M = N\mu \tanh\left(\frac{\mu B}{k_B T}\right).}$$

Heat capacity at fixed B:

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B}.$$

$$\boxed{C_B = Nk_B \left(\frac{\mu B}{k_B T}\right)^2 \frac{1}{\cosh^2(\mu B/k_B T)}.}$$

High-temperature limit:

$$\frac{\mu B}{k_B T} \ll 1, \qquad \tanh x \approx x.$$

Then

$$\boxed{M \approx \frac{N\mu^2 B}{k_B T}.}$$

This is Curie's law:

$$\boxed{M \propto \frac{1}{T}.}$$

Energy:

$$U \approx -\frac{N\mu^2 B^2}{k_B T}.$$

Heat capacity:

$$C_B \approx Nk_B \left(\frac{\mu B}{k_B T}\right)^2 \propto \frac{1}{T^2}.$$

28.1 Negative Temperature

For this system, energy is bounded above:

$$-N\mu B \leq U \leq +N\mu B.$$

Entropy is maximal at $U = 0$. For $U > 0$,

$$\frac{\partial S}{\partial U} < 0,$$

so

$$T < 0.$$

A negative-temperature system is not colder than zero; it is hotter than any positive-temperature system because it will give energy to a positive-temperature object.

29. Magnetic Work and Magnetic Potentials

Given magnetic specimen volume V, total magnetic moment M, auxiliary field H:

$$H = \frac{B}{\mu_0} - \frac{M}{V}.$$

Solenoid relation:

$$H = \frac{NI}{L}.$$

Flux:

$$\Phi = NAB.$$

Induced emf magnitude:

$$\mathcal{E} = \frac{d\Phi}{dt} = NA\frac{dB}{dt}.$$

Power supplied:

$$P = I\mathcal{E} = NIA\frac{dB}{dt}.$$

Since $V = AL$ and $H = NI/L$,

$$P = HV\frac{dB}{dt}.$$

Thus total work:

$$dW_{\text{total}} = VH\mathrm{d}B.$$

Using

$$B = \mu_0\left(H + \frac{M}{V}\right),$$

$$dB = \mu_0\left(dH + \frac{dM}{V}\right).$$

Then

$$dW_{\text{total}} = \mu_0 VH\mathrm{d}H + \mu_0 H\mathrm{d}M.$$

Subtract empty-solenoid field work:

$$\boxed{dW = \mu_0 H\mathrm{d}M.}$$

Thermodynamic identity:

$$\boxed{dU = T\mathrm{d}S + \mu_0 H\mathrm{d}M.}$$

Helmholtz:

$$F = U - TS,$$

$$\boxed{dF = -S\mathrm{d}T + \mu_0 H\mathrm{d}M.}$$

Magnetic enthalpy analogue:

$$H_m = U - \mu_0 HM.$$

$$dH_m = T\mathrm{d}S - \mu_0 M\mathrm{d}H.$$

Magnetic Gibbs analogue:

$$G_m = U - TS - \mu_0 HM.$$

$$\boxed{dG_m = -S\mathrm{d}T - \mu_0 M\mathrm{d}H.}$$

Thus G_m is minimized at fixed T, H.

30. Phase Stability and Phase Boundaries

30.1 Gibbs Free Energy Stability

At fixed T, P, N, the stable phase minimizes G. For molar quantities,

$$dg = -s\mathrm{d}T + v\mathrm{d}P.$$

At fixed P,

$$\left(\frac{\partial g}{\partial T}\right)_P = -s.$$

At fixed T,

$$\left(\frac{\partial g}{\partial P}\right)_T = v.$$

If comparing phases A and B,

$$\Delta g_{AB} = g_B - g_A.$$

If

$$\Delta g_{AB} < 0,$$

then

$$g_B < g_A,$$

so phase B is stable. If

$$\Delta g_{AB} > 0,$$

phase A is stable.

