Lecture 2

What Determines Equilibrium?

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The previous lecture closed by promising two things: the conditions that characterise equilibrium, and the zeroth law. Both come out of a single calculation, which is the subject of this note. The prerequisites are partial derivatives, the first law in the form $dE = đQ + đW$, and the definition of temperature as a derivative of the entropy. Throughout, E denotes internal energy, $đQ$ is heat delivered *to* whichever body is named, and subscripts 1 and 2 label the two bodies of a composite system. Items 2 and 3 of Section 6 fall outside the argument and may be left for a second reading.

Contents

1 The Question the First Law Leaves Open

Put a hot brick against a cold one, wrap the pair in insulation, and wait. Something happens, and then it stops happening. The first law tells us what is conserved while it happens: if the pair exchanges nothing with its surroundings, then

$$E_1 + E_2 = E_{\text{tot}}, \tag{1}$$

with E_{tot} fixed. This is one equation in two unknowns, so it leaves a one-parameter family of possible final states, every one of which conserves energy exactly. Energy conservation restricts the possible final states, but it does not tell us which division of the energy the two bodies will reach. We need an additional condition to select the equilibrium state.

It is worth seeing how wide the remaining choice is. Take a kilogram of water at 20 °C alongside a kilogram at 80 °C, treating the specific heat as constant at $c \approx 4.18\ \mathrm{kJ\,kg^{-1}\,K^{-1}}$ — an approximation good to about one per cent over this range — so that the pair holds roughly 418 kJ above 0 °C. We observe two kilograms at 50 °C, but a final state of 10 °C and 90 °C, or of 0 °C and 100 °C, balances the energy just as exactly. Whatever rules those out is a separate physical principle.

That principle is the second law, and the form we need is not the general statement that entropy increases but a variational statement about this particular composite system. Sections 2 and 3 set it up and extract the equilibrium condition, Section 4 applies the same calculation to other walls, and Section 5 recovers the zeroth law.

2 A Composite System and Its Constraints

Let us replace the bricks with something we can write equations about.

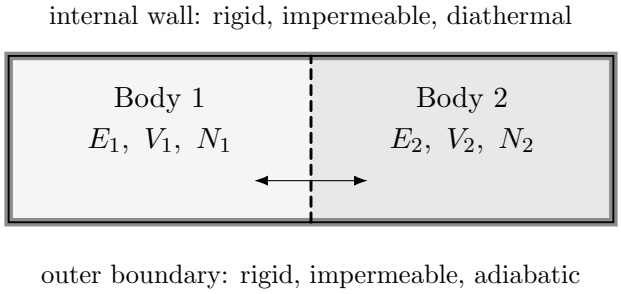

Figure 1: The composite system. Because the outer boundary is rigid, impermeable and adiabatic, E_{tot}, V_{tot} and N_{tot} are fixed. The *internal* wall decides what the two bodies may trade with each other. In Sections 2 and 3 it conducts energy but neither moves nor passes particles, so E_1 is the only freed variable.

Two bodies, each separately in internal equilibrium, are described by (E_i, V_i, N_i) for $i = 1, 2$. They sit inside a common boundary that is rigid, impermeable and adiabatic, so that E_{tot}, V_{tot} and N_{tot} are fixed once and for all. Between them is an internal wall, shown dashed in Figure 1, which for now is rigid and impermeable but conducts energy.

The wall needs describing with care, because it is a *constraint*. While it is adiabatic, E_1 is pinned at whatever value the preparation gave it, and any division of the energy is then a perfectly good equilibrium state of the whole. Making the wall diathermal releases that constraint and leaves E_1 free to take any value consistent with (1). Each problem below has that shape: we identify the variable a released constraint has freed, then find the value it takes.

