Thermodynamics — Math Walk-Through

This is the math walk-through for the Thermodynamics pillar. It stays VMS-first and picks up from the Bridge: count routes, use the right multipliers, minimize the right free-energy. No imported constitutive laws. No new dimensional dials beyond the single action scale $S_0 = \hbar$ (and k_B as an acceptance lock). We move from micro counting → macro levers → fluctuation–response → transport kernels → phase onset, and we pin each ladder to the Thermodynamics Math Appendix for full detail.

0) Setup & Locks

• Single dimensional scale: $S_0 = \hbar$ (SI-locked; fixed once and never tuned).

• Acceptance lock: k_B appears only as the acceptance multiplier for energy; it calibrates the thermometer, not the theory.

• Counting object: route weights use multipliers; when we need phase we use S[path] = ∫ A_d ds, but this pillar is mostly ratios and counts.

• Scope discipline: near-equilibrium, weak gradients, locally stationary statistics; far-from-equilibrium and turbulence live in branches.

No imports (what we do NOT assume)

We do not assume ideal-gas, Fourier/Fick/Newton, Navier–Stokes, or mean-field templates. When those forms appear, they are dictionaries of our counting and kernels—not starting axioms.

Classical bridge — smooth-limit dictionary

In the short-memory and smooth-profile limit, our kernels reduce to the familiar forms: Fourier $q = -\kappa \nabla T$, Fick $J = -D \nabla c$, and Newton $\tau = \eta \nabla v$. The coefficients (κ, D, η) are Green–Kubo integrals of fluctuations.

1) Route counting → entropy, temperature, and the fundamental relation

We start with a count Ω of compatible route-arrangements under macroscopic constraints (energy E, volume V, particle number N). The entropy is the logarithm of that count; the multipliers that weight routes become the thermodynamic variables.

$S = k_B \cdot \ln \Omega$

$\beta = 1/(k_B T)$ (energy multiplier)

Maximize S subject to fixed E, V, N with multipliers (β, βp, $-\beta\mu$). The stationary point gives the familiar fundamental relation.

$dU = T\,dS - p\,dV + \mu\,dN$

Read this in VMS terms: the multipliers we used to weight routes (T, p, μ) are the levers that tie micro counts to the macro changes. We did not assume them—we got them by extremizing the count. (Thermo Appendix §1.)

2) Legendre transform ladder and Maxwell relations (full algebra)

1) Helmholtz: $F = U - T\,S$. Differentiate using the product rule:

$dF = dU - T\,dS - S\,dT = (T\,dS - p\,dV + \mu\,dN) - T\,dS - S\,dT$

$\Rightarrow\ dF = -S\,dT - p\,dV + \mu\,dN$

2) Read off slopes: $S = -(\partial F/\partial T)_{V,N}$, $p = -(\partial F/\partial V)_{T,N}$, $\mu = (\partial F/\partial N)_{T,V}$.

3) Maxwell from equality of mixed partials of F(T,V,N):

$(\partial S/\partial V)_T = -(\partial/\partial V)_T\,(\partial F/\partial T)_{V,N} = -(\partial/\partial T)_V\,(\partial F/\partial V)_{T,N} = (\partial p/\partial T)_V$

Pick the scorecard that matches what you're holding fixed. Legendre transforms swap a fluctuating extensive for its multiplier.

$F(T,V,N) = U - T\,S$

$G(T,p,N) = H - T\,S = F + pV$

$\Omega(T,V,\mu) = U - TS - \mu N$

Write the differentials and take mixed partials to generate the Maxwell relations (all are Jacobian identities).

$(\partial S/\partial V)_T = (\partial p/\partial T)_V$; $(\partial S/\partial N)_T = -(\partial \mu/\partial T)_N$; $(\partial \mu/\partial V)_T = -(\partial p/\partial N)_T$ …

What this means (plain talk)

Once you pick the scorecard (F, G, or Ω), everything you call an EoS number is a slope or curvature. Maxwell relations are symmetry statements about those slopes—pure bookkeeping from consistent multipliers. (Thermo Appendix §2.)

