The Statistical Basis of Thermodynamics

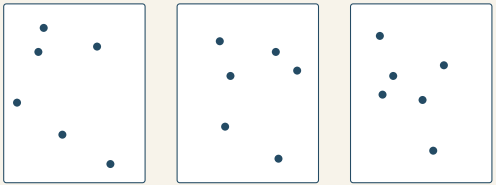
Multiplicity, equilibrium, and the origin of thermodynamic laws

Tsvi Tlusty · UNIST

Convention: $k_B = 1$

Why can a gas be predictable?

ONE MACROSTATE, MANY MICROSTATES



(E, V, N) is the same

Positions are shown schematically; the microscopic momenta are not specified.

THE OBJECT WE COUNT

A macrostate fixes a few bulk variables. A microstate specifies one complete microscopic realization.

$$\Omega(E, V, N) = \text{number of allowed states}$$

> We do not need one microscopic history. We need the weight of each macroscopic possibility.

A first count: two energy levels

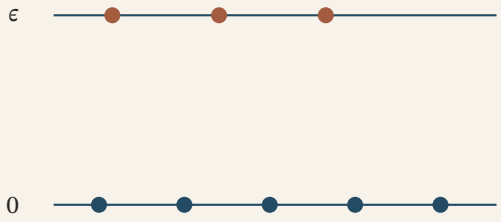
Take N distinguishable objects with energies 0 and ϵ. If m are excited,

$$E = m\epsilon, \qquad \Omega(N, m) = \binom{N}{m}.$$

$$\Omega(10, 5) = 252.$$

> The energy fixes how many are excited, not which objects are excited.

ONE OF THE ALLOWED ARRANGEMENTS



$N = 8, \quad m = 3, \quad \Omega = 56$

Large numbers make a narrow macrostate

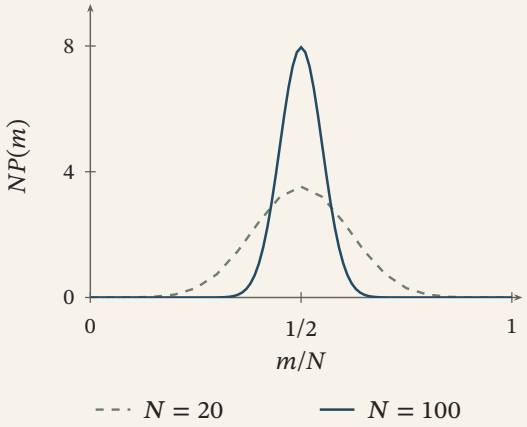
Across all 2^N configurations, each object is excited with probability $1/2$. Then

$$P(m) = 2^{-N}\binom{N}{m}.$$

$$\langle m \rangle = \frac{N}{2}, \qquad \mathrm{Var}(m) = \frac{N}{4}.$$

> Absolute fluctuations grow as $\sqrt{N}$; the fractional uncertainty falls as $N^{-1/2}$.

Exact binomial weights; vertical scale is the density in m/N.



Equal probabilities within the constraints

THE MICROCANONICAL POSTULATE

For an isolated system, assign equal probability to every accessible microstate compatible with the constraints.

$$p_r = \frac{1}{\Omega(E, V, N)}$$

The probabilities sum to one because exactly Ω states are included.

WHAT EQUAL WEIGHT DOES NOT MEAN

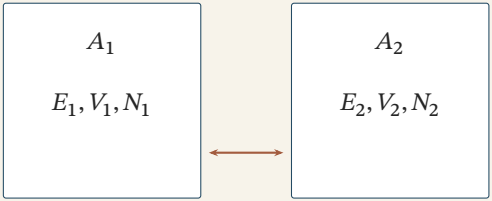
States with the wrong energy, volume, or particle number are excluded. Equal weight is not assigned to all conceivable states.

> The postulate specifies an ensemble. It is a statistical input, not a consequence of state counting alone.

Lecture 2 asks whether mechanics preserves this distribution.

Contact turns counting into equilibrium

WEAK THERMAL CONTACT



energy exchange

$$E_1 + E_2 = E^{(0)}$$

A composite microstate is one choice in A_1 and one choice in A_2. Therefore

$$\Omega^{(0)}(E_1) = \Omega_1(E_1)\Omega_2(E^{(0)} - E_1).$$

The most probable energy division maximizes the product, or its logarithm:

$$\partial_{E_1} \ln \Omega_1 = \partial_{E_2} \ln \Omega_2.$$

> Equilibrium is a maximum of multiplicity.

Entropy and temperature emerge together

THE QUANTITY THAT EQUALIZES

$$\beta \equiv \left(\frac{\partial \ln \Omega}{\partial E} \right)_{V,N}.$$

Thermal equilibrium requires $\beta_1 = \beta_2$.
Thermodynamics requires $T_1 = T_2$.

$$\boxed{S = \ln \Omega}, \qquad \beta = \frac{1}{T}.$$

With units restored: $S = k_{\mathrm{B}} \ln \Omega$, $\beta = (k_{\mathrm{B}} T)^{-1}$.

WHY A LOGARITHM?

Independent systems multiply their state counts, but add their entropies.

$$\ln(\Omega_1 \Omega_2) = \ln \Omega_1 + \ln \Omega_2.$$

> Temperature is the inverse slope of entropy: it measures how much the state count grows when energy is added.

The equilibrium maximum is sharp

Let $S_{\text{tot}}(E_1) = S_1(E_1) + S_2(E^{(0)} - E_1)$. Near its maximum E_1^*,

$$S_{\text{tot}}(E_1) \simeq S_{\text{tot}}(E_1^*) + \frac{1}{2} S''_{\text{tot}}(E_1^*)(E_1 - E_1^*)^2.$$

For two stable phases at the same temperature, $S_i'' = -1/(T^2 C_i)$. Thus

$$\sigma_{E_1}^2 = T^2 \frac{C_1 C_2}{C_1 + C_2}.$$

Since $P(E_1) \propto \mathrm{e}^{S_{\text{tot}}(E_1)}$, the peak is approximately Gaussian.

For ordinary extensive systems, $C_i \sim N$ and $E_i \sim N$. Hence $\sigma_E / E \sim N^{-1/2}$.

The second law is statistical, not mechanical

$$\frac{P(\text{macrostate } B)}{P(\text{macrostate } A)} = \frac{\Omega_B}{\Omega_A} = \mathrm{e}^{S_B - S_A}.$$

WHAT THE COUNT SAYS

A macroscopic entropy increase means an exponentially larger set of microscopic possibilities. A low-entropy preparation is exceptionally atypical.

WHAT THE COUNT DOES NOT SAY

Counting alone does not give a relaxation time, remove dynamical barriers, or make every individual trajectory monotone in entropy.

> The second law concerns typical evolution from a low-entropy preparation, not a new microscopic force.

Three exchanges, three thermodynamic fields

Allow the composite system to exchange energy, volume, or particles. Maximizing total entropy equalizes the corresponding derivatives.

$$\boxed{\mathrm{d}S = \frac{1}{T}\,\mathrm{d}E + \frac{P}{T}\,\mathrm{d}V - \frac{\mu}{T}\,\mathrm{d}N}.$$

ENERGY

$$(\partial_E S)_{V,N} = \frac{1}{T}$$

VOLUME

$$(\partial_V S)_{E,N} = \frac{P}{T}$$

PARTICLES

$$(\partial_N S)_{E,V} = -\frac{\mu}{T}$$

With thermal equilibrium already established, these conditions become equality of T, P, and μ.

Extensivity imposes structure

For a homogeneous bulk system, extensivity means

$$E(\alpha S, \alpha V, \alpha N) = \alpha E(S, V, N).$$

Differentiate in α at $\alpha = 1$:

$$\boxed{E = TS - PV + \mu N}.$$

> Extensive variables set the size; intensive variables do not grow with it.

POTENTIALS CHOOSE THE CONSTRAINTS

$$A = E - TS,$$
$$G = E - TS + PV = \mu N,$$
$$H_{\text{th}} = E + PV.$$

Differentiating Euler's relation and subtracting $\mathrm{d}E$ gives

$$S\,\mathrm{d}T - V\,\mathrm{d}P + N\,\mathrm{d}\mu = 0.$$

Positions alone give the ideal-gas law

THE CLASSICAL IDEAL GAS

$$H = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m}.$$

There is no interaction energy. Each particle can explore the whole volume independently.

$$\Omega(E, V, N) \propto V^N F(E, N).$$

THE EQUATION OF STATE

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

$$\boxed{PV = NT}.$$

> The ideal-gas law follows from the positional count before any momentum integral.

Scaling the box determines the energy

In a cubic box of side L, each one-particle energy at fixed quantum numbers scales as

$$\epsilon_{\mathbf{n}} \propto L^{-2} \propto V^{-2/3}.$$

Under quasistatic adiabatic scaling, the occupied state labels stay fixed. Therefore

$$EV^{2/3} = \text{constant}.$$

WORK CONNECTS GEOMETRY TO ENERGY

$$P = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{2E}{3V}.$$

Combine this result with $PV = NT$:

$$\boxed{E = \frac{3}{2}NT}, \qquad C_V = \frac{3}{2}N.$$

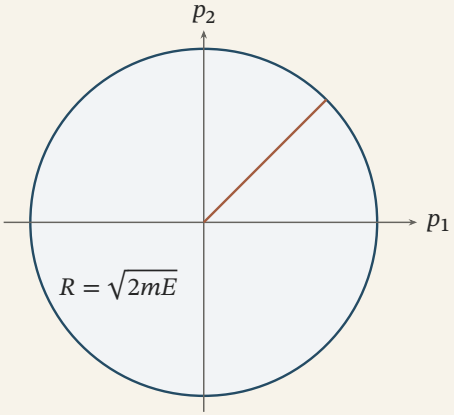
No collision model is needed for these equilibrium relations.

Counting energies is high-dimensional geometry

The momentum constraint $\sum_i \mathbf{p}_i^2 < 2mE$ is a ball in $3N$ dimensions. Positions contribute V^N.

$$\Sigma_{\text{lab}}(E) \simeq \frac{V^N}{h^{3N}} \frac{(2\pi mE)^{3N/2}}{\Gamma(3N/2+1)}.$$

$\Sigma(E)$ counts states below E. A thin energy shell contains $\Omega(E) \simeq \Sigma'(E)\Delta E$ states.



Two-dimensional section of the momentum ball; not physical space.

Spheres and Gaussians share one formula

THE SAME GAUSSIAN IN TWO COORDINATE SYSTEMS

$$\int_{\mathbb{R}^d} \mathrm{e}^{-|\mathbf{x}|^2}\,\mathrm{d}^d x = (\sqrt{\pi})^d = \mathcal{A}_{d-1}\int_0^\infty \mathrm{e}^{-r^2} r^{d-1}\,\mathrm{d}r.$$

$$\int_0^\infty \mathrm{e}^{-r^2} r^{d-1}\,\mathrm{d}r = \frac{1}{2}\Gamma(d/2).$$

$$\mathcal{A}_{d-1} = \frac{2\pi^{d/2}}{\Gamma(d/2)}, \qquad \boxed{V_d(R) = \frac{\pi^{d/2} R^d}{\Gamma(d/2+1)}}.$$

The ideal-gas hypersphere and the canonical Gaussian integral are two versions of the same calculation.

A provisional entropy reveals a missing factor

Take $\ln \Sigma_{\text{lab}}$ and use Stirling's formula, keeping terms extensive in N:

$$S_{\text{lab}} \simeq N \ln\left[\frac{V}{h^3}\left(\frac{4\pi m E}{3N}\right)^{3/2}\right] + \frac{3}{2}N.$$

IT GETS SOME THINGS RIGHT

Differentiation in V and E gives $PV = NT$ and $E = 3NT/2$.

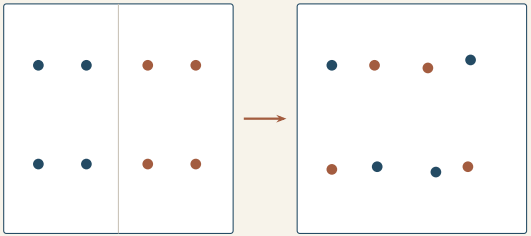
IT FAILS THE SIZE TEST

Under $(E, V, N) \mapsto (\alpha E, \alpha V, \alpha N)$, an unwanted $\alpha N \ln \alpha$ remains.

> The derivatives can look correct while the absolute state count is wrong.

Mixing different gases creates new possibilities

TWO DIFFERENT GASES



before after

Initially the same temperature and density. Each species gains accessible volume.

For different species, each gas expands from V_i to $V = V_1 + V_2$.

$$\Delta S_{\text{mix}} = N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2}.$$

$$N_1 = N_2 = N : \quad \Delta S_{\text{mix}} = 2N \ln 2.$$

This is a real change: the species are physically distinguishable.

The Gibbs paradox is an overcounting problem

NOW USE THE SAME GAS

At the same temperature and density, removing the partition changes no bulk macrostate. There is no extensive entropy of mixing.

> Permanent labels count permutations as different states, although no measurement can distinguish those permutations.

REMOVE THE OVERCOUNTING

$$\Omega = \frac{\Omega_{\text{lab}}}{N!}, \qquad S = S_{\text{lab}} - \ln N!.$$

In the dilute classical limit, each physical arrangement has been counted $N!$ times.

$$\ln N! \simeq N \ln N - N.$$

For a mixture, divide by $N_1!N_2!$, not by $(N_1 + N_2)!$.

Sackur–Tetrode: an extensive entropy

The corrected ideal-gas entropy is now extensive:

$$\boxed{S = N\left\{\ln\left[\frac{V}{N}\left(\frac{4\pi mE}{3Nh^2}\right)^{3/2}\right] + \frac{5}{2}\right\}.}$$

With $E = 3NT/2$, define the thermal wavelength and density:

$$\lambda_T = \frac{h}{\sqrt{2\pi mT}}, \qquad n = \frac{N}{V}.$$

$$S = N\left[\ln\frac{1}{n\lambda_T^3} + \frac{5}{2}\right].$$

Only the intensive ratios E/N and V/N occur inside the logarithm.