30.2 Clausius–Clapeyron Relation

At phase coexistence,

$$g_1 = g_2.$$

Differentiating:

$$dg_1 = dg_2.$$

Using

$$dg = -s\mathrm{d}T + v\mathrm{d}P,$$

$$-s_1\mathrm{d}T + v_1\mathrm{d}P = -s_2\mathrm{d}T + v_2\mathrm{d}P.$$

Thus

$$(s_2 - s_1)\mathrm{d}T = (v_2 - v_1)\mathrm{d}P.$$

Therefore

$$\boxed{\frac{dP}{dT} = \frac{\Delta s}{\Delta v} = \frac{\Delta S}{\Delta V}.}$$

For phases A, B, C:

$$\left(\frac{dP}{dT}\right)_{AB} = \frac{S_B - S_A}{V_B - V_A},$$

$$\left(\frac{dP}{dT}\right)_{AC} = \frac{S_C - S_A}{V_C - V_A},$$

$$\left(\frac{dP}{dT}\right)_{BC} = \frac{S_C - S_B}{V_C - V_B}.$$

If slopes are approximately constant, each boundary is a straight line:

$$P - P_1 = \left(\frac{dP}{dT}\right)(T - T_1).$$

A triple point is the intersection where

$$g_A = g_B = g_C.$$

30.3 Latent Heat Form

For a transition at temperature T,

$$L = T\Delta S.$$

So

$$\boxed{\frac{dP}{dT} = \frac{L}{T\Delta V}.}$$

31. Diamond vs. Graphite

At fixed T, P, stability depends on G, not just entropy:

$$G = U - TS + PV.$$

Diamond has lower entropy than graphite:

$$S_{\text{diamond}} < S_{\text{graphite}}.$$

So entropy alone favors graphite. But diamond has smaller molar volume:

$$V_{\text{diamond}} < V_{\text{graphite}}.$$

At fixed T,

$$\left(\frac{\partial G}{\partial P}\right)_T = V.$$

Graphite's G rises faster with pressure because graphite has larger V. Therefore at high pressure diamond can become stable.

For graphite $\to$ diamond,

$$\Delta V = V_{\text{diamond}} - V_{\text{graphite}} < 0.$$

Increasing pressure lowers $G_{\text{diamond}} - G_{\text{graphite}}$ relative to low pressure:

$$G_{\text{diamond}}(P) - G_{\text{graphite}}(P) = G_{\text{diamond}}(P_0) - G_{\text{graphite}}(P_0) + \int_{P_0}^{P} (V_{\text{diamond}} - V_{\text{graphite}})\mathrm{d}P'.$$

Since the integrand is negative, high pressure favors diamond. Even if carbon entropy decreases,

$$\Delta S_{\text{carbon}} < 0,$$

the environment entropy can increase enough that

$$\Delta S_{\text{total}} > 0.$$

For a T, P reservoir,

$$\boxed{\Delta S_{\text{total}} = -\frac{\Delta G_{\text{system}}}{T}.}$$

So if

$$\Delta G_{\text{system}} < 0,$$

then

$$\Delta S_{\text{total}} > 0.$$

32. Vapor Pressure Under an Inert Gas

Liquid and vapor are in equilibrium. Add inert gas, increasing total pressure P, fixed T. Inert gas does not dissolve in liquid.

For a pure phase:

$$dG = -S\mathrm{d}T + V\mathrm{d}P, \qquad G = N\mu.$$

Divide by N:

$$d\mu = -s\mathrm{d}T + v\mathrm{d}P.$$

At fixed T, for liquid:

$$\boxed{d\mu_l = v_l \mathrm{d}P.}$$

For ideal vapor:

$$\mu_g = \mu_g^0(T) + k_B T \ln P_v.$$

At fixed T,

$$d\mu_g = k_B T \mathrm{d}\ln P_v = k_B T \frac{\mathrm{d}P_v}{P_v}.$$

Equilibrium:

$$\mu_l = \mu_g, \qquad d\mu_l = d\mu_g.$$

So

$$v_l \mathrm{d}P = k_B T \frac{\mathrm{d}P_v}{P_v}.$$

Differential equation:

$$\boxed{\frac{\mathrm{d}P_v}{P_v} = \frac{v_l}{k_B T}\mathrm{d}P.}$$

Integrate from $(P^{(0)}, P_v^{(0)})$ to (P, P_v):

$$\ln \frac{P_v}{P_v^{(0)}} = \frac{v_l}{k_B T}(P - P^{(0)}).$$

Thus

$$\boxed{P_v = P_v^{(0)} \exp\left[\frac{v_l(P - P^{(0)})}{k_B T}\right].}$$

For small v_l,

$$\boxed{\frac{P_v - P_v^{(0)}}{P_v^{(0)}} \approx \frac{v_l(P - P^{(0)})}{k_B T}.}$$

Adding inert gas slightly increases vapor partial pressure because the liquid chemical potential increases with total pressure.

33. van der Waals Equation and Critical Behavior

33.1 van der Waals Equation

For N particles:

$$\boxed{P = \frac{N k_B T}{V - Nb} - \frac{aN^2}{V^2}.}$$

Corrections:

- $b > 0$: excluded volume, reduces available volume.
- $a > 0$: attractions, reduce pressure.

For one mole:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT.$$

33.2 Critical Constants

For one mole:

$$\boxed{V_c = 3b, \qquad P_c = \frac{a}{27b^2}, \qquad T_c = \frac{8a}{27Rb}.}$$

For N particles:

$$V_c = 3Nb, \qquad P_c = \frac{a}{27b^2}, \qquad k_B T_c = \frac{8a}{27b}.$$

Critical point conditions:

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \qquad \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0.$$

33.3 Reduced Variables

$$t = \frac{T}{T_c}, \qquad p = \frac{P}{P_c}, \qquad v = \frac{V}{V_c}.$$

Reduced equation:

$$\boxed{p(v;t) = \frac{8t}{3v - 1} - \frac{3}{v^2}.}$$

This is universal: a, b disappear.

33.4 Expansion Near Critical Point

Let

$$\omega = v - 1.$$

Near $v = 1, t = 1$,

$$\boxed{p \simeq (4t - 3) + 6(1 - t)\omega - \frac{3}{2}\omega^3.}$$

The quadratic term is negligible near coexistence because

$$\omega = O((1 - t)^{1/2}).$$

33.5 Maxwell Construction

Below T_c, the raw van der Waals isotherm has a mechanically unstable region:

$$\left(\frac{\partial P}{\partial V}\right)_T > 0.$$

Stable mechanical equilibrium requires

$$\boxed{\left(\frac{\partial P}{\partial V}\right)_T < 0.}$$

At coexistence, replace oscillating loop with horizontal line P_0 or P_{vap}. At fixed T,

$$dF = -P\mathrm{d}V.$$

Original isotherm from V_l to V_g:

$$F_g - F_l = -\int_{V_l}^{V_g} P(V,T)\mathrm{d}V.$$

Physical coexistence path:

$$F_g - F_l = -P_0(V_g - V_l).$$

Equating:

$$\boxed{\int_{V_l}^{V_g} [P(V,T) - P_0]\,\mathrm{d}V = 0.}$$

Equal-area rule: area above horizontal line equals area below. In reduced variables:

$$\boxed{\int_{v_l}^{v_g} [p(v;t) - p_{\text{vap}}]\,\mathrm{d}v = 0.}$$

33.6 Approximate Vapor Pressure Near Critical Point

Because the near-critical expression is antisymmetric after subtracting $4t - 3$,

$$\boxed{p_{\text{vap}} \simeq 4t - 3.}$$

So

$$P_{\text{vap}} \simeq P_c\left(4\frac{T}{T_c} - 3\right).$$

Slope at critical point:

$$\boxed{\left.\frac{dP}{dT}\right|_c = \frac{4P_c}{T_c} = \frac{R}{2b}.}$$

33.7 Coexisting Volumes and Critical Exponent β

At vapor pressure:

$$6(1-t)\omega - \frac{3}{2}\omega^3 = 0.$$

Solutions:

$$\omega = 0, \qquad \omega = \pm 2\sqrt{1-t}.$$

Thus

$$v_g - v_l = 4\sqrt{1-t}.$$

Therefore

$$\boxed{V_g - V_l = 4V_c\sqrt{1 - \frac{T}{T_c}} = 4V_c\sqrt{\frac{T_c - T}{T_c}}.}$$