3) Euler homogeneity and Gibbs–Duhem

1) Assume first-order homogeneity: $U(\lambda S, \lambda V, \lambda N) = \lambda U(S,V,N)$. Differentiate w.r.t. λ and set λ=1:

$U = (\partial U/\partial S)_{V,N} S + (\partial U/\partial V)_{S,N} V + (\partial U/\partial N)_{S,V} N = T S - p V + \mu N$

2) Differentiate Euler and compare with $dU = T dS - p dV + \mu dN$ to eliminate dU and get:

$S dT - V d p + N d \mu = 0$ (Gibbs–Duhem)

For simple systems the extensive variables scale together. That homogeneity gives the Euler form and Gibbs–Duhem constraint.

$U = T S - p V + \mu N$

$S dT - V dp + N d\mu = 0$

The first says energy is the weighted sum of the conserved tallies; the second says the multipliers are not independent once you fix a material. (Thermo Appendix §3.)

4) From geometry budgets to an EoS (no new scales)

1) Start with $f = f_0 + a\_T \mathcal{T} + a\_S \mathcal{S} + a\_C \mathfrak{C} + \cdots$ · A small state change shifts ($\mathcal{T}$, $\mathcal{S}$, $\mathfrak{C}$):

$\mathcal{T}$ = torsion, $\mathcal{S}$ = shear, $\mathfrak{C}$ = closure; the a• are dimensionless weights fixed in this pillar.

$d f = a\_T d\mathcal{T} + a\_S d\mathcal{S} + a\_C d\mathfrak{C} + \cdots$ with $d\mathcal{T} = (\partial\mathcal{T}/\partial T) dT + (\partial\mathcal{T}/\partial p) dp + \cdots$

Combine to $dF = \int d f dV$ and read EoS outputs from slopes of F (P, κ_T, C_V, …).

Indices & chain rule (one-liners):

$d f = (\partial f/\partial\mathcal{T}) d\mathcal{T} + (\partial f/\partial\mathcal{S}) d\mathcal{S} + (\partial f/\partial\mathfrak{C}) d\mathfrak{C} + \cdots = a\_T d\mathcal{T} + a\_S d\mathcal{S} + a\_C d\mathfrak{C} + \cdots$

2) Each index responds to the control knobs (T, p, …):

$d\mathcal{T} = (\partial\mathcal{T}/\partial T) dT + (\partial\mathcal{T}/\partial p) d p + \cdots$; $d\mathcal{S} = \ldots$; $d\mathfrak{C} = \ldots$

3) Combine to form $dF = \int d f dV$, then read off EoS quantities from slopes of F. Ratios across nearby states cancel calibration constants.

We do not guess an equation of state. We write a free-energy density from our geometry budgets (torsion $\mathcal{T}$, shear $\mathcal{S}$, closure $\mathfrak{C}$) with dimensionless coefficients fixed in this pillar, and then differentiate. That's it.

$f = f_0 + a\_T \cdot \mathcal{T} + a\_S \cdot \mathcal{S} + a\_C \cdot \mathfrak{C} + \cdots$ (a_• dimensionless; no new scales)

Nudge T or p → $\mathcal{T}$, $\mathcal{S}$, $\mathfrak{C}$ shift a little → the slopes of $F = \int f dV$ convert those geometric nudges into EoS outputs (P, κ_T, C_V, …). The Appendix carries full worked examples and validity bands. (Thermo Appendix §4.)

Classical bridge — ideal forms as a dictionary

Ideal-gas and simple-fluid expressions appear when $\mathcal{T}$, $\mathcal{S}$, $\mathfrak{C}$ take their smooth-limit values. We don't import those laws; we land them when the geometry is bland enough.

5) Fluctuation identities (variance ↔ susceptibility)

Canonical energy variance: start with $Z(\beta) = \sum e^{-\beta E_i}$, $\ln Z$ derivatives give averages.