Postulate: entropy maximisation

Each body has an entropy $S_i(E_i, V_i, N_i)$, defined on its equilibrium states, differentiable, and increasing in E_i at fixed V_i and N_i. The entropy of the composite system is the sum, $S_{\text{tot}} = S_1 + S_2$. When an internal constraint is released, the freed variables take the values that maximise S_{tot} over all states consistent with the constraints that remain.

Two clauses there do real work, and are better flagged before use than after. Additivity is an approximation, whose accuracy Section 2.1 estimates; monotonicity in E fails for the systems described in item 3 of Section 6.

2.1. Why the Entropies Add

Additivity is not a matter of definition. If the two bodies interact, the total energy is $E_1 + E_2 + E_{\text{int}}$, and the entropy of the whole is not in general a sum of a function of E_1 and a function of E_2. What makes the sum legitimate is that E_{int} is negligible, and for short-range forces we can estimate by how much.

Interactions of molecular range a contribute only across the contact surface, so the interaction energy is of order $\epsilon A/a^2$, where A is the contact area and ϵ a per-molecule bond energy. The bulk energy of a body of volume V is of order $\epsilon V/a^3$. Their ratio is

$$\frac{E_{\text{int}}}{E_{\text{bulk}}} \sim \frac{aA}{V} \sim \frac{a}{L} \sim N^{-1/3}, \tag{2}$$

with L a linear dimension and N the number of molecules. For a centimetre cube of condensed matter, $a/L \approx 3 \times 10^{-10}\,\text{m}/10^{-2}\,\text{m}$, a few parts in 10^8. Additivity therefore neglects surface contributions relative to bulk ones, and (2) names the two conditions to check before relying on it: short-range forces, and a body large compared with their range.

2.2. Temperature, Pressure and Chemical Potential as Derivatives

We need names for the derivatives that appear when S_{tot} is differentiated. The first was introduced in the previous lecture and is restated here because everything below depends on it; the second follows the same pattern with volume in place of energy. The chemical potential is the new ingredient, and it is needed only from Section 4 onwards.

Definitions

For a body in equilibrium,

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

These are definitions rather than results: nothing so far says that T is what a mercury thermometer reads, and it is the monotonicity clause of the postulate that makes T positive and single-valued in E at fixed V and N. Notice also which combinations appear. The derivatives of the entropy are $1/T$, P/T and $-\mu/T$, so those are the quantities the calculations below equalise; the familiar equalities of T, P and μ have to be recovered from them, as we do in Section 4. The task of the next section is to show that T behaves as a temperature should, finishing equal in two bodies in contact and ordering the direction of flow between them.

3 Maximising the Total Entropy

Hold V_1, V_2, N_1, N_2 fixed and let E_1 be the freed variable. Using (1) to eliminate $E_2 = E_{\text{tot}} - E_1$ makes the total entropy a function of one variable,

$$S_{\text{tot}}(E_1) = S_1(E_1, V_1, N_1) + S_2(E_{\text{tot}} - E_1, V_2, N_2). \tag{3}$$

Differentiating, the chain rule supplies a minus sign on the second term, because raising E_1 lowers E_2 by exactly as much:

$$\frac{dS_{\text{tot}}}{dE_1} = \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2,N_2} = \frac{1}{T_1} - \frac{1}{T_2}. \tag{4}$$

Setting the slope to zero gives the condition we were after, stated below with the assumptions it needs.

Thermal equilibrium

For two internally equilibrated bodies that can exchange energy, with their volumes and particle numbers fixed and with additive entropy, an interior equilibrium maximum requires equal temperatures. This condition first identifies a stationary point. If the total entropy is concave on the allowed energy interval, that stationary point is a maximum; strict concavity makes it unique.

Three things in that box deserve unpacking. A vanishing slope locates a stationary point and nothing more; it is concavity across the allowed interval that makes the point a maximum, and that also identifies the local maximum with the global one, so without concavity a stable local maximum may be only metastable. We assumed the maximum is interior: if S_{tot} increased across the whole range of E_1 the maximum would sit at an endpoint, where (4) need not vanish. And the derivatives are taken at fixed volume and particle number, which changes the result — $(\partial S/\partial E)$ at fixed V is a different function from the same derivative at fixed P, and only the first is $1/T$ as defined.