One entropy gives isotherms and adiabats

REVERSIBLE CHANGES

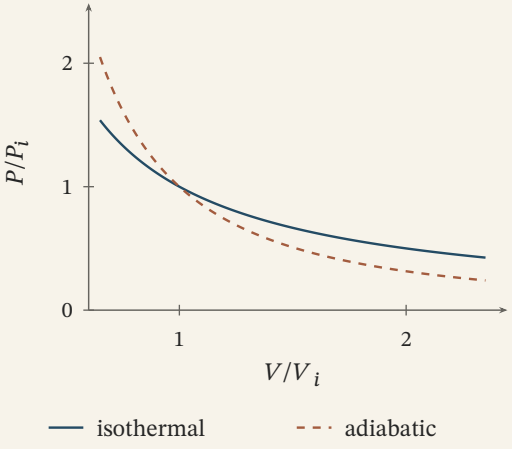
For an isothermal change, E is fixed and

$$\Delta S = N \ln \frac{V_f}{V_i}.$$

For a reversible adiabatic change, S is fixed:

$$TV^{2/3} = \text{const.}, \quad PV^{5/3} = \text{const.}$$

$C_P = 5N/2$, so $\gamma = C_P/C_V = 5/3$.



The same count gives the chemical potential

Using $E = 3NT/2$ and the corrected entropy,

$$A = E - TS = NT[\ln(n\lambda_T^3) - 1].$$

ADDING ONE PARTICLE

$$\boxed{\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = T\ln(n\lambda_T^3)}$$

THE CLASSICAL REGIME

$$n\lambda_T^3 \ll 1 \quad \Longrightarrow \quad \mu < 0.$$

> λ_T supplies the quantum counting scale even when the motion is treated classically.

From multiplicity to thermodynamics

COUNT

$$\Omega(E, V, N) \quad \longrightarrow \quad S = \ln \Omega$$

Many microscopic realizations give one macroscopic description. For ordinary large systems, relative fluctuations become small.

DIFFERENTIATE

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

Temperature, pressure, and chemical potential are derivatives of the entropy, not additional microscopic assumptions.

> Correct counting needs both the quantum cell h^{3N} and the permutation factor $N!$. Next: how does an ensemble move through phase space?

Theory of Ensembles

Phase-space flow, invariant measures, and the size of one state

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Convention: $k_{\mathrm{B}} = 1$

Mechanics becomes a flow in phase space

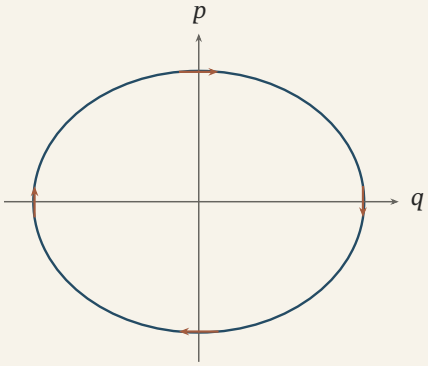
A classical microstate is one point in $6N$ dimensions:

$$\Gamma = (q_1, \dots, q_{3N}; p_1, \dots, p_{3N}).$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}.$$

For a time-independent Hamiltonian, $\mathrm{d}H/\mathrm{d}t = 0$. The trajectory stays on an energy surface.

A HARMONIC ORBIT



$H(q, p) = E$

Newton's law in phase-space form

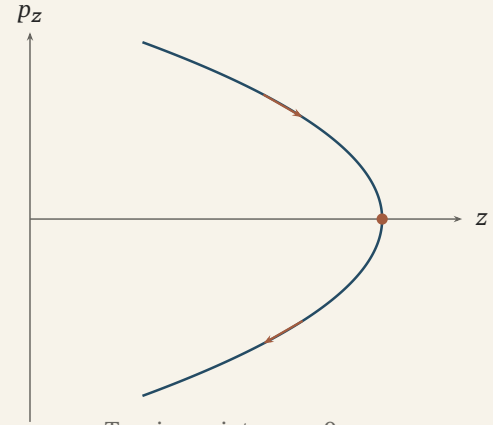
ONE CONCRETE HAMILTONIAN

$$H = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz.$$

$$\dot{z} = \frac{p_z}{m}, \qquad \dot{p}_z = -mg.$$

The vertical energy $E_z = p_z^2/(2m) + mgz$ is constant. Upward motion slows, turns, and falls.

VERTICAL MOTION AT FIXED ENERGY



Turning point: $p_z = 0$, $z = E_z/(mg)$.

From one history to a distribution of possibilities

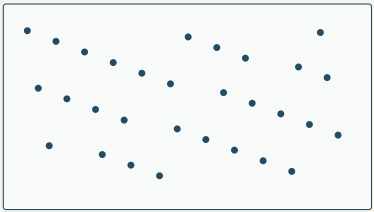
An ensemble is a distribution of possible microscopic states, not a new physical system.

$$\int \rho(\Gamma, t)\, \mathrm{d}\Gamma = 1.$$

The probability in a small phase-space volume is $\rho(\Gamma, t)\, \mathrm{d}\Gamma$.

> An observable is averaged over the possible preparations.

$$\boxed{\langle f \rangle (t) = \int f(\Gamma)\rho(\Gamma, t)\, \mathrm{d}\Gamma}.$$



an ensemble of phase points

Time averages versus ensemble averages

WHAT A LABORATORY OFTEN MEASURES

$$\overline{f} = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} f[\Gamma(t)]\, \mathrm{d}t.$$

This follows one realization for a long time.

WHAT AN ENSEMBLE CALCULATES

$$\langle f \rangle = \int f(\Gamma) \rho(\Gamma)\, \mathrm{d}\Gamma.$$

This averages over microscopic preparations at one time.

> Ergodicity can connect the two averages. It is a property of the dynamics and measure, not a consequence of having many degrees of freedom.

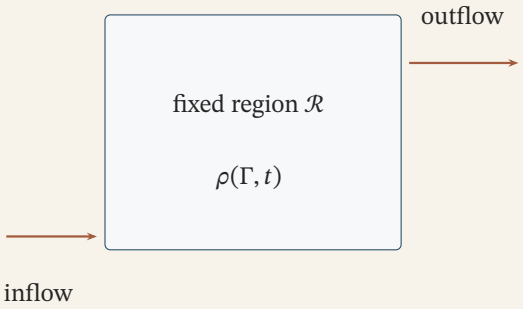
Probability obeys a continuity equation

For a fixed region $\mathcal{R}$ in phase space, probability changes only through its boundary:

$$\frac{\partial}{\partial t}\int_{\mathcal{R}} \rho \, \mathrm{d}\Gamma = -\oint_{\partial\mathcal{R}} \rho \mathbf{v}\cdot\hat{\mathbf{n}} \, \mathrm{d}\sigma.$$

The divergence theorem, for arbitrary $\mathcal{R}$, gives the local conservation law.

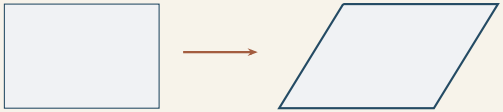
$$\boxed{\partial_t \rho + \nabla_\Gamma \cdot (\rho \mathbf{v}) = 0}.$$



Hamiltonian flow is incompressible

Hamilton's equations make the divergence of the phase-space velocity vanish:

$$\nabla_\Gamma \cdot \mathbf{v} = \sum_i \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = \sum_i \left(\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right) = 0.$$



$\mathcal{R}(0)$ $\mathcal{R}(t)$

The cloud can shear, stretch, and fold, but its phase-space volume is unchanged.

$$\mathrm{Vol}\,\mathcal{R}(t) = \mathrm{Vol}\,\mathcal{R}(0).$$

Liouville's theorem: density travels unchanged

Since $\nabla_\Gamma \cdot \mathbf{v} = 0$, the continuity equation becomes

$$\partial_t \rho + \sum_i \left(\dot{q}_i \, \partial_{q_i} \rho + \dot{p}_i \, \partial_{p_i} \rho \right) = 0.$$

POISSON-BRACKET FORM

$$\boxed{\partial_t \rho + \{\rho, H\} = 0}.$$

FOLLOW A MOVING PHASE POINT

$$\boxed{\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0}.$$

$\{A, B\} = \sum_i [(\partial_{q_i} A)(\partial_{p_i} B) - (\partial_{p_i} A)(\partial_{q_i} B)]$. The same convention is used throughout.

A conserved density is not necessarily stationary

MATERIAL DERIVATIVE

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = \partial_t \rho + \mathbf{v} \cdot \nabla_\Gamma \rho = 0.$$

A moving phase point carries a constant density. The surrounding distribution may still change at any fixed location.

STATIONARITY

$$\partial_t \rho = 0.$$

A stationary ensemble has an unchanging density at each fixed location. It must additionally satisfy $\{\rho, H\} = 0$.

> Incompressible motion does not mean motionless probability.

Functions of conserved quantities are stationary

For a time-independent Hamiltonian, let

$$\rho(\Gamma) = F[H(\Gamma)].$$

$$\{F(H), H\} = F'(H)\{H, H\} = 0.$$

More generally, a function of conserved quantities is stationary.

EXAMPLES AND A LIMITATION

A constant weight on an energy shell is stationary. So is a Boltzmann weight $e^{-\beta H}$, once normalized.

> Stationarity does not select the equilibrium ensemble uniquely. The imposed constraints and statistical assumptions select the weights.

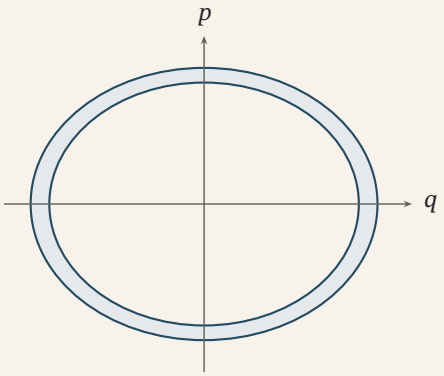
An energy shell defines the ensemble

Define the phase-space volume per unit energy,

$$\omega(E) = \int \delta[H(\Gamma) - E]\, \mathrm{d}\Gamma.$$

$$\boxed{\rho_{\mathrm{mc}}(\Gamma) = \frac{\delta[H(\Gamma) - E]}{\omega(E)}}.$$

Equivalently, use a uniform thin shell of width ΔE, then take a suitably narrow-shell limit.



A schematic energy shell, shown for an oscillator.

What Liouville proves – and what it does not

THE INVARIANT SURFACE MEASURE

$$\int f\,\delta(H-E)\,\mathrm{d}\Gamma = \int_{H=E} \frac{f\,\mathrm{d}\Sigma}{|\nabla_\Gamma H|}.$$

Uniform in a thin phase-space shell does not mean uniform Euclidean area on the surface $H = E$.

MECHANICS AND STATISTICS

Liouville's theorem preserves the chosen microcanonical measure. It does not prove equal a priori probability or convergence to equilibrium.

> The microcanonical postulate chooses the measure. Hamiltonian dynamics makes that choice consistent in time.

The ideal-gas phase volume

For N ideal-gas particles, the positions contribute V^N and the momenta fill a $3N$-dimensional ball:

$$\Phi(E) = \int_{H<E} \mathrm{d}\Gamma = V^N \frac{(2\pi m E)^{3N/2}}{\Gamma(3N/2+1)}.$$

$$\omega(E) = \frac{\partial \Phi}{\partial E} = \frac{V^N (2\pi m)^{3N/2}}{\Gamma(3N/2)} E^{3N/2-1}.$$

> Φ and $\omega \Delta E$ are still dimensional volumes, not numbers of quantum states.

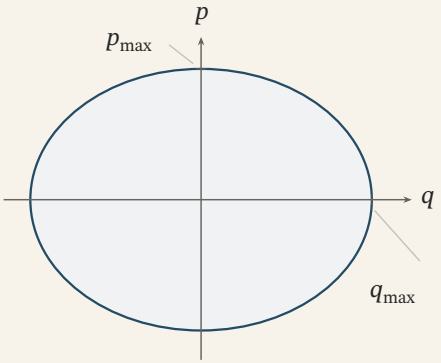
An oscillator's area is an action

$$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 q^2.$$

$$q_{\max} = \sqrt{\frac{2E}{m\omega^2}}, \qquad p_{\max} = \sqrt{2mE}.$$

The area enclosed by the orbit is

$$\boxed{\mathcal{A}(E) = \pi q_{\max} p_{\max} = \frac{2\pi E}{\omega}}.$$



An action: area has units of position × momentum.

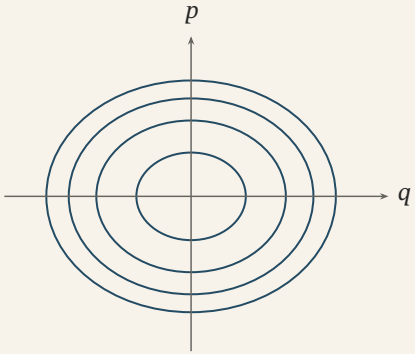
One added quantum contributes an area h

The oscillator spectrum has equally spaced energies:

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega.$$

Adjacent levels differ by $\Delta E = \hbar\omega$. Therefore

$$\boxed{\Delta\mathcal{A} = \frac{2\pi}{\omega}\Delta E = 2\pi\hbar = h}.$$



The radii grow as $\sqrt{n + 1/2}$; adjacent annuli have equal area h.

The uncertainty scale is not the counting factor

UNCERTAINTY FIXES THE SCALE

$$\Delta q \, \Delta p \geq \frac{\hbar}{2}.$$

Quantum states cannot be localized arbitrarily sharply in both variables.

STATE COUNTING FIXES THE FACTOR

one state per h^f in $2f$ dimensions.

The oscillator, or the spacing of wavevectors in a box, gives the exact semiclassical counting factor.

> The phase-space cell is a counting rule, not a claim that every quantum state occupies a disjoint rectangular tile.

From phase volume to state count

For a phase-space region $\mathcal{R}$ with f canonical pairs, the semiclassical count is

$$\#\ \text{states} \simeq \frac{1}{h^f} \int_{\mathcal{R}} \mathrm{d}^f q\ \mathrm{d}^f p.$$

FOR A DILUTE IDENTICAL GAS

$$\boxed{\Omega(E, V, N) \simeq \frac{\omega(E)\Delta E}{N! h^{3N}}}.$$

TWO DISTINCT CORRECTIONS

h^{3N} converts a phase volume into a state count.

$N!$ removes permutations of identical particles.

These factors cancel in normalized classical averages, but not in entropy or chemical potential.