$\langle E \rangle = -\partial \ln Z / \partial\beta$, $\mathrm{Var}(E) = \partial^2 \ln Z / \partial\beta^2$

Chain rule $\beta = 1/(k_B T) \Rightarrow \partial/\partial\beta = -k_B T^2\, \partial/\partial T$, hence:

$\mathrm{Var}(E) = k_B T^2 C_V$, $C_V = (\partial\langle E\rangle/\partial T)_V$

Grand canonical particle variance: $\Xi = \sum e^{-\beta(E_i - \mu N_i)}$:

$\langle N \rangle = (1/\beta)\, \partial \ln \Xi / \partial \mu$, $\mathrm{Var}(N) = (1/\beta)\, \partial\langle N\rangle/\partial \mu = k_B T\, (\partial N/\partial \mu)_{T,V}$

Cross-covariance (E,N): mixed derivatives of $\ln \Xi$ yield:

$\mathrm{Cov}(E,N) = k_B T^2\, (\partial N / \partial T)_{\mu,V}$

Route-counting variances give you the static responses—two faces of the same coin. This is why noise levels lock down response strengths.

$\mathrm{Var}(E) = k_B T^2 \cdot C_V$

$\mathrm{Var}(N) = k_B T \cdot (\partial N/\partial\mu)_{T,V}$

$\mathrm{Cov}(E,N) = k_B T^2 \cdot (\partial N/\partial T)_{\mu,V}$

Pack these into a covariance matrix and you have the full static susceptibility block. These are data-friendly because variances and covariances are measured directly. (Thermo Appendix §5.)

6) Green–Kubo kernels and Onsager reciprocity (time-domain view)

1) Start from entropy production rate $\sigma = \sum_a J_a X_a$. Linear response posits $J = L \cdot X$.

2) Kubo: a small time-dependent tilt X drives a mean current $\langle J_a(t)\rangle$ proportional to an equilibrium correlation:

$L_{ab} = \int_0^\infty \langle J_a(0)\, J_b(t)\rangle_{eq}\, dt$

3) Onsager symmetry: under time reversal, currents change sign; microscopic reversibility of route weights enforces $L_{ab} = L_{ba}$.

Linear response says small drifts are proportional to small tilts. The coefficients are correlation integrals of spontaneous fluctuations.

$L_{ab} = \int_0^\infty \langle J_a(0)\, J_b(t)\rangle_{eq} \, dt$

$J_a = \sum_b L_{ab} \cdot X_b$, $L_{ab} = L_{ba}$

Here X_b are the right gradients (multipliers' gradients): $X_T = \nabla(1/T)$, $X_N = -\nabla(\mu/T)$, $X_{mom} \propto \nabla v$. Time-reversal of the route weights gives $L_{ab} = L_{ba}$ (Onsager). (Thermo Appendix §6.)

Classical bridge — why Fourier/Fick/Newton appear

Short memory + local stationarity → the integrals collapse to constants (κ, D, η) and the kernels reduce to $q = -\kappa \nabla T$, $J = -D \nabla c$, $\tau = \eta \nabla v$.

7) Cross-effects (2×2 block and names you know)

Write the coupled system and identify reciprocity explicitly:

⌈ J_q \; J_N ⌉^T = ⌈ L_{qq} L_{qN} \; L_{Nq} L_{NN} ⌉⌈ ∇(1/T) \; −∇(μ/T) ⌉ ,   L_{qN} = L_{Nq}

Names map onto off-diagonal gates: Seebeck/Peltier (heat–charge), Soret/Dufour (heat–mass). We compute L's from correlation integrals.

Couple two conserved tallies and write the force–flux block explicitly. The off-diagonal gates come in Onsager-paired matches.

⌈ J_q \; J_N ⌉^T = ⌈ L_{qq} L_{qN} \; L_{Nq} L_{NN} ⌉ ⌈ ∇(1/T) \; −∇(μ/T) ⌉

Names you know live here as dictionaries: Seebeck/Thomson/Peltier (thermoelectric), Soret/Dufour (heat–mass). We compute the L's via correlation integrals; the names attach in the smooth limit. (Thermo Appendix §7.)

8) Worked numerics (illustrative, ratio-first)

A) Diffusion (Einstein): $\mu_d = 5.0\times10^{-9}$ m²·N⁻¹·s⁻¹, T = 298 K.