3.1. The Direction of Energy Flow

Equality of temperature tells us where the process stops. Equation (4) also tells us which way it runs before it stops, which is what connects the defined quantity T to the everyday notions of hot and cold.

Consider a spontaneous change in the isolated composite system, in which a small amount of energy δE_1 actually passes into body 1. The second law requires the total entropy not to decrease, so to first order

$$\delta S_{\text{tot}} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \delta E_1 \;\geq\; 0. \tag{5}$$

Suppose $T_1 > T_2 > 0$. Then $1/T_1 < 1/T_2$, the bracket is negative, and (5) forces $\delta E_1 \leq 0$: energy leaves the hotter body. When the temperatures are equal the bracket vanishes and so does the first-order change in S_{tot}. That is a necessary condition for equilibrium, but on its own it settles neither stability nor the absence of exchange: the first variation describes admissible changes about a state, not the dynamics of the approach to it, and equality of temperature says nothing about the further exchanges that a different wall would permit.

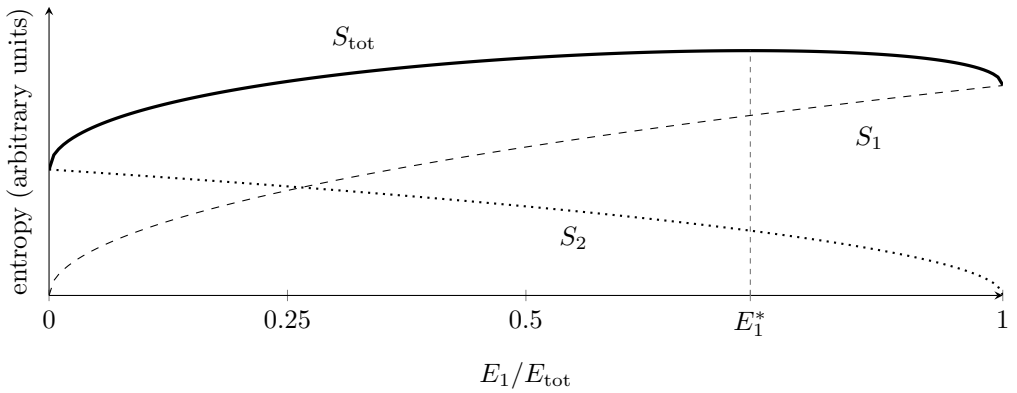

Figure 2: Total entropy as the freed variable E_1 ranges over the values allowed by conservation, for two bodies with $S_i \propto \sqrt{E_i}$ — a concave choice, so that the stationary point shown is the unique maximum. Both components are plotted against E_1, so body 1 gains as body 2 loses; each is monotonic, and yet the sum has an interior maximum at E_1^*, where the two curves have slopes of equal magnitude and opposite sign. That is what equation (4) says when it vanishes.

Key Point

Written in terms of $\beta = 1/k_B T$, the first-order change reads $\delta S_{\text{tot}} = k_B(\beta_1 - \beta_2)\,\delta E_1 \geq 0$, so the sign of the transfer is fixed by the difference of the two β's, and the stationary condition is $\beta_1 = \beta_2$. When both temperatures are positive a larger β means a lower T, and this reproduces the familiar statement. Item 3 of Section 6 describes a case in which ordering by T and by β disagree.