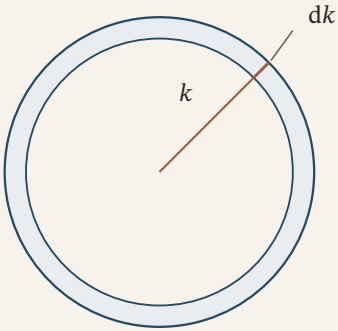
The same rule counts electromagnetic modes

In a large periodic box, one wavevector state occupies $(2\pi)^3/V$ in $\mathbf{k}$ space.

$$\mathrm{d}\mathcal{N} = 2\frac{V}{(2\pi)^3}4\pi k^2\,\mathrm{d}k.$$

The factor 2 is the number of transverse polarizations. With $\omega = ck$,

$$\boxed{\mathrm{d}\mathcal{N} = \frac{V\omega^2}{\pi^2 c^3}\,\mathrm{d}\omega}.$$



A section of the wavevector shell. The full shell is three-dimensional.

States, motion, measure, and counting

MECHANICS

$$(q, p) \longrightarrow (\dot{q}, \dot{p})$$

Hamilton's equations move microstates. Liouville's theorem preserves phase volume and transports density.

STATISTICAL DESCRIPTION

$$\rho(\Gamma) \longrightarrow \langle f \rangle$$

The ensemble weights possible states. Quantum mechanics supplies the counting scale h^f.

> An isolated system uses an energy-shell measure. Next, thermal contact replaces the fixed energy by a Boltzmann weight.

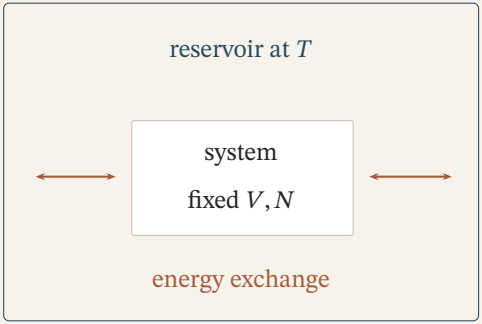
The Canonical Ensemble

Boltzmann weights, response, and the limits of equipartition

Tsvi Tlusty · UNIST

Convention: $k_{\mathrm{B}} = 1$

A heat bath replaces the fixed energy



Weak coupling makes the composite energy approximately additive.

For a microstate r of energy E_r, the reservoir has energy $E^{(0)} - E_r$.

$$p_r \propto \Omega_R(E^{(0)} - E_r).$$

$$S_R(E^{(0)} - E_r) \simeq S_R(E^{(0)}) - \beta E_r.$$

The reservoir's entropy slope supplies the factor $\mathrm{e}^{-\beta E_r}$, with $\beta = 1/T$.

The canonical probability law

$$\boxed{p_r = \frac{\mathrm{e}^{-\beta E_r}}{Q_N}}, \qquad Q_N(T,V) = \sum_r \mathrm{e}^{-\beta E_r}.$$

A MICROSTATE PROBABILITY

$$\frac{p_r}{p_s} = \mathrm{e}^{-\beta(E_r - E_s)}.$$

The ratio depends on the energy difference. Normalization is supplied by Q_N.

AN ENERGY-LEVEL PROBABILITY

$$P(E_i) = \frac{g_i \mathrm{e}^{-\beta E_i}}{Q_N}.$$

An energy shared by g_i microstates has an extra degeneracy factor. Do not confuse a state with an energy level.

The same law from a maximum of multiplicity

Take $\mathcal{N}$ distinguishable copies. If n_r copies occupy microstate r,

$$W = \frac{\mathcal{N}!}{\prod_r n_r!}, \qquad \sum_r n_r = \mathcal{N}, \qquad \sum_r n_r E_r = \mathcal{N} U.$$

Maximize $\ln W$ under the two constraints. Stirling gives

$$\ln W \simeq \mathcal{N} \ln \mathcal{N} - \sum_r n_r \ln n_r.$$

The stationary occupations satisfy

$$\frac{n_r^*}{\mathcal{N}} = \frac{\mathrm{e}^{-\beta E_r}}{Q_N}.$$

The multiplicity is exponentially sharp in $\mathcal{N}$. This reproduces the reservoir construction.

The first derivative gives the mean energy

For a spectrum independent of temperature, differentiate the normalization sum:

$$\frac{\partial Q_N}{\partial \beta} = -\sum_r E_r \mathrm{e}^{-\beta E_r} = -Q_N \langle E \rangle .$$

$$\boxed{U = \langle E \rangle = -\left(\frac{\partial \ln Q_N}{\partial \beta} \right)_{V,N}}.$$

> The partition function is a generator: its logarithmic derivatives are equilibrium observables.

Entropy identifies the Helmholtz free energy

Since $-\ln p_r = \beta E_r + \ln Q_N$, averaging over the canonical ensemble gives

$$S = -\sum_r p_r \ln p_r = \beta U + \ln Q_N.$$

Use $A = U - TS$:

$$\boxed{A(T, V, N) = -T \ln Q_N}.$$

TWO IMPORTANT LIMITS

For Ω equally probable states, $S = \ln \Omega$.

As $T \to 0^+$, a nondegenerate ground state has $p_0 \to 1$ and $S \to 0$.

> A ground-state degeneracy g_0 instead leaves a residual entropy $\ln g_0$.

One potential generates the thermodynamics

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

$$S = -\left(\partial_T A\right)_{V,N}, \quad P = -\left(\partial_V A\right)_{T,N}, \quad \mu = \left(\partial_N A\right)_{T,V}.$$

If an external parameter λ changes the Hamiltonian,

$$\frac{\partial A}{\partial \lambda} = \left\langle \frac{\partial H}{\partial \lambda} \right\rangle.$$

The conjugate generalized force is

$$X_\lambda = -\partial_\lambda A.$$

Pressure is the case $\lambda = V$.

The partition function is a Laplace transform

RESOLVE THE STATE COUNT BY ENERGY

Let $D(E)\,\mathrm{d}E$ be the number of states in an energy interval. Then

$$\boxed{Q_N(\beta) = \int D(E)\mathrm{e}^{-\beta E}\,\mathrm{d}E}.$$

The canonical partition function is a Laplace transform of the density of states.

KEEP THE THREE COUNTS DISTINCT

$$D(E) = \frac{\mathrm{d}\Sigma}{\mathrm{d}E},$$

$$\Sigma(E) = \int^{E} D(E')\,\mathrm{d}E',$$

$$\Omega(E) \simeq D(E)\Delta E.$$

> D is a density, Σ is cumulative, and Ω counts a thin shell.

Classical weights in phase space

For N identical particles in the dilute Maxwell–Boltzmann regime,

$$Q_N = \frac{1}{N! h^{3N}} \int \mathrm{e}^{-\beta H(\mathbf{q},\mathbf{p})}\, \mathrm{d}^{3N}q\, \mathrm{d}^{3N}p.$$

$$\langle f \rangle = \frac{\int f(\Gamma) \mathrm{e}^{-\beta H(\Gamma)}\, \mathrm{d}\Gamma}{\int \mathrm{e}^{-\beta H(\Gamma)}\, \mathrm{d}\Gamma}.$$

> The counting factors matter for A, S, and μ, but cancel in normalized classical averages.

The ideal gas becomes a Gaussian integral

For an ideal gas, the positions give V^N and each momentum integral is Gaussian:

$$\int_{\mathbb{R}^3} \mathrm{e}^{-\beta p^2/(2m)}\, \mathrm{d}^3 p = (2\pi m T)^{3/2}.$$

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

THE ENTIRE CALCULATION IN ONE FORMULA

$$\boxed{Q_N = \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N}.$$

Taking the logarithm before differentiating makes the thermodynamics immediate.

> Validity requires $n\lambda_T^3 \ll 1$: quantum exchange is then negligible.

The ideal gas: differentiate once

$$\ln Q_N = -\ln N! + N \ln V - 3N \ln \lambda_T.$$

ENERGY AND PRESSURE

$$U = -\partial_\beta \ln Q_N = \frac{3}{2} NT,$$

$$P = T \partial_V \ln Q_N = \frac{NT}{V}.$$

FREE ENERGY AND ENTROPY

$$A = NT[\ln(n\lambda_T^3) - 1],$$

$$S = N[\ln(1/(n\lambda_T^3)) + 5/2].$$

$$C_V = \frac{3}{2} N, \qquad \mu = T \ln(n\lambda_T^3).$$

Recovering the density of states

Write the canonical result as $Q_N = C_N \beta^{-a}$, with $a = 3N/2$ and $C_N = V^N (2\pi m)^{3N/2} / (N! h^{3N})$.

$$\int_0^\infty \frac{E^{a-1}}{\Gamma(a)} \mathrm{e}^{-\beta E} \, \mathrm{d}E = \beta^{-a}.$$

$$\boxed{D(E) = \frac{V^N (2\pi m)^{3N/2}}{N! h^{3N} \Gamma(3N/2)} E^{3N/2-1}}.$$

> The canonical Gaussian integral recovers the microcanonical hypersphere count.

Energy fluctuations are a response coefficient

Differentiate the mean energy once more:

$$\frac{\partial^2 \ln Q_N}{\partial \beta^2} = \langle E^2 \rangle - \langle E \rangle^2 = \mathrm{Var}(E) = -\frac{\partial U}{\partial \beta}.$$

Since $\mathrm{d}T/\,\mathrm{d}\beta = -T^2$,

$$\boxed{\mathrm{Var}(E) = T^2 C_V}.$$

The same coefficient controls a spontaneous fluctuation and a response to changing temperature.

> For a temperature-independent canonical Hamiltonian, $C_V \geq 0$.

Many energies, one narrow window

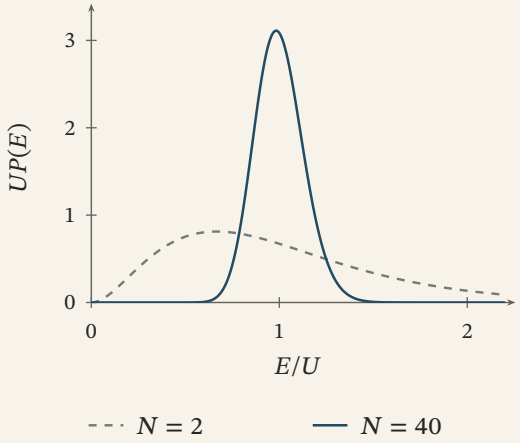
The full energy probability includes the density of states:

$$P(E) = \frac{D(E)\mathrm{e}^{-\beta E}}{Q_N}.$$

For an ideal gas, $a = 3N/2$ and $P(E)$ is a gamma distribution:

$$U = aT, \quad E^* = (a-1)T, \quad \sigma_E^2 = aT^2.$$

Mean and mode differ by T, a relative difference of order $1/N$.



The saddle point explains ensemble equivalence

Choose a fixed microscopic bin ΔE_0 and define $S_B(E) = \ln[D(E)\Delta E_0]$. The dominant energy satisfies

$$\partial_E S_B(E^*) = \beta, \qquad S_B''(E^*) \simeq -\frac{1}{T^2 C_V}.$$

$$P(E) \simeq \frac{1}{\sqrt{2\pi T^2 C_V}} \exp\left[-\frac{(E-E^*)^2}{2T^2 C_V}\right].$$

> For an ordinary bulk phase, $U \sim N$ and $C_V \sim N$, so $\sigma_E/U \sim N^{-1/2}$.

A subextensive cost for the width

The same saddle point estimates the partition function itself:

$$Q_N \simeq \frac{\sqrt{2\pi T^2 C_V}}{\Delta E_0}\, \mathrm{e}^{S_B(E^*)-\beta E^*}.$$

$$A \simeq E^* - T S_B(E^*) - T \ln \frac{\sqrt{2\pi T^2 C_V}}{\Delta E_0}.$$

> The first two terms are extensive. The width contributes only $O(T \ln N)$, which vanishes per particle.

An integration-by-parts identity does the work

Let x_j be a phase-space variable. If the boundary term vanishes, integrate by parts:

$$0 = \int \partial_{x_j}\!\left(x_i \mathrm{e}^{-\beta H}\right) \mathrm{d}\Gamma = \delta_{ij} \int \mathrm{e}^{-\beta H}\, \mathrm{d}\Gamma - \beta \int x_i \partial_{x_j} H\, \mathrm{e}^{-\beta H}\, \mathrm{d}\Gamma.$$

$$\boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = T \delta_{ij}}.$$

> The boundary assumption is automatic for Gaussian momenta, but needs care at hard coordinate walls.

One quadratic term gives T/2

If an unconstrained variable enters only through a quadratic term, $H \supset ax^2$, then

$$\langle x \partial_x H \rangle = 2 \langle ax^2 \rangle = T.$$

$$\boxed{\langle ax^2 \rangle = T/2}.$$

COUNT QUADRATIC TERMS

A monatomic gas has $3N$ translational terms: $U = 3NT/2$.

A set of N one-dimensional oscillators has $2N$ terms: $U = NT$.

> Equipartition is classical. A quantum degree of freedom freezes out when its energy spacing exceeds T.

The virial theorem connects forces to pressure

For a confined system, define the virial coordinate $G = \sum_i \mathbf{r}_i \cdot \mathbf{p}_i$. In equilibrium,

$$0 = \langle \dot{G} \rangle = 2 \langle K \rangle + \left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i \right\rangle .$$

THE WALL CONTRIBUTION

$$\left\langle \sum_i \mathbf{r}_i \cdot \mathbf{F}_i^{\text{wall}} \right\rangle = -P \oint \mathbf{r} \cdot \mathrm{d}\mathbf{S} = -3PV .$$

THE GEOMETRIC STEP

$$\oint \mathbf{r} \cdot \mathrm{d}\mathbf{S} = \int_V \nabla \cdot \mathbf{r} \, \mathrm{d}V = 3V .$$

Confinement or bounded virial motion is needed to set the long-time average of $\dot{G}$ to zero.

Interactions correct the ideal-gas pressure

For pair forces, action and reaction combine as $\mathbf{r}_i \cdot \mathbf{F}_{ij} + \mathbf{r}_j \cdot \mathbf{F}_{ji} = \mathbf{r}_{ij} \cdot \mathbf{F}_{ij}$. Hence

$$\boxed{PV = NT + \frac{1}{3}\left\langle \sum_{i<j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \right\rangle}.$$

A CENTRAL PAIR POTENTIAL

$$PV = NT - \frac{1}{3}\left\langle \sum_{i<j} r_{ij} u'(r_{ij}) \right\rangle.$$

attraction



$\mathbf{r}_{ij} \cdot \mathbf{F}_{ij} < 0$

$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$; $\mathbf{F}_{ij}$ is the force on i due to j.

The classical oscillator has two quadratic terms

$$q_1 = \frac{1}{h}\int \mathrm{d}p\ \mathrm{d}q\, \mathrm{e}^{-\beta[p^2/(2m)+m\omega^2 q^2/2]} = \frac{T}{\hbar\omega}.$$

INDEPENDENT LOCALIZED MODES

$$Q_N = q_1^N = (\beta\hbar\omega)^{-N}.$$

There is no particle-permutation factor $1/N!$ for distinct oscillator modes.