$k_B T = (1.380649\times10^{-23})(298) = 4.114\times10^{-21}$ J

$D = \mu_d k_B T = (5.0\times10^{-9})(4.114\times10^{-21}) = 2.06\times10^{-29}$ m²/s (illustrative numbers)

B) Thermal conductivity (Green–Kubo): suppose the integral gives 0.28 $W\cdot m^{-1}\cdot K^{-1}$ for your volume and T:

κ = (1/(k_B T^2 V)) ∫_0^∞ ⟨J_q(0) J_q(t)⟩ dt → κ ≈ 0.28 W·m^{-1}·K^{-1}

C) Viscosity (stress autocorrelation): report η from the measured integral and meta-data:

η = (V/(k_B T)) ∫_0^∞ ⟨P_{xy}(0) P_{xy}(t)⟩ dt

We prefer ratio-first checks; absolutes are shown for scale only. These three micro-examples are fully reproducible with the Appendix code.

A) Diffusion from mobility (Einstein relation). Take $\mu_d = 5.0\times10^{-9}$ $m^2\cdot N^{-1}\cdot s^{-1}$ at T = 298 K.

$D = \mu_d k_B T \approx (5.0\times10^{-9})(1.380649\times10^{-23})(298) \approx 2.06\times10^{-29}$ m²/s

Ratio-first: repeat at T_2 and publish $D(T_2)/D(T_1)$; most calibration nuisances divide out. (Thermo Appendix §8A.)

B) Thermal conductivity from a heat-current autocorrelation. Suppose a finite-volume run yields $\int_0^\infty \langle J_q(0)J_q(t)\rangle\, dt / (k_B T^2 V) = 0.28$ $W\cdot m^{-1}\cdot K^{-1}$ (illustrative).

κ = (1/(k_B T^2 V)) ∫_0^∞ ⟨J_q(0) J_q(t)⟩ \, dt → κ ≈ 0.28 W·m^{-1}·K^{-1}

Show $\kappa(T_2)/\kappa(T_1)$ for robustness; absolute κ can be posted as secondary. (Thermo Appendix §8B.)

C) Shear viscosity from stress correlations. For a simple shear, use P_{xy} and integrate its autocorrelation over time:

$$\eta = (V/(k_B T)) \int_0^\infty \langle P_{xy}(0)\, P_{xy}(t)\rangle \, dt$$

Insert your measured integral and volume/temperature to report η; again, ratio-first across nearby states is cleaner. (Thermo Appendix §8C.)

9) Validity, limits, and failure modes

Where this kernel picture holds: near-equilibrium, weak gradients, local stationarity, short to moderate memory. Where to be cautious: strong gradients, turbulence, critical opalescence (long memory), and far-from-equilibrium drives. We call those out explicitly in the Appendix so tests don't over-reach.

10) Pointers into the Thermodynamics Math Appendix (exact sections)

§1 Counting and multipliers → S, T, ensembles
§2 Legendre ladder → Maxwell relations (worked Jacobians)
§3 Euler homogeneity → Gibbs–Duhem
§4 Geometry budgets → $f(\mathcal{T}, \mathcal{S}, \mathfrak{C})$ → EoS examples
§5 Fluctuation identities → variance–susceptibility blocks
§6 Green–Kubo + Onsager → transport kernels
§7 Cross-effects 2×2 → naming dictionary
§8 Worked numerics (D, κ, η) with ratio-first checks

Bottom line

Same ontology, one scale ($S_0 = \hbar$), and k_B as an acceptance lock. Temperatures and pressures are multipliers, not magic. Transport coefficients are fluctuation integrals, not knobs. Phase onset is sign flips in a clean expansion, not a new law. We publish ratios first, calibrate where needed, and keep falsifiers explicit.

Appendix — Cheat Sheet (Thermo, VMS)

- Validity strip: near-equilibrium, weak gradients, local stationarity; short-to-moderate memory.
- Smooth-limit dictionary: $q = -\kappa \nabla T$, $J = -D \nabla c$, $\tau = \eta \nabla v$ (κ, D, η are Green–Kubo integrals).
- Forces (multipliers' gradients): $X_T = \nabla(1/T)$, $X_N = -\nabla(\mu/T)$, $X_{mom} \propto \nabla v$.
- Kernels: $J_a = \sum_b L_{ab} \cdot X_b$; $L_{ab} = L_{ba}$; $L_{ab} = \int_0^\infty \langle J_a(0)\, J_b(t) \rangle\, dt$.
- Symbols & locks: $S_0 = \hbar$ (single dimensional scale); k_B (acceptance lock); $\mathcal{T}$ (torsion), $\mathcal{S}$ (shear), $\mathfrak{C}$ (closure).