3.2. A Worked Example: Two Ideal Gases

Equality of temperature is a statement about derivatives; to watch it produce a number we need an entropy function. For a monatomic ideal gas the energy dependence of the entropy is

$$S_i(E_i, V_i, N_i) = \tfrac{3}{2} N_i k_B \ln(E_i/E_0) + f(V_i, N_i), \tag{6}$$

where E_0 is an arbitrary reference energy keeping the logarithm's argument dimensionless, and f collects everything independent of E_i, including the constant a change of E_0 produces. The complete expression — the Sackur–Tetrode equation — carries the volume and particle-number dependence and a constant fixed by quantum mechanics, and we shall derive it once we have the machinery. None of it is needed here, since only the E_i dependence survives differentiation at fixed V_i and N_i:

$$\frac{1}{T_i} = \left(\frac{\partial S_i}{\partial E_i}\right)_{V_i, N_i} = \frac{3 N_i k_B}{2 E_i} \qquad \Longleftrightarrow \qquad E_i = \tfrac{3}{2} N_i k_B T_i. \tag{7}$$

That is equipartition, three quadratic degrees of freedom per atom, and here it follows from (6) and the definition of T rather than being assumed separately.

Equality of temperature requires $E_1/N_1 = E_2/N_2$ by (7), so the energy divides to make the energy *per atom* match, not to make the energies match. Combining (7) with (1) gives the common final temperature,

$$T_f = w_1 T_1^{(0)} + w_2 T_2^{(0)}, \qquad w_i = \frac{C_i}{C_1 + C_2}, \qquad C_i = \tfrac{3}{2} N_i k_B, \tag{8}$$

where $T_i^{(0)}$ are the initial temperatures and C_i is the constant-volume heat capacity of sample i. The weights are positive and satisfy $w_1 + w_2 = 1$, so T_f is a weighted mean of the initial temperatures, lying between them. For these gases $w_i = N_i/(N_1 + N_2)$. This is also why the two kilograms of water in Section 1 met in the middle: their heat capacities were equal, and they would not have met in the middle had one of them been half a kilogram.

We can now check the second law rather than invoke it. Substituting (8) into (6) and using the same weights,

$$\Delta S_{\text{tot}} = C_1 \ln \frac{T_f}{T_1^{(0)}} + C_2 \ln \frac{T_f}{T_2^{(0)}} = (C_1 + C_2) \left[\ln \left(\sum_i w_i T_i^{(0)} \right) - \sum_i w_i \ln T_i^{(0)} \right]. \tag{9}$$

The bracket compares the logarithm of a weighted mean with the weighted mean of the logarithms. Because the logarithm is strictly concave and the weights are positive and sum to one, Jensen's inequality makes the first at least as large as the second, with equality only when the two temperatures coincide. So $\Delta S_{\text{tot}} \geq 0$, strictly so whenever the samples start at different temperatures, the equality case being the one in which nothing happens. The reason is visible in the definition of T: at fixed volume $dS = đQ/T$, so a given quantity of energy is worth more entropy to the colder body, and its gain outweighs the hot body's loss. Both (8) and (9) assume C_i constant, true for a monatomic ideal gas at fixed volume but not in general.

Numbers

Two argon samples with $N_1 = 2N_2$, initially at 300 K and 600 K, so that $w_1 = 2/3$ and $w_2 = 1/3$. Equation (8) gives $T_f = (2 \cdot 300 + 600)/3 = 400$ K, pulled towards the larger sample. Equation (9) gives $\Delta S_{\text{tot}} = \frac{3}{2} N_2 k_B \left[2 \ln \frac{4}{3} + \ln \frac{2}{3} \right] \approx 0.25\, N_2 k_B > 0$. The final energies stand in the ratio 2 to 1: equal temperature, not equal energy.

4 Which Wall Equalises Which Quantity?

The calculation in Section 3 did not depend on the exchanged quantity being energy: it used only that a released constraint freed one additive conserved quantity, and that the entropy is differentiable in it. A different wall frees a different quantity, and the same differentiation yields a different equality.