CLASSICAL THERMODYNAMICS

$$U = NT, \qquad C_V = N,$$

$$A = NT\ln(\beta\hbar\omega),$$

$$S = N[1 - \ln(\beta\hbar\omega)].$$

Quantum oscillators: discrete excitation

The quantum levels are $E_n = (n + 1/2)\hbar\omega$. A geometric series gives

$$q_1 = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega(n+1/2)} = \frac{1}{2\sinh(\beta\hbar\omega/2)}.$$

For N independent modes, $Q_N = q_1^N$. Differentiate its logarithm as before.

ZERO-POINT PLUS THERMAL ENERGY

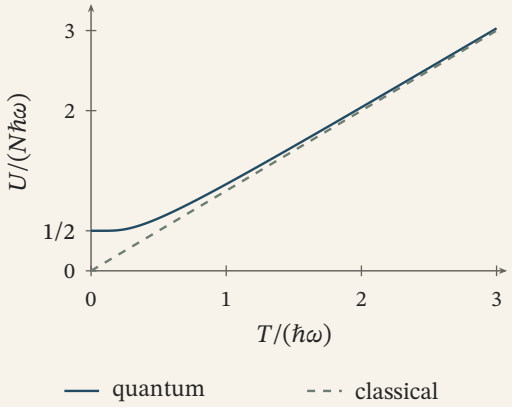
$$\boxed{\frac{U}{N} = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega} - 1}}.$$

$$\frac{C_V}{N} = \frac{x^2\mathrm{e}^x}{(\mathrm{e}^x - 1)^2}, \qquad x = \frac{\hbar\omega}{T}.$$

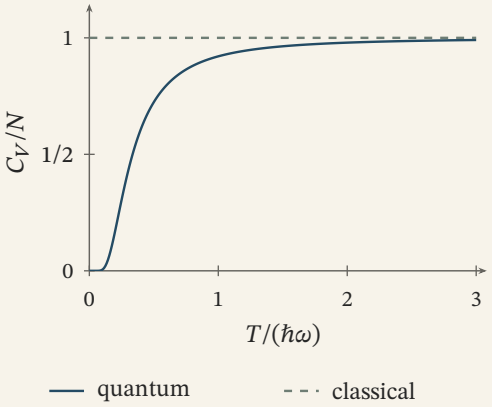
> Discreteness replaces classical equipartition at low temperature.

Equipartition is the high-temperature limit

ENERGY



HEAT CAPACITY



The oscillator count agrees

Put R identical excitation quanta into N distinguishable oscillator modes. The energy and multiplicity are

$$E = \frac{N}{2}\hbar\omega + R\hbar\omega, \qquad \Omega_R = \binom{R+N-1}{R}.$$

STARS AND BARS



$(2,1,0,3)$: $N = 4,\ R = 6$

Stirling's formula and $\beta = \partial_E \ln \Omega_R$ give

$$\frac{R}{N} = \frac{1}{e^{\beta\hbar\omega} - 1}.$$

Classical moments in a magnetic field

A localized classical dipole of magnitude μ_s in field B has $E(\theta) = -\mu_s B\cos\theta$. Write $x = \mu_s B/T$.

$$q_1 = \int \mathrm{e}^{x\cos\theta}\,\mathrm{d}\Omega = 4\pi\frac{\sinh x}{x}.$$

The total moment is $M = T\partial_B \ln Q_N$, with $Q_N = q_1^N$.

THE LANGEVIN FUNCTION

$$\boxed{\frac{M}{N\mu_s} = L(x) = \coth x - \frac{1}{x}}.$$

$$L(x) \simeq \frac{x}{3} \quad (x \ll 1),$$

$$L(x) \to 1 \quad (x \to \infty).$$

Weak fields give Curie's law: $\chi = \partial_B M = N\mu_s^2/(3T)$.

Quantum moments: discrete projections

Label the $2J+1$ moment projections by $m = -J, \dots, J$. Write $\mu_{\mathrm{sat}} = g_J \mu_{\mathrm{B}} J$ and $x = \mu_{\mathrm{sat}} B / T$. Then $E_m = -\mu_{\mathrm{sat}} B m / J$.

$$q_1 = \sum_{m=-J}^{J} \mathrm{e}^{x m / J} = \frac{\sinh[(2J+1)x/(2J)]}{\sinh[x/(2J)]}.$$

$$\boxed{\frac{M}{N \mu_{\mathrm{sat}}} = B_J(x)}, \qquad B_J(x) = \frac{2J+1}{2J} \coth \frac{(2J+1)x}{2J} - \frac{1}{2J} \coth \frac{x}{2J}.$$

μ_{B} is the Bohr magneton; g_J sets the moment scale. The finite geometric sum replaces the angular integral.

Curie response crosses over to saturation

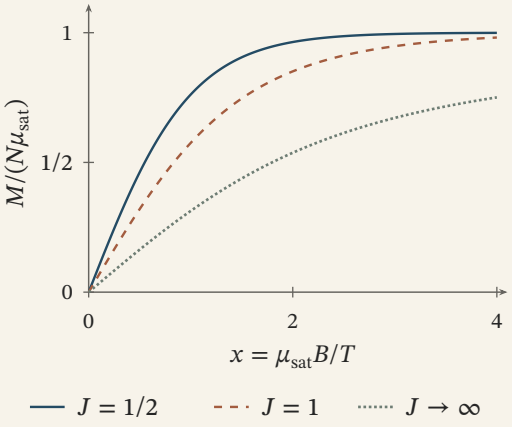
The small-field limit is

$$B_J(x) \simeq \frac{J+1}{3J}x, \quad \chi = \frac{N(g_J\mu_B)^2 J(J+1)}{3T}.$$

For $J = 1/2$, $B_{1/2}(x) = \tanh x$.

At fixed saturation moment, $J \to \infty$ gives the classical Langevin function.

In LS coupling, $g_J = 1 + \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}$ for $J > 0$.



Two levels and negative temperature

For N independent two-level units with energies $-\epsilon$ and $+\epsilon$,

$$Q_N = [2\cosh(\beta\epsilon)]^N.$$

$$\begin{aligned} U &= -N\epsilon\tanh(\beta\epsilon), \\ S &= N[\ln(2\cosh(\beta\epsilon)) - \beta\epsilon\tanh(\beta\epsilon)], \\ C &= N(\beta\epsilon)^2\operatorname{sech}^2(\beta\epsilon). \end{aligned}$$

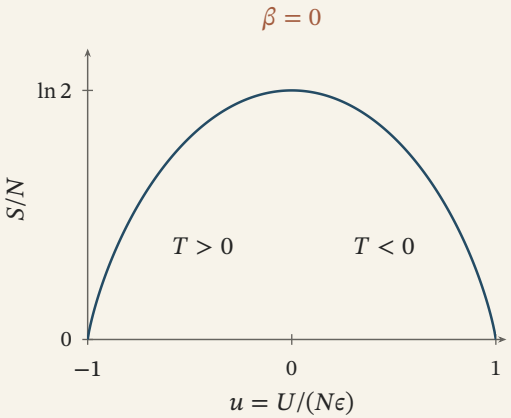
> The bounded spectrum keeps the partition function finite even when $\beta < 0$.

Beyond the entropy maximum

Let $u = U/(N\epsilon)$. The upper and lower fractions are $(1+u)/2$ and $(1-u)/2$. Counting gives

$$\frac{S}{N} = -\frac{1+u}{2}\ln\frac{1+u}{2} - \frac{1-u}{2}\ln\frac{1-u}{2}.$$

$$\boxed{\beta = \frac{\partial S}{\partial U} = \frac{1}{2\epsilon}\ln\frac{1-u}{1+u}}.$$



Adding energy beyond the maximum lowers S.

Negative temperature is hotter, not colder

Transfer a small energy $\delta Q > 0$ from system A to system B. The total entropy change is

$$\delta S_{\text{tot}} = -\beta_A \delta Q + \beta_B \delta Q = (\beta_B - \beta_A)\delta Q.$$

THE THERMAL ORDER

If $\beta_A < \beta_B$, energy flow from A to B increases total entropy. A negative-β system can heat any positive-β system.

THE PHYSICAL RESTRICTION

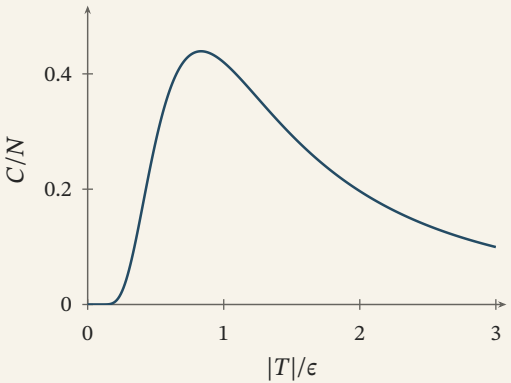
Negative temperature needs an upper-bounded accessible spectrum and isolation from unbounded degrees of freedom, such as free-particle motion.

The Schottky peak is a redistribution window

$$\frac{C}{N} = x^2 \operatorname{sech}^2 x, \qquad x = \frac{\epsilon}{|T|}.$$

At low $|T|$, almost all units occupy one extreme level. At high $|T|$, the populations approach equality and the energy saturates.

> The heat capacity is largest where thermal energy can most effectively redistribute the populations.



Peak at $|T|/\epsilon \simeq 0.834$; $C/N \simeq 0.439$.

Infinite temperature is a regular point in beta

For a finite one-unit spectrum $\{\epsilon_n\}_{n=1}^{q}$, let the overbar be the uniform average and $\sigma_\epsilon^2 = \overline{\epsilon^2} - \bar{\epsilon}^2$. Near $\beta = 0$,

$$\ln q_1 = \ln q - \beta\bar{\epsilon} + \frac{\beta^2}{2}\sigma_\epsilon^2 + O(\beta^3).$$

$$\frac{U}{N} = \bar{\epsilon} - \beta\sigma_\epsilon^2 + O(\beta^2), \qquad \frac{S}{N} = \ln q - \frac{\beta^2}{2}\sigma_\epsilon^2 + O(\beta^3).$$

> $\beta = 0$ is the maximum-entropy state. Entropy is even in β only for a spectrum symmetric about its mean.

The canonical toolkit

THE CANONICAL TOOLKIT

$$p_r = \frac{e^{-\beta E_r}}{Q_N}, \qquad A = -T \ln Q_N.$$

$$U = -\partial_\beta \ln Q_N, \qquad \mathrm{Var}(E) = T^2 C_V.$$

One normalization sum generates the equilibrium thermodynamics and the fluctuations around it.

THE LESSON FROM THE EXAMPLES

Classical quadratic variables equipartition. Quantum level spacing freezes motion out. Bounded spectra can pass through $\beta = 0$ into population inversion.

> The canonical ensemble allows energy exchange. Lecture 4 adds particle exchange, and the chemical potential enters the statistical weight.

The Grand Canonical Ensemble

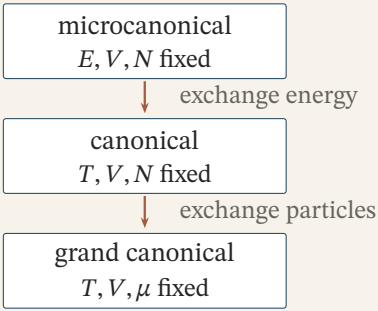
Fugacity, fluctuations, and the geometry of phase coexistence

Tsvi Tlusty · UNIST

Convention: $k_B = 1$

What changes when particles may enter?

THE HIERARCHY OF CONSTRAINTS



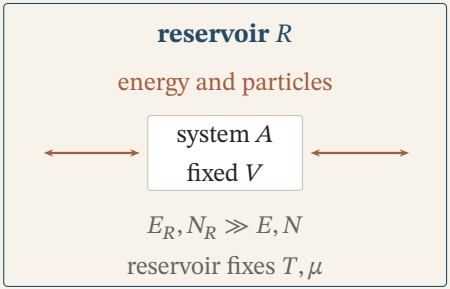
THE CENTRAL MOVE

The reservoir replaces two conserved quantities by two intensive variables:

$$E \longleftrightarrow T, \qquad N \longleftrightarrow \mu.$$

> The volume is held fixed. Energy and particle number fluctuate, while T and μ remain imposed by the reservoir.

The reservoir prices a microstate



For a system microstate (N, r) with energy $E_{N,r}$,

$$p_{N,r} \propto \Omega_R(E^{(0)} - E_{N,r}, N^{(0)} - N).$$

Expand the reservoir entropy $S_R = \ln \Omega_R$:

$$\begin{aligned} S_R &\simeq S_R^{(0)} - \left(\frac{\partial S_R}{\partial E_R}\right) E_{N,r} - \left(\frac{\partial S_R}{\partial N_R}\right) N \\ &= S_R^{(0)} - \frac{E_{N,r}}{T} + \frac{\mu N}{T}. \end{aligned}$$

> Energy costs E/T; admitting N particles returns $\mu N/T$.

The grand-canonical probability law

NORMALIZATION OVER ALL PARTICLE-NUMBER SECTORS

$$p_{N,r} = \frac{\mathrm{e}^{-\beta(E_{N,r}-\mu N)}}{\mathcal{Q}} \qquad \mathcal{Q} = \sum_{N=0}^{\infty} \sum_{r} \mathrm{e}^{-\beta(E_{N,r}-\mu N)}.$$

Introduce

$$\alpha = -\beta\mu, \qquad z = \mathrm{e}^{\beta\mu} = \mathrm{e}^{-\alpha}.$$

Then the weight is $\mathrm{e}^{-\alpha N - \beta E_{N,r}}$.

> The probability is attached to a *microstate*. A probability for an energy interval must also include the density of states.

When N is fixed, $\mathrm{e}^{\beta\mu N}$ cancels and the canonical ensemble is recovered.

The same law from many copies

Take $\mathcal{N} \gg 1$ distinguishable copies and let $m_{N,r}$ be the number in state (N, r).

$$\sum_{N,r} m_{N,r} = \mathcal{N}, \qquad \sum_{N,r} N m_{N,r} = \mathcal{N}\bar{N},$$

$$\sum_{N,r} E_{N,r} m_{N,r} = \mathcal{N} U.$$

The multiplicity is

$$W = \frac{\mathcal{N}!}{\prod_{N,r} m_{N,r}!}.$$

Maximize $\ln W$ under the three constraints:

$$\frac{m^*_{N,r}}{\mathcal{N}} \propto \mathrm{e}^{-\alpha N - \beta E_{N,r}}, \qquad \sum_{N,r} \frac{m^*_{N,r}}{\mathcal{N}} = 1.$$

> In the many-copy limit, the most probable frequencies become the grand-canonical probabilities.