Critical exponent:

$$\boxed{\beta = \frac{1}{2}.}$$

33.8 Latent Heat Near Critical Point

Clapeyron:

$$L = T(V_g - V_l)\frac{dP_{\text{vap}}}{dT}.$$

Using the results above:

$$\boxed{L(T) \simeq 16 P_c V_c t\sqrt{1-t}.}$$

Thus

$$L \to 0$$

as

$$(T_c - T)^{1/2}.$$

33.9 Critical Isotherm Exponent δ

At $t = 1$,

$$p - 1 = -\frac{3}{2}(v-1)^3.$$

Thus

$$P - P_c \propto (V - V_c)^3,$$

so

$$\boxed{\delta = 3.}$$

33.10 Compressibility Exponent γ

Isothermal compressibility:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

In reduced variables,

$$\kappa = -\frac{1}{P_c v}\left[\left(\frac{\partial p}{\partial v}\right)_t\right]^{-1}.$$

Near critical:

$$\frac{\partial p}{\partial v} \simeq 6(1-t) - \frac{9}{2}(v-1)^2.$$

Above critical, $t > 1$, use $v = 1$:

$$\boxed{\kappa_+ \simeq \frac{1}{6P_c(t-1)}.}$$

Below critical, use coexistence branch

$$(v-1)^2 = 4(1-t).$$

Then

$$\boxed{\kappa_- \simeq \frac{1}{12P_c(1-t)}.}$$

Thus

$$\boxed{\gamma = \gamma' = 1.}$$

34. Virial Expansion

Real gas deviations from ideal gas:

$$\boxed{PV = nRT\left[1 + \frac{B(T)}{V/n} + \frac{C(T)}{(V/n)^2} + \cdots\right].}$$

Equivalently,

$$\frac{PV}{nRT} = 1 + B(T)\frac{n}{V} + C(T)\left(\frac{n}{V}\right)^2 + \cdots.$$

For nitrogen, $B(T)$ is negative at low T and positive at high T. Physical meaning:

- Low T: attractions dominate, pressure lower than ideal, so $B(T) < 0$.
- High T: repulsion/excluded volume dominates, effective pressure higher, so $B(T) > 0$.

34.1 van der Waals Virial Coefficients

Start from

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}.$$

Multiply:

$$\frac{PV}{nRT} = \frac{V}{V - nb} - \frac{an}{RTV}.$$

Now

$$\frac{V}{V - nb} = \frac{1}{1 - nb/V} = 1 + \frac{nb}{V} + \frac{n^2b^2}{V^2} + \cdots.$$

Therefore

$$\frac{PV}{nRT} = 1 + \left(b - \frac{a}{RT}\right)\frac{n}{V} + b^2\left(\frac{n}{V}\right)^2 + \cdots.$$

Thus

$$\boxed{B(T) = b - \frac{a}{RT}, \qquad C(T) = b^2.}$$

35. Anharmonic Thermal Expansion

A classical particle in potential $u(x)$ has Boltzmann distribution

$$p(x) = \frac{e^{-\beta u(x)}}{Z_x}, \qquad Z_x = \int_{-\infty}^{\infty} e^{-\beta u(x)}\mathrm{d}x.$$

Average position:

$$\boxed{\langle x\rangle = \frac{\int_{-\infty}^{\infty} x e^{-\beta u(x)}\mathrm{d}x}{\int_{-\infty}^{\infty} e^{-\beta u(x)}\mathrm{d}x}.}$$

Expand around minimum x_0:

$$u(x) = u(x_0) + (x - x_0)u'(x_0) + \frac{1}{2}(x - x_0)^2u''(x_0) + \frac{1}{3!}(x - x_0)^3u'''(x_0) + \cdots.$$