Let the internal wall be movable and permeable as well as diathermal, so that E_1, V_1 and N_1 are all free subject to the three conservation conditions. Using the definitions of Section 2.2, the first-order change in the total entropy is

$$\begin{aligned} dS_{\text{tot}} = {} & \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 \\ & - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1. \end{aligned} \tag{10}$$

Whether the three displacements may be varied independently is a question about the constraints, not a matter of convention. Here the wall's conductivity, its mobility and its permeability are separate physical properties, and each can be adjusted without the others, so dE_1, dV_1 and dN_1 are independent and each bracket must vanish on its own. The order in which we read off the consequences matters: the first bracket gives $T_1 = T_2$, and only with that in hand do the other two reduce to $P_1 = P_2$ and $\mu_1 = \mu_2$.

Internal wall	Freed variables	Condition for an interior stationary point of S_{tot}
rigid, impermeable, diathermal	E_1	$T_1 = T_2$
movable, impermeable, diathermal	E_1, V_1	$T_1 = T_2$ and $P_1 = P_2$
rigid, permeable, diathermal	E_1, N_1	$T_1 = T_2$ and $\mu_1 = \mu_2$
movable, permeable, diathermal	E_1, V_1, N_1	$T_1 = T_2$, $P_1 = P_2$ and $\mu_1 = \mu_2$
movable, impermeable, insulating	V_1, and E_1 through the piston's motion	$P_1 = P_2$ describes mechanical balance only; unequal temperatures may persist through that stage, and what happens afterwards depends on the mechanical model (see below)

Table 1: Conditions for an interior stationary point of S_{tot} under each set of constraints, for additive entropies and bodies each internally equilibrated; concavity on the allowed interval is what makes such a point a maximum. Every quantity the wall passes contributes one equality between entropic derivatives, and the equalities in T, P and μ follow from those in $1/T$, P/T and μ/T only once the temperatures agree.

The last row of Table 1 needs the care it is given there. An insulating piston can still exchange energy with the gases through its motion. For a reversible adiabatic change of either gas we may write $dE_i = -P_i\,dV_i$, so its entropy stays constant along that path. A freely released piston need not follow this path: it can accelerate, store kinetic energy, and take part in dissipative relaxation. We must therefore specify the mechanical model before treating the energy and volume variations as independent, or before imposing a relation between them. Substituting $dE_i = -P_i\,dV_i$ into (10) and finding $dS_{\text{tot}} = 0$ once $P_1 = P_2$, whatever the temperatures, is a consequence of that imposed relation rather than a result about the released piston [10].

For a horizontal, unloaded piston of finite mass with negligible friction, the usual ideal-gas treatment separates two mechanisms of very different timescale. The faster damps the piston's motion and brings the gases to mechanical balance, $P_1 = P_2$, while their temperatures may still differ. The slower works through fluctuations: collisions make the piston's position fluctuate, and the momentum transfer carries energy between the gases even though the piston conducts no heat. In that model the gases do reach a common temperature, as molecular dynamics confirms [11,12]. This picture belongs to that model and should not be carried over to every piston, and a *fixed* insulating wall is a different constraint again: it frees nothing and imposes no condition.

Key Point

The equilibrium conditions depend on which exchanges the wall permits. We must therefore specify the remaining constraints before asking whether two bodies are in equilibrium, and a composite system held by a constraint can sit indefinitely in a state that is not the maximum-entropy state of its parts.

5 The Zeroth Law and What a Thermometer Measures

The zeroth law states that two bodies each in thermal equilibrium with a third are in thermal equilibrium with each other. Within the description set up in Section 2 we can see where this comes from. If bodies 1 and 3 are joined by a diathermal wall and reach an interior, stable maximum of their total entropy, then $T_1 = T_3$; the same argument for bodies 2 and 3 gives $T_2 = T_3$. These are equalities between real numbers, so $T_1 = T_2$. Equality of the common temperature variable is transitive because numerical equality is.