The reservoir and maximum-multiplicity constructions are two views of the same ensemble.

One potential contains the thermodynamics

Let $q = \ln \mathcal{Q}$. From $\ln p_{N,r} = -q - \alpha N - \beta E_{N,r}$,

$$S = -\sum p \ln p = q + \alpha N + \beta U.$$

Using $\alpha = -\mu/T$ and $\beta = 1/T$ gives

$$\boxed{\Phi_G \equiv U - TS - \mu N = -T \ln \mathcal{Q}}$$

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

For a homogeneous macroscopic phase,

$$\Phi_G = -PV, \qquad q = \frac{PV}{T}.$$

Φ_G is the natural potential when T, V, μ are controlled. Stable equilibrium minimizes it.

Fugacity makes a generating function

Group microstates by particle number:

$$\boxed{\mathcal{Q}(z,V,T)=\sum_{N=0}^{\infty} z^N Q_N(V,T)}, \qquad z=\mathrm{e}^{\beta\mu}.$$

FIRST DERIVATIVES: MEANS

$$N = z\left(\frac{\partial q}{\partial z}\right)_{T,V}, \quad U = T^2\left(\frac{\partial q}{\partial T}\right)_{z,V}.$$

$$P = T\left(\frac{\partial q}{\partial V}\right)_{T,z}.$$

LEGENDRE RETURN TO FIXED N

$$A = \Phi_G + \mu N = -Tq + NT\ln z,$$

$$S = q + \frac{U}{T} - N\ln z.$$

> Second derivatives of q give fluctuations and response functions.

Example: the classical ideal gas

For independent indistinguishable particles in the Maxwell–Boltzmann regime,

$$Q_N = \frac{[Vf(T)]^N}{N!}.$$

Therefore

$$\mathcal{Q} = \sum_{N=0}^{\infty} \frac{[zVf(T)]^N}{N!} = \exp[zVf(T)], \qquad q = zVf(T).$$

$$N = zVf(T), \quad P = zTf(T), \quad PV = NT.$$

$$\frac{U}{N} = T^2 \frac{\mathrm{d}}{\mathrm{d}T} \ln f(T).$$

If $f(T) \propto T^\nu$, then $U = \nu NT$ and $C_V = \nu N$.

> Internal states change U and C_V, but not the ideal-gas equation of state.

A different sum: independent localized units

If each localized unit has partition function $\phi(T)$ and distinct locations,

$$Q_N = \phi(T)^N, \qquad \mathcal{Q} = \sum_{N=0}^{\infty} [z\phi(T)]^N = \frac{1}{1 - z\phi(T)}.$$

Write $x = z\phi(T)$. Then

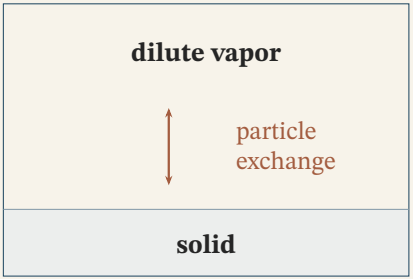
$$N = \frac{x}{1-x}, \qquad \frac{U}{N} = T^2 \frac{\phi'(T)}{\phi(T)}.$$

For one harmonic degree of freedom,

$$\phi_{\mathrm{qm}} = \frac{1}{2\sinh(\hbar\omega/2T)}, \quad \phi_{\mathrm{cl}} = \frac{T}{\hbar\omega}.$$

This is a formal localized-unit model, not a complete compressible solid. It has $\mathrm{Var}(N) = N(N+1)$, so relative number fluctuations do not vanish.

Solid–vapor equilibrium is equality of fugacity



At equilibrium,

$$\mu_g = \mu_s \quad \Longleftrightarrow \quad z_g = z_s.$$

For a dilute gas, $z_g = N_g/[V_g f(T)]$. For a macroscopic localized phase, $z_s \phi(T) \simeq 1$. Hence

$$\frac{N_g}{V_g} \simeq \frac{f(T)}{\phi(T)}, \qquad P_{\text{sat}}(T) = \frac{T f(T)}{\phi(T)}.$$

For a monatomic vapor above an Einstein solid,

$$P_{\text{sat}} = \frac{T}{\lambda_T^3}[2\sinh(\hbar\omega/2T)]^3 \mathrm{e}^{-\epsilon/T}.$$

Fluctuations and compressibility

Since $N = -\partial_\alpha q$,

$$\mathrm{Var}(N) = \partial_\alpha^2 q = T\left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

For one homogeneous component, Gibbs–Duhem gives $(\mathrm{d}\mu)_T = \mathrm{d}P/n$, while $(\partial n/\partial P)_T = n\kappa_T$. Therefore

$$\boxed{\frac{\mathrm{Var}(N)}{N^2} = \frac{\mathrm{Var}(n)}{n^2} = \frac{T\kappa_T}{V}}.$$

Away from a transition, κ_T is finite, so $\sqrt{\mathrm{Var}(N)}/N \sim N^{-1/2}$.

For an ideal gas, $\kappa_T = 1/P$ and $\mathrm{Var}(N) = N$ (the Poisson law).

High compressibility means large spontaneous density fluctuations.

Energy fluctuations: a second channel

At fixed fugacity,

$$\mathrm{Var}(E) = T^2 \left(\frac{\partial U}{\partial T} \right)_{z,V}.$$

But changing T at fixed z changes both the energy per particle and the mean particle number. For a smooth bulk equation of state,

$$\boxed{\mathrm{Var}(E)_{\mathrm{GC}} = T^2 C_V + \left(\frac{\partial U}{\partial N} \right)^2_{T,V} \mathrm{Var}(N)}.$$

Canonical energy fluctuation

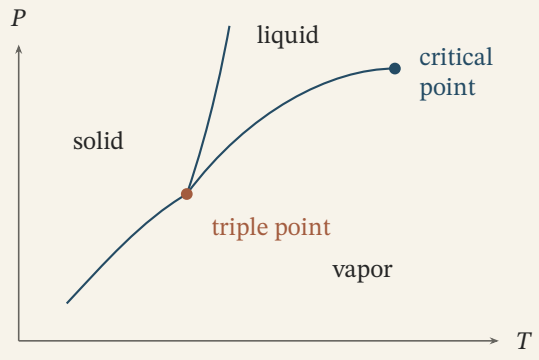
Energy redistributes at fixed N.

Particle-number contribution

Particles enter and leave.

Grand-canonical energy noise is never smaller than the canonical energy noise of the same bulk phase.

Coexistence: equal chemical potentials



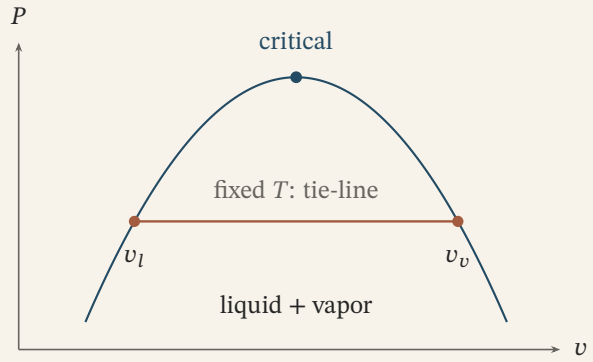
Two phases A and B coexist when transferring one particle costs no Gibbs energy:

$$\boxed{\mu_A(T,P) = \mu_B(T,P)}.$$

- A coexistence curve solves this equality.
- Three curves meet where $\mu_S = \mu_L = \mu_V$.
- Only the liquid–vapor line ends at a critical point.

At criticality, liquid and vapor become one phase.

A line in P–T becomes a region in P–v



At fixed T and coexistence pressure, the endpoints are the pure phases. Intermediate volumes change only the phase fraction:

$$v = (1 - x)v_l + xv_v,$$

$$x = \frac{v - v_l}{v_v - v_l}.$$

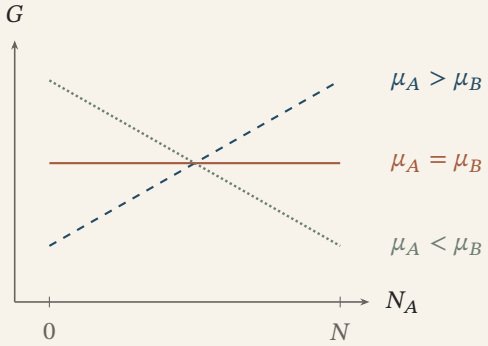
> The tie-line fixes the two phases; the lever rule fixes their proportions.

At criticality, v_l and v_v merge and the region closes.

Gibbs energy at coexistence

At fixed T, P, N, let $N_A + N_B = N$. Neglecting interfaces,

$$G = G_A(T, P, N_A) + G_B(T, P, N_B), \qquad \mathrm{d}G = (\mu_A - \mu_B)\,\mathrm{d}N_A.$$



$$G = N\mu_B + N_A(\mu_A - \mu_B).$$

Away from coexistence, the minimum lies at one endpoint: one pure phase wins.

> At $\mu_A = \mu_B$, the bulk Gibbs energy is flat. Changing the phase fraction costs no bulk Gibbs energy.

The Clapeyron equation

Along a coexistence curve, $\mu_A(T,P) = \mu_B(T,P)$. Since

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

differentiating the equality gives

$$-s_A\,\mathrm{d}T + v_A\,\mathrm{d}P = -s_B\,\mathrm{d}T + v_B\,\mathrm{d}P.$$

$$\boxed{\frac{\mathrm{d}P_{\mathrm{coex}}}{\mathrm{d}T} = \frac{\Delta s}{\Delta v} = \frac{\ell}{T\Delta v}}, \qquad \ell = T\Delta s.$$

For vaporization, $\Delta s > 0$ and $\Delta v > 0$: the slope is positive.

For melting, Δv may have either sign. Water has a negative slope because liquid water is denser than ice.

Latent heat and volume discontinuity determine the geometry of the phase boundary.

Lecture 4: the structure to retain

EXCHANGE

$$p_{N,r} \propto \mathrm{e}^{-\beta(E_{N,r}-\mu N)}.$$

The fugacity $z = \mathrm{e}^{\beta\mu}$ turns $\mathcal{Q}$ into a generating function for the canonical sectors.

FLUCTUATIONS

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

$$\frac{\mathrm{Var}(N)}{N^2} = \frac{T\kappa_T}{V}.$$

THERMODYNAMICS

$$\Phi_G = -T \ln \mathcal{Q},$$
$$\mathrm{d}\Phi_G = -S\,\mathrm{d}T - P\,\mathrm{d}V - N\,\mathrm{d}\mu.$$

COEXISTENCE

$$\mu_A = \mu_B, \qquad \frac{\mathrm{d}P}{\mathrm{d}T} = \frac{\Delta s}{\Delta v}.$$

> Exchange turns equilibrium into a calculus: first derivatives give means, second derivatives give fluctuations, and equal chemical potentials draw phase boundaries.

Formulation of Quantum Statistics

Density operators, exchange symmetry, and the classical limit

Tsvi Tlusty · UNIST

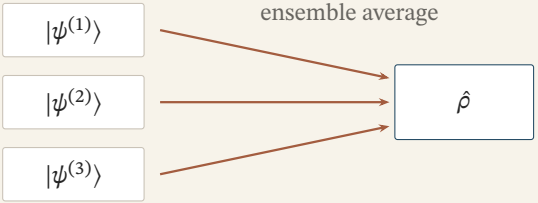
Convention: $k_B = 1$

Why a density operator?

TWO LAYERS OF PROBABILITY

A wavefunction already predicts probabilities for measurements on one system.

An ensemble adds uncertainty about which state was prepared.



WHAT MUST BE RETAINED?

Averaging the wavefunctions would lose phase-sensitive information. Instead average products of amplitudes:

$$\rho_{mn} = \overline{a_m a_n^*}.$$

> The density operator stores exactly the information needed to predict every observable, without confusing quantum uncertainty with statistical uncertainty.

Definition and three essential properties

For an ensemble with preparation probabilities w_k,

$$\boxed{\hat{\rho} = \sum_k w_k |\psi_k\rangle\langle\psi_k|}, \qquad w_k \geq 0, \quad \sum_k w_k = 1.$$

In a basis $\{|\phi_n\rangle\}$,

$$\rho_{mn} = \sum_k w_k a_m^{(k)} a_n^{(k)*}.$$

NORMALIZED

$$\operatorname{Tr}\rho = 1.$$

HERMITIAN

$$\rho^\dagger = \rho, \quad \rho_{mn} = \rho_{nm}^*.$$

POSITIVE

$$\langle\chi|\rho|\chi\rangle \geq 0.$$

Diagonal entries are measurement probabilities in the chosen basis; off-diagonal entries are coherences, not transition probabilities.

Dynamics and stationarity

Differentiate $\rho = \sum_k w_k |\psi_k\rangle\langle\psi_k|$ and use the Schrödinger equation:

$$\boxed{i\hbar\dot{\rho} = [H, \rho]}.$$

This is the quantum counterpart of Liouville's equation.

For a time-independent Hamiltonian, equilibrium requires

$$[H, \rho] = 0.$$

In the energy basis, $(E_m - E_n)\rho_{mn} = 0$.

> Stationarity removes coherences between different energies, but does not by itself select Boltzmann weights.

Coherences may remain inside a degenerate energy subspace.

Every observable is a trace

For an observable G,

$$\langle G \rangle = \sum_k w_k \langle \psi_k | G | \psi_k \rangle$$
$$= \sum_{m,n} \rho_{mn} G_{nm} = \boxed{\operatorname{Tr}(\rho G)}.$$

The trace is basis-independent. Choose the representation that makes either ρ or G simplest.

For an unnormalized statistical operator R,

$$\langle G \rangle = \frac{\operatorname{Tr}(RG)}{\operatorname{Tr} R}.$$

This is convenient when $R = \mathrm{e}^{-\beta H}$.

> The density operator specifies the ensemble; the Hamiltonian specifies the spectrum; the trace turns both into measurable averages.