At the minimum,

$$u'(x_0) = 0.$$

Purely quadratic approximation predicts no expansion:

$$\langle x \rangle = x_0.$$

Include a small cubic term. Let

$$y = x - x_0, \qquad k = u''(x_0), \qquad g = u'''(x_0).$$

Then leading shift:

$$\boxed{\langle x \rangle - x_0 = -\frac{u'''(x_0)}{2[u''(x_0)]^2} k_B T.}$$

For Lennard-Jones:

$$u(x) = u_0 \left[\left(\frac{x_0}{x} \right)^{12} - 2 \left(\frac{x_0}{x} \right)^{6} \right].$$

At $x = x_0$,

$$u'(x_0) = 0,$$
$$u''(x_0) = \frac{72 u_0}{x_0^2},$$
$$u'''(x_0) = -\frac{1512 u_0}{x_0^3}.$$

Then

$$\langle x \rangle - x_0 = \frac{7}{48} x_0 \frac{k_B T}{u_0}.$$

Linear expansion coefficient:

$$\boxed{\alpha = \frac{1}{x_0} \frac{d \langle x \rangle}{dT} = \frac{7}{48} \frac{k_B}{u_0}.}$$

36. Fuel Cells and Gibbs Free Energy

For a chemical reaction at fixed T, P, maximum non-expansion work is

$$\boxed{W_{\text{nonexp,max}} = -\Delta G.}$$

For a fuel cell, ideal electrical work:

$$\boxed{W_{\text{elec,max}} = -\Delta G.}$$

Reaction:

$$\mathrm{CH_4} + 2\mathrm{O_2} \rightarrow 2\mathrm{H_2O}(\ell) + \mathrm{CO_2}.$$

Use formation values:

$$\Delta H^\circ = \sum \nu_i \Delta H^\circ_{f,\text{products}} - \sum \nu_i \Delta H^\circ_{f,\text{reactants}},$$
$$\Delta G^\circ = \sum \nu_i \Delta G^\circ_{f,\text{products}} - \sum \nu_i \Delta G^\circ_{f,\text{reactants}}.$$

HW result:

$$\Delta H^\circ = -890.36\,\text{kJ/mol},$$
$$\Delta G^\circ = -817.90\,\text{kJ/mol}.$$

Maximum electrical work:

$$\boxed{W_{\text{elec,max}} = 817.90\,\text{kJ/mol}.}$$

Waste heat:

$$Q_{\text{waste}} = (-\Delta H^\circ) - (-\Delta G^\circ) = 72.46\,\text{kJ/mol}.$$

Cell voltage:

$$\boxed{E = \frac{-\Delta G}{n_e F}.}$$

For methane, $n_e = 8$, so

$$E = \frac{817.90 \times 10^3}{8F} \approx 1.06\,\text{V}.$$

37. Grand Potential Application: Hydrogen Ionization Stability

Single proton can be unoccupied or occupied by one electron. Neglect spin and excited states.

Unoccupied:

$$U = 0, \qquad S = 0, \qquad N = 0,$$

so

$$\Phi_{\text{unocc}} = 0.$$

Occupied:

$$U = -13.6\,\text{eV}, \qquad S = 0, \qquad N = 1.$$

$$\Phi_{\text{occ}} = U - TS - \mu N = -13.6\,\text{eV} - \mu_e.$$

Classical ideal gas electron chemical potential:

$$\boxed{\mu_e = k_B T \ln\!\left(n_e \lambda_T^3\right),}$$

where

$$\lambda_T = \frac{h}{\sqrt{2\pi m_e k_B T}}.$$

At $T = 5800\,\text{K}$ and $n_e = 2 \times 10^{19}\,\text{m}^{-3}$,

$$\mu_e \approx -8.89\,\text{eV}.$$

Thus

$$\Phi_{\text{occ}} = -13.6 - (-8.89) = -4.71\,\text{eV}.$$

Since

$$\Phi_{\text{occ}} < \Phi_{\text{unocc}},$$

the occupied state is more stable. Equal stability:

$$\Phi_{\text{occ}} = 0 \qquad \Rightarrow \qquad \mu_e = -13.6\,\text{eV}.$$

Solve

$$k_B T \ln\left[n_e \left(\frac{h}{\sqrt{2\pi m_e k_B T}}\right)^3\right] = -13.6\,\text{eV}.$$