Reading that as a statement about mutual thermal equilibrium uses assumptions we have already made, and it is worth saying which. Each body must have a well-defined temperature, which is the content of the postulate; the contact between 1 and 2 must be of the same diathermal kind as the other two; and the state identified by $T_1 = T_2$ must be a stable maximum rather than merely a stationary point, which is the concavity assumption of Section 3. What we have is therefore transitivity within a particular thermodynamic description, not an assumption-free derivation of the empirical zeroth law. The traditional presentation runs the other way, taking transitivity as the empirical input and concluding that it *implies* an empirical temperature whose equality characterises mutual equilibrium; Lieb and Yngvason [5] give an axiomatic version in which the entropy's existence is itself a conclusion.

Transitivity alone does not fix a scale. If θ is an empirical temperature then so is $g(\theta)$ for any strictly increasing g: the two agree about which pairs of bodies are in equilibrium and disagree about every numerical value. Equality at equilibrium therefore determines temperature only up to a monotonic relabelling. What fixes the scale is the second law, through $1/T = (\partial S/\partial E)_{V,N}$, which determines T to within a single multiplicative constant; and that constant is now a matter of convention, since the SI fixes $k_B = 1.380649 \times 10^{-23}\ \mathrm{J\,K^{-1}}$ exactly.

A thermometer is this argument put to work. Bring a small body into diathermal contact with a large one, wait, and read off some property of it — a length, a resistance, a pressure — that varies monotonically with its temperature. Equilibrium guarantees the two temperatures are equal, and a calibration curve turns the reading into a number.

The word *small* needs a quantitative meaning, because the measurement changes what it measures, and Section 3.2 already says by how much. For heat capacities that can be treated as constant over the relevant range, the weighted mean (8) gives

$$T_f - T_{\mathrm{sys}} = -\,\frac{C_{\mathrm{th}}}{C_{\mathrm{sys}} + C_{\mathrm{th}}}\,(T_{\mathrm{sys}} - T_{\mathrm{th}}) \;\approx\; -\,\frac{C_{\mathrm{th}}}{C_{\mathrm{sys}}}\,(T_{\mathrm{sys}} - T_{\mathrm{th}})\,. \tag{11}$$

A good thermometer is one whose heat capacity is small compared with that of the thing measured, which is not the same as being physically small. Equation (11) also assumes the two actually reach equilibrium, and how long that takes is a question thermodynamics cannot answer.

6 What the Result Leaves Open

1. **Stationary is not maximum.** The sign of $d^2S_{\mathrm{tot}}/dE_1^2$ decides whether the stationary point is a maximum, and it brings in the heat capacities of both bodies. A system can satisfy $T_1 = T_2$ and remain unstable, and the states excluded on those grounds are the ones that matter for phase separation. This is the subject of the lecture on stability.

2. **Additivity can fail** (optional reading). The estimate (2) assumed short-range forces. Gravitational energy grows with the bulk of a system rather than its surface, so the entropy of a

self-gravitating system is not additive; its microcanonical heat capacity can be negative, and the microcanonical and canonical descriptions stop agreeing [8,9]. Little of Section 3 survives there, and the two-body argument should be read as a statement about short-range forces.

3. **Monotonicity can fail** (optional reading). An upper bound on a system's energy spectrum *permits* negative temperatures but does not by itself establish them. The condition for $T < 0$ is $(\partial S/\partial E)_{V,N} < 0$ over some range of E, which requires $S(E)$ to turn over and decrease. The standard realisation is a set of nuclear spins in a magnetic field, treated as an isolated subsystem on timescales short compared with spin–lattice relaxation: the spin entropy rises, peaks when the levels are equally populated, and falls as the upper level fills. There (5) still holds, and β is the variable to read it with, since any $\beta < 0$ lies below every $\beta > 0$ and such a spin system gives up energy to any body at positive temperature. Purcell and Pound [6] prepared such a state; Ramsey [7] worked out the thermodynamics.