Pure states and mixtures are not the same

In the basis $\{|0\rangle, |1\rangle\}$, compare

$$|+\rangle = \frac{|0\rangle + |1\rangle}{\sqrt{2}}.$$

COHERENT PURE STATE

$$\rho_+ = \frac{1}{2}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad \operatorname{Tr}\rho_+^2 = 1.$$

INCOHERENT MIXTURE

$$\rho_{\text{mix}} = \frac{1}{2}\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \operatorname{Tr}\rho_{\text{mix}}^2 = \frac{1}{2}.$$

Both give probabilities $1/2, 1/2$ in this basis, but another measurement distinguishes them.

$$S = -\operatorname{Tr}(\rho \ln \rho), \qquad \operatorname{Tr}\rho^2 = 1 \text{ only for a pure state.}$$

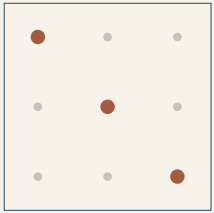
Random phases and dephasing

Write $a_n = |a_n| e^{i\theta_n}$. If relative phases are independently random,

$$\overline{e^{i(\theta_m - \theta_n)}} = 0 \qquad (m \neq n).$$

Therefore

$$\rho_{mn} = \overline{|a_m||a_n| e^{i(\theta_m - \theta_n)}} = \overline{|a_n|^2}\, \delta_{mn}.$$



only populations remain

> Dephasing is an ensemble statement in a specified basis. It does not determine the diagonal populations, and it is not a universal property of every mixed state.

The three quantum ensembles

ENSEMBLE	DENSITY OPERATOR	MEANING OF THE TRACE
Microcanonical	$\rho_{\mathrm{mc}} = \dfrac{\Pi_{E,\Delta}}{\Gamma}, \quad \Gamma = \operatorname{Tr} \Pi_{E,\Delta}$	Equal weight over physical states in an energy window.
Canonical	$\rho_N = \dfrac{\mathrm{e}^{-\beta H_N}}{Q_N}, \quad Q_N = \operatorname{Tr}_N \mathrm{e}^{-\beta H_N}$	Trace over the physical N-particle Hilbert space.
Grand canonical	$\rho_{\mathrm{GC}} = \dfrac{\mathrm{e}^{-\beta(H-\mu\hat{N})}}{\mathcal{Q}}$	Trace over all N sectors; $\mathcal{Q} = \sum_N z^N Q_N$.

> Exchange symmetry determines which many-particle states belong in these traces. It is not an extra correction appended afterwards.

Example: one spin in a magnetic field

For an electron, write $\hat{\mu}_z = -\mu_s \sigma_z$ and

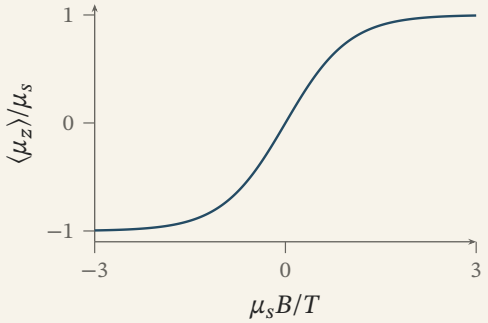
$$H = -\hat{\mu}_z B = \mu_s B \sigma_z .$$

With $x = \mu_s B/T$,

$$\rho = \frac{\mathrm{e}^{-x\sigma_z}}{2\cosh x} = \frac{1}{2\cosh x}\begin{pmatrix} \mathrm{e}^{-x} & 0 \\ 0 & \mathrm{e}^{x} \end{pmatrix}.$$

Hence

$$\boxed{\langle \mu_z \rangle = \mu_s \tanh(\mu_s B/T)}.$$



Weak field: $\langle \mu_z \rangle \simeq \mu_s^2 B/T$.

Strong field: saturation.

Example: the free-particle heat kernel

For $H = -\hbar^2\nabla^2/(2m)$ in a large periodic box,

$$K(\mathbf{r},\mathbf{r}';\beta) = \langle \mathbf{r}|\mathrm{e}^{-\beta H}|\mathbf{r}'\rangle \simeq \frac{1}{(2\pi)^3}\int \mathrm{d}^3k\, \mathrm{e}^{-\beta\hbar^2k^2/(2m)+\mathrm{i}\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}.$$

The Fourier transform is Gaussian:

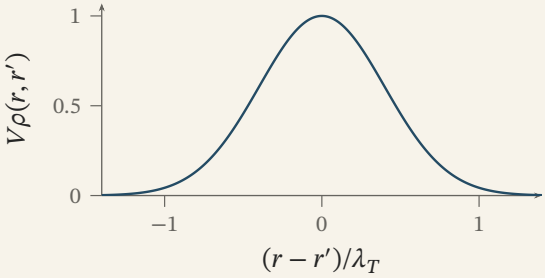
$$\boxed{K(\mathbf{r},\mathbf{r}';\beta) = \frac{1}{\lambda_T^3}\exp\!\left[-\pi\frac{|\mathbf{r}-\mathbf{r}'|^2}{\lambda_T^2}\right]}, \qquad \lambda_T = \frac{h}{\sqrt{2\pi m T}}.$$

> The thermal wavelength λ_T is the coherence length generated by imaginary-time propagation.

Thermal wavelength and the classical energy

The normalized density kernel is

$$\rho(\mathbf{r},\mathbf{r}') = \frac{1}{V}\exp\!\left[-\pi\frac{|\mathbf{r}-\mathbf{r}'|^2}{\lambda_T^2}\right].$$



The diagonal is uniform:

$$\rho(\mathbf{r},\mathbf{r}) = \frac{1}{V}.$$

The trace gives

$$Q_1 = \frac{V}{\lambda_T^3}, \quad U = -\partial_\beta \ln Q_1 = \frac{3}{2}T.$$

> High temperature shortens off-diagonal coherence while the quantum trace approaches the classical ideal-gas energy.

Example: the harmonic oscillator

For a harmonic oscillator,

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right).$$

The energy basis turns the trace into a geometric sum:

$$Q_1 = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta\hbar\omega(n+1/2)} = \frac{1}{2\sinh(\beta\hbar\omega/2)}.$$

$$U = \frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right).$$

Low temperature: $U \longrightarrow \hbar\omega/2$.

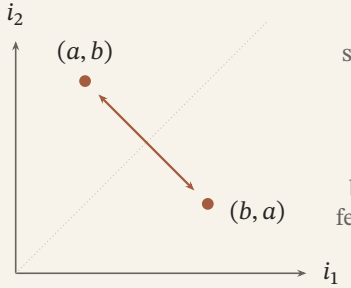
High temperature: $U \longrightarrow T$.

The density operator is basis-independent; computational effort is not.

Indistinguishability: count occupations

For noninteracting identical particles,

$$H = \sum_{j=1}^{N} h_j, \qquad \sum_i n_i = N, \qquad E = \sum_i n_i \epsilon_i.$$



same occupation list

$i_1 = i_2$: bosons allowed, fermions excluded

Particle labels do not define different physical preparations.

An occupation list labels one many-particle state; exchange symmetry decides which lists are allowed.

Exchange symmetry and Pauli exclusion

For two identical particles,

$$P_{12}\Psi_B = +\Psi_B, \qquad P_{12}\Psi_F = -\Psi_F.$$

BOSONS

$$\Psi_B \propto \sum_{P \in S_N} P\Phi.$$

Occupation numbers are unrestricted:

$$n_i = 0, 1, 2, \ldots$$

FERMIONS

$$\Psi_F = \frac{1}{\sqrt{N!}} \det[u_{i_a}(q_b)].$$

If two complete one-particle states coincide, two rows coincide and the determinant vanishes: $n_i = 0$ or 1.

Pauli exclusion applies to a complete one-particle state, including spin and all internal labels.

The symmetry projector

In the labeled tensor-product space,

$$\Pi_\eta = \frac{1}{N!} \sum_{P \in S_N} \chi_\eta(P) P, \quad \chi_B(P) = 1, \quad \chi_F(P) = \mathrm{sgn}(P).$$

Project the free-particle heat kernel into the bosonic or fermionic sector:

$$\boxed{K_N^{(\eta)}(R, R'; \beta) = \frac{1}{N! \lambda_T^{3N}} \sum_{P \in S_N} \chi_\eta(P) \exp\left[-\frac{\pi}{\lambda_T^2} \sum_i |\mathbf{r}_i - \mathbf{r}'_{P(i)}|^2 \right]}.$$

Identity permutation: 1

(classical contribution)

Transposition (ij) on the diagonal:

$\pm e^{-2\pi r_{ij}^2 / \lambda_T^2}$ (first exchange correction)

Exchange matters when particles approach within one thermal wavelength.

Quantum counting yields classical phase space

When the gas is dilute,

$$\boxed{n\lambda_T^3 \ll 1},$$

exchange permutations are rare. Retaining only the identity term gives

$$Q_N \simeq \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N.$$

Equivalently,

$$Q_N = \frac{1}{N!h^{3N}} \int \mathrm{d}^{3N}q\ \mathrm{d}^{3N}p\, \mathrm{e}^{-\beta \sum_i p_i^2/(2m)}.$$

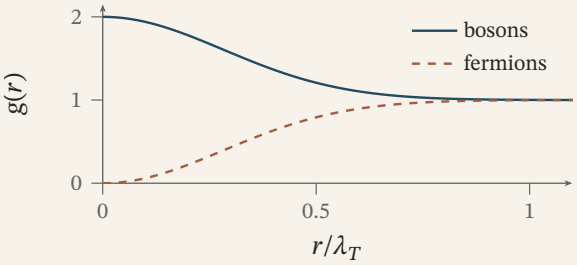
Quantum state counting supplies both the phase-space cell h^{3N} and the Gibbs factor $1/N!$.

Exchange correlation without force

For two free identical particles in one internal state,

$$\boxed{g_{\pm}(r) = 1 \pm \mathrm{e}^{-2\pi r^2/\lambda_T^2}}.$$

The upper sign is bosonic; the lower sign is for identical-spin fermions.



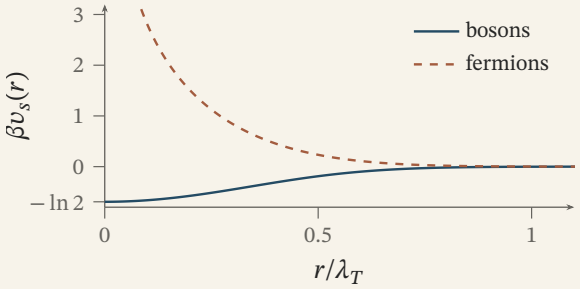
- Bosons bunch: $g_+(0) = 2$.
- Identical-spin fermions have an exchange hole: $g_-(0) = 0$.
- Both become uncorrelated for $r \gg \lambda_T$.

The Hamiltonian remains free; the correlation comes from state counting.

The statistical potential

Define v_s by $e^{-\beta v_s(r)} = g(r)$:

$$\boxed{\beta v_s^{(\pm)}(r) = -\ln[1 \pm e^{-2\pi r^2/\lambda_T^2}]}.$$



Bosonic v_s is attractive; fermionic v_s is repulsive and diverges at the origin.

It represents an equal-time pair correlation, not a force. Longer cycles need not be pairwise.

Lecture 5: the structure to retain

ENSEMBLES

$$\rho = \sum_k w_k |\psi_k\rangle\langle\psi_k|, \qquad i\hbar\dot{\rho} = [H, \rho],$$

$$\langle G \rangle = \mathrm{Tr}(\rho G).$$

$$\rho_N = \frac{e^{-\beta H_N}}{Q_N}, \qquad \rho_{\mathrm{GC}} = \frac{e^{-\beta(H-\mu\hat{N})}}{\mathcal{Q}}.$$

INDISTINGUISHABILITY

Bosons are symmetric; fermions are antisymmetric. The trace contains only physical states.

$$n\lambda_T^3 \ll 1 \quad \Longrightarrow \quad Q_N \simeq \frac{1}{N!}\left(\frac{V}{\lambda_T^3}\right)^N.$$

$$g_{\pm}(r) = 1 \pm e^{-2\pi r^2/\lambda_T^2}.$$

> The density operator organizes uncertainty; exchange symmetry reorganizes the states being counted. Together they lead smoothly from quantum statistics to classical phase space.

The Theory of Simple Gases

Occupation statistics, fluctuations, pressure, and effusion

Tsvi Tlusty · UNIST

Convention: $k_{\mathrm{B}} = 1$

The problem is counting, not dynamics

For an ideal gas,

$$H = \sum_j n_j \epsilon_j .$$

The energy is additive. The nontrivial question is how many many-particle states correspond to a given occupation profile.

THREE RULES

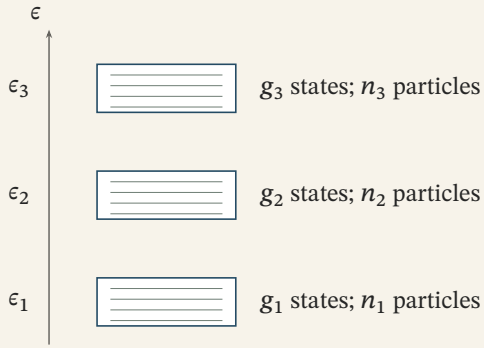
- Bosons: any occupation is allowed.
- Fermions: each complete state holds at most one particle.
- Classical particles: exchange becomes negligible.

> The same one-particle spectrum produces different thermodynamics because the many-particle states are counted differently.

Two routes meet at the same law: maximize multiplicity, or factorize the grand sum.

Coarse-graining the spectrum

Group nearby one-particle levels into narrow cells. Cell i has representative energy ϵ_i, contains $g_i \gg 1$ states, and holds n_i particles.



The macroscopic constraints are

$$\sum_i n_i = N, \qquad \sum_i n_i \epsilon_i = E.$$

> g_i counts available states; n_i counts particles. Confusing them destroys the combinatorics.

Each cell is narrow on the thermal scale, yet broad enough to contain many levels.

Three counting rules

For one cell with n particles and g states:

STATISTICS	MULTIPLICITY	PHYSICAL RULE
Bose–Einstein	$w_B(n,g) = \binom{n+g-1}{n}$	Stars and bars: empty states and multiple occupancy are allowed.
Fermi–Dirac	$w_F(n,g) = \binom{g}{n}$	Choose the occupied states; $0 \le n \le g$.
Maxwell–Boltzmann	$w_{\mathrm{MB}}(n,g) = \dfrac{g^n}{n!}$	Classical state choices, with the Gibbs factor already included.

When $n/g \ll 1$, both quantum multiplicities reduce to the Maxwell–Boltzmann form.