Result:

$$T_* \approx 8.59 \times 10^3\,\text{K}.$$

38. Maximum-Entropy Gaussian Distribution

Given continuous probability density $p(x)$, maximize

$$S[p] = -\int_{-\infty}^{\infty} p(x)\ln p(x)\mathrm{d}x$$

subject to

$$\int p(x)\mathrm{d}x = 1,$$

$$\int xp(x)\mathrm{d}x = \alpha,$$

$$\int (x-\alpha)^2 p(x)\mathrm{d}x = \beta^2.$$

Use Lagrange multipliers:

$$\mathcal{F}[p] = -\int p\ln p\mathrm{d}x - \lambda_0\left(\int p\mathrm{d}x - 1\right) - \lambda_1\left(\int xp\mathrm{d}x - \alpha\right) - \lambda_2\left(\int (x-\alpha)^2 p\mathrm{d}x - \beta^2\right).$$

Variation gives

$$\ln p(x) = -1 - \lambda_0 - \lambda_1 x - \lambda_2(x-\alpha)^2.$$

So

$$p(x) = A\exp\left[-\lambda_1 x - \lambda_2(x-\alpha)^2\right].$$

Mean constraint forces $\lambda_1 = 0$. Then

$$p(x) = Ae^{-\lambda_2(x-\alpha)^2}.$$

Normalization and variance give

$$\lambda_2 = \frac{1}{2\beta^2}, \qquad A = \frac{1}{\sqrt{2\pi\beta^2}}.$$

Thus

$$\boxed{p(x) = \frac{1}{\sqrt{2\pi\beta^2}}\exp\left[-\frac{(x-\alpha)^2}{2\beta^2}\right].}$$

So the maximum-entropy distribution with fixed mean and variance is Gaussian.

39. Exam-Style Recognition Guide

39.1 Most Probable Macrostate

Use

$$\Omega_{\text{total}} = \Omega_A\Omega_B, \qquad S_{\text{total}} = S_A + S_B.$$

Maximize entropy:

$$dS_{\text{total}} = 0.$$

Usually gives equal intensive variables:

$$T_A = T_B, \qquad P_A = P_B, \qquad \mu_A = \mu_B.$$

For Einstein solids:

$$\frac{q_A}{N_A} = \frac{q_B}{N_B}.$$

39.2 Fixed Constraints

If fixed T, V, N, use Helmholtz free energy:

$$F = U - TS.$$

Equilibrium minimizes F.

If fixed T, P, N, use Gibbs free energy:

$$G = U - TS + PV.$$

Equilibrium minimizes G.

If fixed T, V, μ, use grand potential:

$$\Phi = U - TS - \mu N.$$

Equilibrium minimizes Φ.

39.3 Phase Boundary Slope

Use Clausius–Clapeyron:

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}.$$

Or with latent heat:

$$\frac{dP}{dT} = \frac{L}{T\Delta V}.$$

39.4 van der Waals Coexistence

Use Maxwell equal-area rule:

$$\int_{V_l}^{V_g} [P(V,T) - P_0]\mathrm{d}V = 0.$$

Mechanical instability means

$$\left(\frac{\partial P}{\partial V}\right)_T > 0.$$

39.5 Shift All Energy Levels

Use

$$Z' = e^{-\beta\epsilon} Z, \qquad P'_s = P_s, \qquad U' = U + \epsilon, \qquad F' = F + \epsilon, \qquad S' = S.$$

39.6 Probability Distribution from Energy

Use canonical ensemble:

$$P_s = \frac{e^{-\beta E_s}}{Z}.$$

For continuous coordinate:

$$p(x) = \frac{e^{-\beta u(x)}}{\int e^{-\beta u(x)}\mathrm{d}x}.$$

For velocities:

$$f(\vec{v}) \propto e^{-\beta m v^2/2}.$$

39.7 Heat Capacity from Entropy

Use

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V, \qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P.$$