4. **Finite systems fluctuate.** The maximum identifies the most probable division of the energy, not the only one. For ordinary extensive systems, with correlations short compared with the system size and away from critical points, relative energy fluctuations scale as $N^{-1/2}$, which is what makes the maximum sharp enough to be called *the* equilibrium state. Near a critical point, or where correlations are long ranged, that estimate does not apply; and for a small system "the equilibrium value of E_1" becomes a mean rather than a value. Quantifying this needs the canonical machinery.

5. **Nothing here concerns time.** The postulate identifies the state the system ends in, not when it arrives, and Section 4 has already shown that a timescale argument can decide which of two conditions is met first.

The gap the next lecture closes is a practical one. Every argument above needed the composite system to be isolated, so that E_{tot} was fixed and the entropy of the whole was the thing to maximise, and almost no experiment is arranged that way. A sample on a bench sits in a room whose temperature is fixed and whose energy is not; what is held fixed is T and V, and the sample's own entropy is free to fall. The maximum-entropy principle remains true but is no longer expressed in the variables an experimenter controls. So if equilibrium maximises entropy, why does a system at fixed temperature and volume minimise the Helmholtz free energy instead, and what is being maximised when it does?

Appendix A: The Same Calculation with Lagrange Multipliers

Section 3 eliminated E_2 using the constraint and then differentiated with respect to the single surviving variable. That is the quickest route for two bodies and one conserved quantity, but it becomes awkward with several of each. The multiplier form generalises without effort, and its multipliers turn out to be quantities we have already named.

Let M bodies be free to exchange n additive conserved quantities $X^1, \ldots, X^n$; for us these are $(X^1, X^2, X^3) = (E, V, N)$. Write X_i^a for the amount of quantity a held by body i. The totals are fixed,

$$\sum_{i=1}^{M} X_i^a = X^a, \qquad a = 1, \ldots, n, \tag{12}$$

and we maximise $S_{\mathrm{tot}} = \sum_i S_i(X_i^1, \ldots, X_i^n)$ subject to (12). Introducing one multiplier λ_a per constraint,

$$\mathcal{L} = \sum_{i=1}^{M} S_i(X_i^1, \ldots, X_i^n) - \sum_{a=1}^{n} \lambda_a \left(\sum_{i=1}^{M} X_i^a - X^a \right), \tag{13}$$

the stationarity conditions $\partial\mathcal{L}/\partial X_i^a = 0$ read

$$\left(\frac{\partial S_i}{\partial X_i^a} \right)_{X_i^b,\ b \neq a} = \lambda_a \qquad \text{for every body } i \text{ and every quantity } a. \tag{14}$$

The point of (14) is that its right-hand side carries no index i: each entropic derivative takes the same value in every body, and that common value is the multiplier. With the definitions of Section 2.2,

$$\lambda_E = \frac{1}{T}, \qquad \lambda_V = \frac{P}{T}, \qquad \lambda_N = -\frac{\mu}{T}, \tag{15}$$

so all M bodies share a temperature and, once that holds, a pressure and a chemical potential. Putting $M = 2$, $n = 1$ and eliminating the multiplier recovers (4).

Each multiplier inherits the units of the entropy derivative it equals, so λ_E is measured in K^{-1}: it is a reciprocal temperature, not the β of statistical mechanics. The two differ by a factor of k_B, because β is the multiplier obtained by maximising the dimensionless entropy S/k_B rather than the dimensional S:

$$\lambda_E = \frac{1}{T}, \qquad \beta = \frac{1}{k_B T} = \frac{\lambda_E}{k_B}. \tag{16}$$

Rescaling the objective by $1/k_B$ rescales every multiplier the same way, so that $\lambda_V/k_B = P/k_B T$ and $\lambda_N/k_B = -\mu/k_B T$; it is these that appear in the canonical and grand-canonical distributions, and we shall meet β again in that form. The multipliers are therefore not bookkeeping devices: up to that normalisation they are the equilibrium values of the intensive quantities themselves.

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