The dominant occupation profile

For large cells, the thermodynamic entropy is controlled by the profile of largest multiplicity:

$$S \simeq \ln W\{n_i^*\}, \qquad W = \prod_i w_i(n_i, g_i).$$

Introduce $a = -1$ (Bose), $a = +1$ (Fermi), and $a = 0$ (Maxwell–Boltzmann). Stirling's approximation gives, for $a = \pm 1$,

$$\frac{\partial \ln w_i}{\partial n_i} = \ln\!\left(\frac{g_i}{n_i} - a\right).$$

Maximize

$$\mathcal{L} = \ln W - \alpha \sum_i n_i - \beta \sum_i n_i \epsilon_i.$$

One formula, three statistics

The stationary condition is

$$\ln\left(\frac{g_i}{n_i^*} - a\right) = \alpha + \beta\epsilon_i.$$

Therefore the mean occupation per state is

$$\boxed{f_i \equiv \frac{n_i^*}{g_i} = \frac{1}{\mathrm{e}^{\alpha+\beta\epsilon_i} + a} = \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon_i} + a}}.$$

BOSONS

$$f_B = \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon} - 1}.$$

FERMIONS

$$f_F = \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon} + 1}.$$

CLASSICAL

$$f_{\mathrm{MB}} = z\mathrm{e}^{-\beta\epsilon}.$$

A single sign decides whether a state can accumulate particles or saturates at one.

Thermodynamic meaning of the multipliers

At the constrained maximum,

$$\beta = \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}, \qquad \alpha = \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{\mu}{T}.$$

Thus

$$z = \mathrm{e}^{\beta\mu}.$$

Substituting the occupation profile back into the entropy gives the bulk pressure:

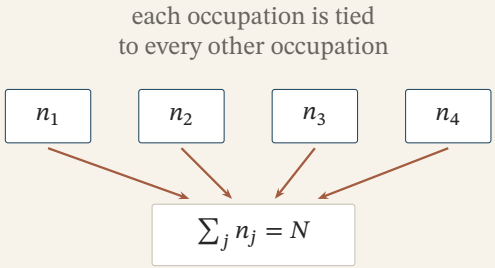
$$\boxed{\frac{PV}{T} = \frac{1}{a}\sum_i g_i \ln(1 + az\mathrm{e}^{-\beta\epsilon_i})},$$

The $a \to 0$ limit is continuous. The multipliers become inverse temperature and minus chemical potential divided by temperature.

Why the canonical sum does not factorize

For individual one-particle states j,

$$Q_N = \sum_{\{n_j\}:\, \sum_j n_j = N} \exp\left(-\beta \sum_j n_j \epsilon_j\right).$$



Although the energy is additive, the fixed-N constraint couples the modes.

The canonical partition function is not a product of one-state sums because the occupations must add to exactly N.

The grand sum factorizes mode by mode

Multiply by z^N and sum over all particle numbers. The global constraint disappears:

$$\mathcal{Q} = \prod_j \mathcal{Z}_j, \qquad y_j = z\mathrm{e}^{-\beta\epsilon_j}.$$

STATISTICS	ONE-STATE SUM
Bose	$\mathcal{Z}_j = (1 - y_j)^{-1}$
Fermi	$\mathcal{Z}_j = 1 + y_j$
Classical	$\mathcal{Z}_j = \mathrm{e}^{y_j}$

For $a = \pm 1$,

$$q \equiv \ln \mathcal{Q} = \frac{1}{a} \sum_j \ln(1 + a y_j).$$

Differentiate one level:

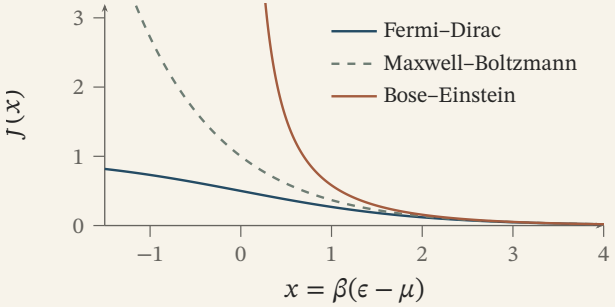
$$\langle n_j \rangle = \frac{y_j}{1 + a y_j}.$$

Summing over N is exact: each occupation list belongs to one and only one particle-number sector.

Three occupation curves

Let $x = \beta(\epsilon - \mu)$. Then

$$f_B = (\mathrm{e}^x - 1)^{-1}, \qquad f_F = (\mathrm{e}^x + 1)^{-1}, \qquad f_{\mathrm{MB}} = \mathrm{e}^{-x}.$$



- Bosons require $x > 0$, or $\mu < \epsilon$.
- Fermions approach unit occupation for $x \ll 0$.
- All three agree when $x \gg 1$.

> The classical limit is low occupation, not simply high energy.

One-mode fluctuations

A second derivative of q gives the occupation variance:

$$\boxed{\mathrm{Var}(n_j) = f_j(1 - a f_j)}.$$

BOSONS

$$\mathrm{Var}(n) = f + f^2.$$

Bunching makes the fluctuations super-Poissonian.

FERMIONS

$$\mathrm{Var}(n) = f - f^2.$$

Exclusion suppresses fluctuations near full occupation.

CLASSICAL

$$\mathrm{Var}(n) = f.$$

The variance equals the mean.

For a highly occupied Bose mode, $\mathrm{Var}(n)/\langle n\rangle^2 \to 1$: macroscopic occupation does not imply a sharply defined occupation in the grand ensemble.

The full one-mode distributions

The one-state partition function normalizes the complete probability law:

STATISTICS	PROBABILITY OF OCCUPATION n	DISTRIBUTION
Bose–Einstein	$\Pr(n) = \dfrac{f^n}{(1+f)^{n+1}}, \quad n = 0, 1, 2, \ldots$	Geometric; most probable n is zero.
Fermi–Dirac	$\Pr(0) = 1 - f, \quad \Pr(1) = f$	Bernoulli.
Maxwell–Boltzmann	$\Pr(n) = \mathrm{e}^{-f} \dfrac{f^n}{n!}$	Poisson.

A mean occupation and a most probable occupation are different statements. A Bose mode may have a large mean but mode zero.

When does quantum statistics matter?

For a nonrelativistic gas with one internal state,

$$\boxed{n\lambda_T^3 \sim 1}, \qquad \lambda_T = \frac{h}{\sqrt{2\pi m T}}.$$

The classical regime is

$$n\lambda_T^3 \ll 1,$$

or equivalently

$$T \gg \frac{h^2}{2\pi m} n^{2/3}.$$

If there are g equally populated internal states, the degeneracy per internal state is

$$\frac{n\lambda_T^3}{g}.$$

Quantum statistics matters when thermal wave packets overlap: λ_T becomes comparable with the mean spacing $n^{-1/3}$.

Pressure from the dispersion relation

For an isotropic gas with dispersion $\epsilon(p)$,

$$P = \frac{4\pi T}{ah^3} \int_0^\infty p^2 \ln(1 + aze^{-\beta\epsilon(p)})\,\mathrm{d}p.$$

Integrating by parts and writing $u = \mathrm{d}\epsilon/\,\mathrm{d}p$ gives

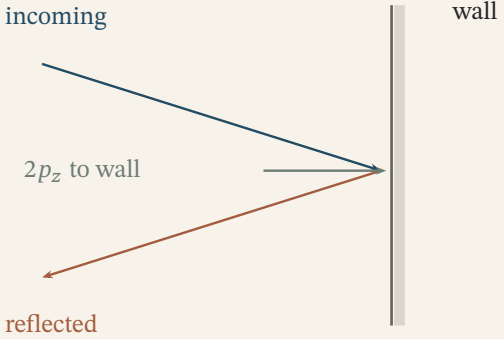
$$\boxed{P = \frac{1}{3} n \langle pu \rangle}.$$

This average uses the actual Bose, Fermi, or classical occupation function.

If $\epsilon = Cp^s$, then $pu = s\epsilon$ and $PV = sU/3$.

- Nonrelativistic: $s = 2$, so $PV = 2U/3$.
- Massless: $s = 1$, so $PV = U/3$.

Pressure as momentum transfer



Particles with $u_z > 0$ strike the wall at a rate proportional to u_z. Specular reflection transfers $2p_z$ per collision:

$$P = 2n \int_{u_z>0} p_z u_z F(\mathbf{u})\, \mathrm{d}^3u.$$

Extend the even integrand to the full sphere and use isotropy:

$$P = n\langle p_z u_z \rangle = \frac{1}{3} n \langle pu \rangle .$$

Thermodynamic pressure is momentum flux into a boundary.

Effusion through a small aperture

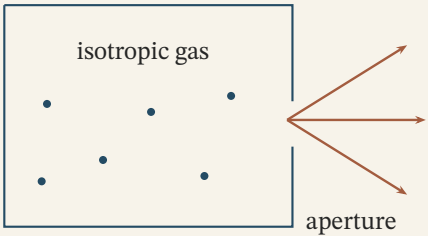
Replace a small part of the wall by a hole. The outward number flux is

$$R = n \int_{u_z>0} u_z F(\mathbf{u})\, \mathrm{d}^3u.$$

Write $u_z = u\cos\theta$. Isotropy separates speed from direction:

$$\int_{\text{outward}} \cos\theta\, \mathrm{d}\Omega = \pi, \qquad p(u) = 4\pi u^2 F(u).$$

$$\boxed{R = \frac{1}{4} n \langle u \rangle}.$$



The factor $1/4$ is half-space selection multiplied by the average projection $\cos\theta$.

The aperture must be ballistic: effusion is not hydrodynamic flow.

Why effusion cools a gas

The probability that a particle escapes is weighted by its speed. The escaping speed distribution is

$$p_{\mathrm{esc}}(u) \propto u\, p(u).$$

For a classical Maxwell gas,

$$p_{\mathrm{esc}}(u) \propto u^3 \mathrm{e}^{-mu^2/(2T)}.$$

$$\langle \epsilon \rangle_{\mathrm{esc}} = 2T, \qquad \langle \epsilon \rangle_{\mathrm{bulk}} = \frac{3}{2} T.$$

> Fast particles reach the aperture more often. They remove more than the average energy per particle, so the re-equilibrating gas left behind cools. The same outward-hemisphere geometry reappears for blackbody radiation as the factor $c/4$.

Lecture 6: the structure to retain

OCCUPATION STATISTICS

$$f(\epsilon) = \frac{1}{z^{-1}e^{\beta\epsilon} + a}, \qquad a = -1, +1, 0.$$

$$q = \frac{1}{a}\sum_j \ln(1 + aze^{-\beta\epsilon_j}).$$

$$\mathrm{Var}(n) = f(1 - af).$$

MOTION AND FLUX

$$P = \frac{1}{3}n\langle pu\rangle, \qquad \epsilon \propto p^s \Longrightarrow PV = \frac{s}{3}U.$$

$$R = \frac{1}{4}n\langle u\rangle, \qquad \langle\epsilon\rangle_{\mathrm{esc}} = 2T.$$

> Counting fixes the occupation law; derivatives fix its fluctuations; momentum transfer gives pressure; directional flux explains effusion.

Ideal Bose Systems

Condensation, saturation, and blackbody radiation

Tsvi Tlusty · UNIST

Convention: $k_B = 1$

One Bose rule, two thermodynamic constraints

MASSIVE BOSONS

Particle number is conserved. The chemical potential adjusts so that the imposed density is maintained.

$$N = \sum_j \frac{1}{z^{-1}\mathrm{e}^{\beta\epsilon_j} - 1}, \quad z = \mathrm{e}^{\beta\mu} \leq 1.$$

If the excited states saturate, excess particles must accumulate in the ground state.

PHOTONS

Matter can create and absorb photons. Photon number is not constrained, so equilibrium fixes $\mu = 0$.

$$\langle n_{\mathbf{k}\sigma} \rangle = \frac{1}{\mathrm{e}^{\beta\hbar\omega_{\mathbf{k}}} - 1}.$$

The same Bose law now determines a temperature-controlled radiation spectrum.

The counting rule is identical; the constraint is not. That difference separates condensation from blackbody radiation.

The continuum can erase the ground state

For a large three-dimensional box,

$$D(\epsilon)\,\mathrm{d}\epsilon = \frac{2\pi V}{h^3}(2m)^{3/2}\epsilon^{1/2}\,\mathrm{d}\epsilon.$$

The density of states vanishes at $\epsilon = 0$, yet the discrete ground state is one genuine quantum state.



Separate it before replacing the excited-state sum by an integral:

$$N = N_0 + N_e, \qquad N_0 = \frac{z}{1-z},$$

$$N_e = \int_0^\infty \frac{D(\epsilon)\,\mathrm{d}\epsilon}{z^{-1}\mathrm{e}^{\beta\epsilon} - 1}.$$

An isolated point has zero measure in the integral, but its occupation can be of order N.

Bose functions organize the thermodynamics

Define

$$\boxed{g_s(z) = \frac{1}{\Gamma(s)} \int_0^\infty \frac{x^{s-1}\,dx}{z^{-1}e^x - 1} = \sum_{\ell=1}^{\infty} \frac{z^\ell}{\ell^s}}$$

with $z\,dg_s/dz = g_{s-1}(z)$.

GRAND POTENTIAL

$$q \equiv \ln \mathcal{Q} = -\ln(1-z) + \frac{V}{\lambda_T^3} g_{5/2}(z).$$

PARTICLE NUMBER

$$N = \frac{z}{1-z} + \frac{V}{\lambda_T^3} g_{3/2}(z).$$

The ground state contributes one logarithm to q, but it may contribute an extensive number of particles to N.

The condensate carries number, not pressure

If $N_0 \propto N$, then

$$z = \frac{N_0}{N_0 + 1}, \qquad -\ln(1 - z) = \ln(N_0 + 1).$$

Thus the ground-state contribution to q/V vanishes as $\ln N/V$, while N_0/V remains finite.

The bulk pressure comes from the excited continuum:

$$\boxed{P = \frac{T}{\lambda_T^3} g_{5/2}(z)}.$$

The energy is

$$U = \frac{3}{2} \frac{VT}{\lambda_T^3} g_{5/2}(z), \qquad U = \frac{3}{2} PV.$$

The zero-energy ground state has no volume derivative in this model. Macroscopic occupation need not imply macroscopic pressure or energy.

The classical limit is small fugacity

When $n\lambda_T^3 \ll 1$, the fugacity is small:

$$g_s(z) = z + \frac{z^2}{2^s} + \cdots .$$

LEADING ORDER

$$n\lambda_T^3 \simeq z, \qquad P \simeq \frac{Tz}{\lambda_T^3} = nT.$$

The Maxwell–Boltzmann equation of state is recovered.