39.8 P-V and T-S Diagram Reasoning

Remember:

$$W = \int P\mathrm{d}V.$$

Clockwise cycle gives positive work. For ideal gas:

$$T \propto PV.$$

For monatomic ideal gas entropy:

$$S = nR\left(\frac{3}{2}\ln T + \ln V\right) + \text{constant}.$$

39.9 Which Phase is Stable?

The stable phase has lower Gibbs free energy G at fixed T, P. If

$$\Delta g_{AB} = g_B - g_A < 0,$$

then B is stable. If

$$\Delta g_{AB} > 0,$$

then A is stable.

39.10 Why Can System Entropy Decrease?

The second law applies to system plus environment:

$$\Delta S_{\text{total}} \geq 0.$$

At fixed T, P,

$$\Delta S_{\text{total}} = -\frac{\Delta G_{\text{system}}}{T}.$$

So system entropy can decrease if environment entropy increases more.

40. Must-Memorize Formula Box

$$S = k_B \ln \Omega$$

$$S = -k_B \sum_s P_s \ln P_s$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

$$dU = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N$$

$$F = U - TS$$

$$dF = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}N$$

$$G = U - TS + PV$$

$$dG = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}N$$

$$\Phi = U - TS - \mu N$$

$$d\Phi = -S\mathrm{d}T - P\mathrm{d}V - N\mathrm{d}\mu$$

$$P_s = \frac{e^{-\beta E_s}}{Z}$$

$$Z = \sum_s e^{-\beta E_s}$$

$$F = -k_B T \ln Z$$

$$U = -\frac{\partial}{\partial \beta} \ln Z$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$C_P - C_V = \frac{TV\beta^2}{\kappa_T}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$PV = Nk_B T$$

$$U_{\mathrm{mono}} = \frac{3}{2} N k_B T$$

$$Z_{\mathrm{tr}} = \frac{V(2\pi m k_B T)^{3/2}}{h^3}$$

$$Z_{\mathrm{ho}} = \frac{1}{1 - e^{-\beta\epsilon}}$$

$$U_{\mathrm{ho}} = \frac{\epsilon}{e^{\beta\epsilon} - 1}$$

$$D_3(v) \propto v^2 e^{-mv^2/(2k_B T)}$$

$$v_{\mathrm{mp}}^{3D} = \sqrt{\frac{2k_B T}{m}}$$

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

$$v_{\mathrm{rms}} = \sqrt{\frac{3k_B T}{m}}$$

$$D_2(v) = \frac{m}{k_B T} v e^{-mv^2/(2k_B T)}$$

$$v_{\mathrm{mp}}^{2D} = \sqrt{\frac{k_B T}{m}}$$

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

$$\int_{V_l}^{V_g} [P(V,T) - P_0]\mathrm{d}V = 0$$

$$p = \frac{8t}{3v - 1} - \frac{3}{v^2}$$

$$B(T) = b - \frac{a}{RT}$$

$$C(T) = b^2$$

$$M = N\mu \tanh\left(\frac{\mu B}{k_B T}\right)$$

$$U_{\mathrm{para}} = -N\mu B \tanh\left(\frac{\mu B}{k_B T}\right)$$

$$\eta_{\mathrm{Carnot}} = 1 - \frac{T_c}{T_h}$$

$$W = \int P\mathrm{d}V$$

$$\Delta U = Q - W$$

$$\Omega_{\mathrm{Einstein}} = \binom{q + N - 1}{q}$$

$$\Delta S_{\mathrm{mix}} = -N k_B [(1-x)\ln(1-x) + x \ln x]$$

$$\Omega_{\mathrm{DNA}}(q) = \binom{L}{q} 3^q$$

$$S_{\mathrm{DNA}}(x) \approx L[-x \ln x - (1-x)\ln(1-x) + x \ln 3]$$

$$x_{\max} = \frac{3}{4}$$