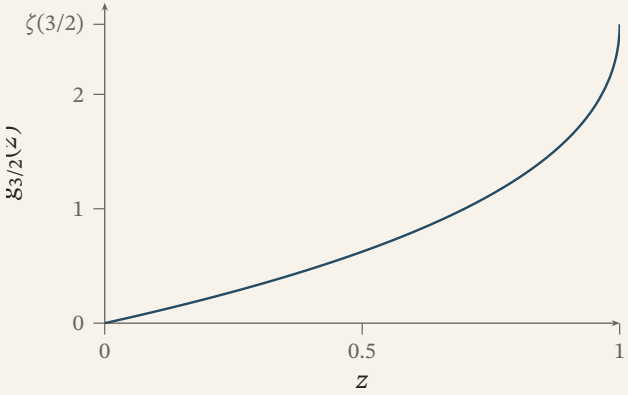
FIRST BOSE CORRECTION

$$\frac{PV}{NT} = 1 - \frac{n\lambda_T^3}{2^{5/2}} + O\big((n\lambda_T^3)^2\big).$$

The negative sign is the thermodynamic trace of bosonic bunching.

> The dilute expansion cannot reveal condensation, where $z \to 1$ and the discrete ground state becomes essential.

Excited states have a finite capacity



$$g_{3/2}(1) = \zeta(3/2) \simeq 2.612.$$

Therefore

$$\boxed{N_e^{\max}(T) = \frac{V}{\lambda_T^3}\zeta(3/2)}.$$

Increasing μ fills the excited states, but μ cannot exceed the ground-state energy. At fixed T, the excited cloud has a true maximum capacity.

Critical temperature from capacity

Condensation begins when the imposed number first equals the maximum number that the excited states can hold:

$$N = N_e^{\max}(T_c) = V\left(\frac{2\pi m T_c}{h^2}\right)^{3/2} \zeta(3/2).$$

$$\boxed{T_c = \frac{h^2}{2\pi m}\left[\frac{n}{\zeta(3/2)}\right]^{2/3}}.$$

ABOVE T_c

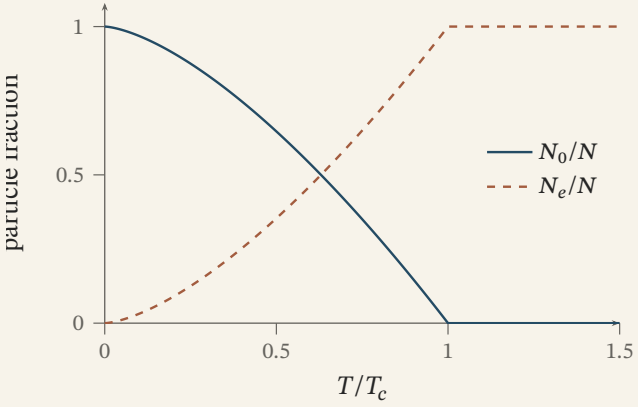
A fugacity $z < 1$ accommodates the particles in excited states; $N_0/N \to 0$.

T_c is fixed by density and mass, not fitted.

BELOW T_c

The bulk fugacity is pinned at $z \to 1$. The excited population falls as $T^{3/2}$; the excess occupies the ground state.

The condensate fraction follows from saturation



For $T \leq T_c$,

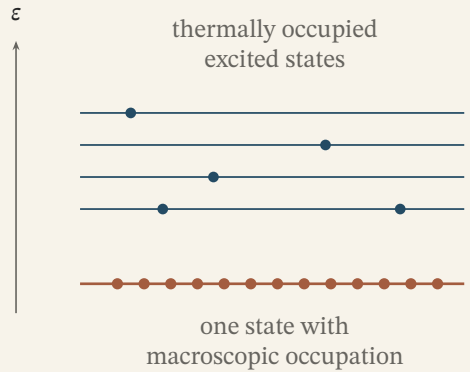
$$N_e = N\left(\frac{T}{T_c}\right)^{3/2}.$$

Therefore

$$\boxed{\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}}.$$

For a finite system, z remains slightly below one: $1 - z \simeq 1/N_0$.

Condensation occurs in state space

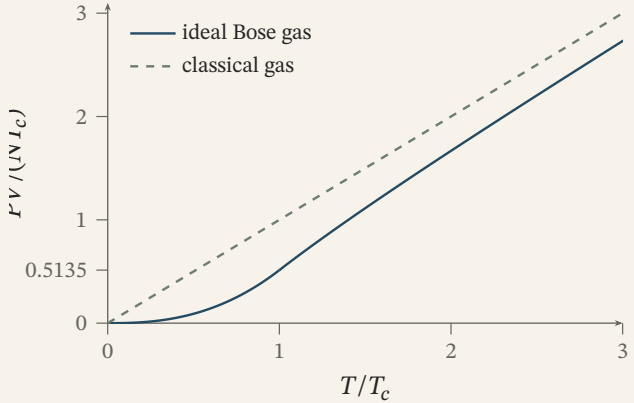


Bose–Einstein condensation is macroscopic occupation of a single one-particle state.

In a uniform box that state is spatially extended. Condensation therefore does not mean that an attractive force has formed a real-space droplet.

The condensate and thermal cloud are components of the same gas, not automatically two spatial phases.

Pressure and energy through T_c



The same curve gives $2U/(3NT_c)$. Above T_c, determine $z(T)$ from the particle-number equation.

Below T_c,

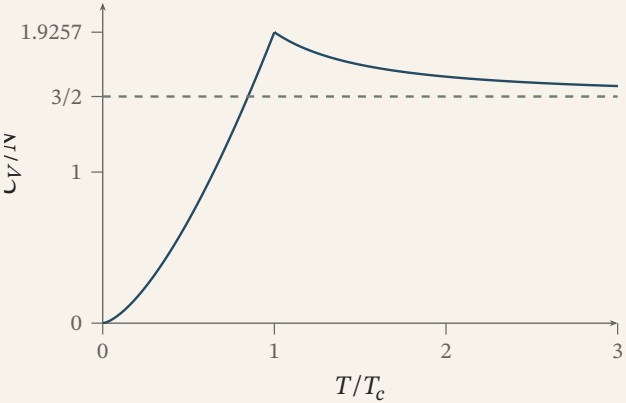
$$P = \frac{T}{\lambda_T^3}\zeta(5/2) \propto T^{5/2}.$$

At the transition,

$$\frac{P_c}{nT_c} = \frac{\zeta(5/2)}{\zeta(3/2)} \simeq 0.5135.$$

> Adding condensate particles at fixed $T < T_c$ does not change the ideal-gas pressure.

The ideal gas has a finite heat-capacity cusp



The ideal gas predicts a cusp, not the sharp λ anomaly of interacting liquid helium.

Below T_c,

$$\frac{C_V}{N} = \frac{15}{4}\frac{\zeta(5/2)}{\zeta(3/2)}\left(\frac{T}{T_c}\right)^{3/2}.$$

At T_c,

$$\frac{C_V}{N} \simeq 1.9257.$$

C_V is continuous, but its slope jumps. At high T, $C_V/N \to 3/2$.

What the ideal gas explains—and what it does not

WHAT SURVIVES

- A quantum-degeneracy scale set by $n\lambda_T^3$.
- Macroscopic occupation of one state below a critical temperature.
- A thermodynamic signature near T_c.
- A natural framework for dilute ultracold atomic gases.

WHAT REQUIRES INTERACTIONS

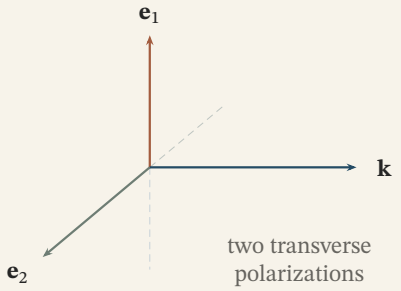
- The quantitative behavior of liquid ^{4}He.
- The sharp λ anomaly.
- Finite compressibility and collective sound.
- The relation between condensate fraction and superfluid fraction.

> Condensation and superfluidity are related but distinct statements. The ideal-gas condensate is not a complete theory of a superfluid liquid.

Photons: the same Bose law with $\mu = 0$

A photon mode is labeled by wavevector $\mathbf{k}$ and transverse polarization $\sigma = 1, 2$:

$$\epsilon_{\mathbf{k}} = \hbar\omega_{\mathbf{k}} = \hbar c|\mathbf{k}|, \qquad \mathbf{k} \cdot \mathbf{e}_\sigma = 0.$$



Because the walls emit and absorb photons,

$$\mu = 0, \qquad z = 1.$$

Each mode is a Bose oscillator:

$$\mathcal{Z}_{\mathbf{k}\sigma} = \frac{1}{1 - \mathrm{e}^{-\beta\hbar\omega_{\mathbf{k}}}}, \quad \langle n_{\mathbf{k}\sigma} \rangle = \frac{1}{\mathrm{e}^{\beta\hbar\omega_{\mathbf{k}}} - 1}.$$

Count the two polarizations once: in the mode density or an explicit polarization sum, never both.

Mode counting gives Planck's spectrum

Including both polarizations, the number of modes in $[\omega, \omega + \mathrm{d}\omega]$ is

$$D_\gamma(\omega)\,\mathrm{d}\omega = \frac{V\omega^2}{\pi^2 c^3}\,\mathrm{d}\omega.$$

Multiply by the mean energy per mode:

$$\hbar\omega\,\langle n\rangle = \frac{\hbar\omega}{\mathrm{e}^{\hbar\omega/T} - 1}.$$

$$\boxed{u_\omega(T) = \frac{\hbar\omega^3}{\pi^2 c^3}\,\frac{1}{\mathrm{e}^{\hbar\omega/T} - 1}}.$$

$u_\omega\,\mathrm{d}\omega$ is energy per volume in an angular-frequency interval: mode density times photon energy times Bose occupation.

Why radiation scales as T^4

Set $x = \hbar\omega/T$:

$$u \equiv \frac{U}{V} = \frac{T^4}{\pi^2\hbar^3c^3}\int_0^\infty \frac{x^3\,\mathrm{d}x}{\mathrm{e}^x - 1}.$$

Use the Bose expansion

$$\frac{1}{\mathrm{e}^x - 1} = \sum_{\ell\geq 1} \mathrm{e}^{-\ell x}.$$

Then

$$\int_0^\infty \frac{x^3\,\mathrm{d}x}{\mathrm{e}^x - 1} = 6\sum_{\ell\geq 1}\ell^{-4} = \frac{\pi^4}{15}.$$

$$\boxed{u = \frac{\pi^2}{15}\frac{T^4}{(\hbar c)^3}}.$$

Three powers of T count accessible modes; one more comes from the energy carried by each photon.

Radiation thermodynamics

For the linear dispersion $\epsilon = cp$,

$$P = \frac{u}{3} = \frac{\pi^2}{45}\frac{T^4}{(\hbar c)^3}.$$

Because $\mu = 0$,

$$G = 0, \qquad A = -PV = -\frac{U}{3}.$$

Therefore

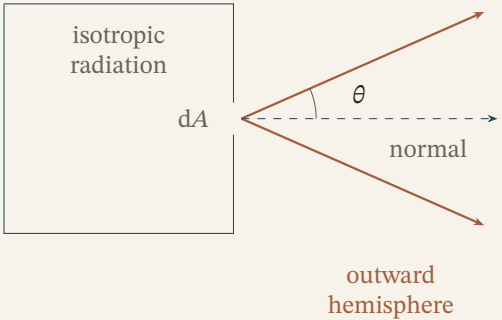
$$S = \frac{4U}{3T}, \qquad C_V = \frac{4U}{T}.$$

Explicitly,

$$C_V = \frac{4\pi^2 V}{15}\frac{T^3}{(\hbar c)^3}.$$

> Once $u(T)$ is known, pressure, free energy, entropy, and heat capacity follow without introducing a photon chemical potential.

Blackbody flux is $cu/4$



A ray at angle θ crosses the aperture with projection factor $\cos\theta$:

$$I = \frac{cu}{4\pi}\int_{\text{outward}} \cos\theta \, \mathrm{d}\Omega.$$

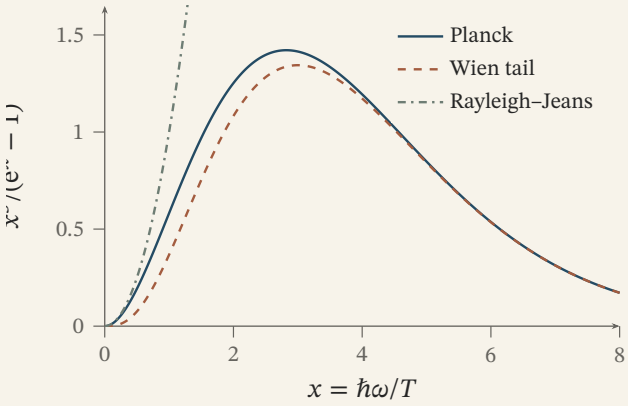
Since

$$\int_{\text{outward}} \cos\theta \, \mathrm{d}\Omega = \pi,$$

$$\boxed{I = \frac{c}{4}u = \frac{\pi^2}{60\hbar^3 c^2}T^4}.$$

The same half-space projection factor appeared in molecular effusion. Directional geometry, not a new thermodynamic assumption, produces the $1/4$.

Planck's law joins two limiting regimes



For $x \ll 1$,

$$u_\omega \simeq \frac{T\omega^2}{\pi^2 c^3}.$$

For $x \gg 1$,

$$u_\omega \simeq \frac{\hbar\omega^3}{\pi^2 c^3} e^{-\hbar\omega/T}.$$

The exact spectrum peaks at $x \simeq 2.821$.

The low-frequency classical law rises as ω^2; the quantum exponential tail prevents the ultraviolet catastrophe.

Lecture 7: the structure to retain

CONSERVED MASSIVE BOSONS

$$N = N_0 + \frac{V}{\lambda_T^3} g_{3/2}(z), \quad P = \frac{T}{\lambda_T^3} g_{5/2}(z).$$

$$N_e^{\max} = \frac{V}{\lambda_T^3}\zeta(3/2), \quad \frac{N_0}{N} = 1 - (T/T_c)^{3/2}.$$

The ground state carries number but no bulk pressure in the ideal model.

EQUILIBRIUM PHOTONS

$$\mu = 0, \quad u_\omega = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/T} - 1}.$$

$$u = \frac{\pi^2 T^4}{15(\hbar c)^3}, \quad P = \frac{u}{3}, \quad I = \frac{c}{4}u.$$

Photon number adjusts; temperature fixes the spectrum.

> One Bose counting rule, two constraints: fixed particle number produces saturation and condensation; variable photon number produces Planck radiation.