4 Temperature

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4a Gas thermometer

An equilibrium macrostate $x_{h,u}$ of a pair of non-interacting systems (recall Sect. 3a) is

$$x_{h,u} = \operatorname{grad}\Lambda(-\beta h) = \operatorname{grad}\Lambda_1(-\beta h_1) \oplus \operatorname{grad}\Lambda_2(-\beta h_2)$$

for β such that $u = \langle h, \operatorname{grad}\Lambda(-\beta h)\rangle$. That is,

$$\begin{aligned} h &= h_1 \oplus h_2\,, \\ x_{h,u} &= x_{h_1,u_1} \oplus x_{h_2,u_2}\,, \\ x_{h_1,u_1} &= \operatorname{grad}\Lambda_1(-\beta_1 h_1)\,, \\ x_{h_2,u_2} &= \operatorname{grad}\Lambda_2(-\beta_2 h_2)\,, \end{aligned} \qquad \beta_1 = \beta_2\,.$$

In equilibrium the two systems have the same β. (See also Sect. 1e.) We may guess that the temperature is a function of β. The same function for all systems. However, which function? What do we really mean by temperature?

Historically, first thermometers were based on thermal expansion of air and other substances.[1] Accordingly, physics defines temperature via "gas thermometer" — a portion of ideal gas.[2] It appears that PV (the pressure times the volume) is proportional to $1/\beta$, which is why the temperature is defined to be proportional to $1/\beta$. We'll prove that $PV\beta = \text{const}$, but first

[1] Philo the Jew of Alexandria (20 BCE – 50 CE); Drebbel, Fludd, Galileo, Sanctorius (16–17th centuries). See "Thermometer" in Wikipedia.

[2] "It is well known that the determination of a temperature scale in classical thermodynamics is connected (through the concept of the gas thermometer) to the laws of ideal gases." R. Balescu, "Equilibrium and nonequilibrium statistical mechanics", 1975, Sect. 4.4, page 125.

we have to realize what do we really mean by the pressure (of the gas, not an arbitrary system).

As was said in 3a4, the ideal gas may be treated as a combination of the coordinate subsystem and three one-dimensional momentum subsystems. For now we consider the coordinate subsystem only: Ω is a domain in $\mathbb{R}^3$ ('container'), μ is the Lebesgue measure (three-dimensional) on Ω, and $h : \Omega \to \mathbb{R}$ ('potential energy'). Mathematically this is just our general framework, since there is nothing special in a domain in $\mathbb{R}^3$ treated as a measure space. However, sometimes we'll recall that now $\mu(\Omega)$ is the volume of the container, etc.

Roughly, the pressure determines the amount of mechanical energy (work) needed in order to displace the gas out of a small part of the container.

4a1 Exercise. For every isothermal quasistatic process (as defined in Sect. 3a) the mechanical part (work) of the received energy is

$$\int_0^1 \langle h_t', x_t \rangle \, \mathrm{d}t = -\frac{1}{\beta} \big(\Lambda(-\beta h_1) - \Lambda(-\beta h_0) \big) \, ,$$

and the thermal part (heat) is

$$\int_0^1 \langle h_t, x_t' \rangle \, \mathrm{d}t = \frac{1}{\beta} \big(S(x_1) - S(x_0) \big) \, .$$

Prove it.

By the way, the energy $u_t = \langle h_t, x_t \rangle$ is $\frac{1}{\beta} \big(S(x_t) - \Lambda(-\beta h_t) \big)$.

Assume that $\mu(\Omega) = V < \infty$ (a finite-volume container), $\beta > 0$, and choose $A \subset \Omega$, $\mu(A) = \Delta V$. We consider the change of

$$\Lambda(-\beta U 1\!\!1_A) = \ln \int \mathrm{e}^{-\beta U 1\!\!1_A} \, \mathrm{d}\mu = \ln \big(1 \cdot (V - \Delta V) + \mathrm{e}^{-\beta U} \cdot \Delta V \big)$$

when the potential U runs from 0 to ∞:

$$\lim_{U \to 0+} \Lambda(-\beta U 1\!\!1_A) = \ln V \, ; \quad \lim_{U \to +\infty} \Lambda(-\beta U 1\!\!1_A) = \ln(V - \Delta V) \, .$$

Imagine an isothermal process that starts at $h_0 = U_0 1\!\!1_A$ with a small U_0 and finishes at $h_1 = U_1 1\!\!1_A$ with a high U_1. By 4a1, the work is close to

$$-\frac{1}{\beta} (\ln(V - \Delta V) - \ln V) \, .$$

This is the work per particle, needed in order to displace the gas out of the part ΔV of the volume V. For small ΔV the work is close to $n\frac{1}{\beta}\frac{\Delta V}{V}$, which means the pressure

$$P = \frac{n}{\beta V} \,. \tag{4a2}$$

The momentum subsystems do not invalidate this formula; their states do not change in the isothermal process, and no heat is transferred between the four subsystems. (Think how to turn this into a formal argument.)

The pressure is usually associated with elastic collisions of gas molecules with the walls of the container.[1] The higher the temperature, the faster the molecules and the higher the pressure. However, in our approach motion of particles is never mentioned, and still, the pressure is well-defined and depends on the temperature. A paradox?

It is instructive to observe dependence of $-\frac{1}{\beta}\big(\Lambda(-\beta U 1\!\!1_A) - \ln V\big)$ on U (and β):

$$-\frac{1}{\beta}\big(\Lambda(-\beta U 1\!\!1_A) - \ln V\big) \approx \begin{cases} U\frac{\Delta V}{V} & \text{for } U \ll 1/\beta, \\ \frac{1}{\beta}\frac{\Delta V}{V} & \text{for } U \gg 1/\beta. \end{cases}$$

Roughly, U has to cross $1/\beta$ in order to displace the gas out of A. This is why the work is proportional to $1/\beta$.

An adiabatic process leads to the same result (4a2), which is easy to guess: for small ΔV the work is small, thus, the heating is also small. The detailed calculation follows, first, for the coordinate subsystem only.

The energy:

$$u = \langle h, \nu \rangle = \frac{\int h \mathrm{e}^{-\beta h} \, \mathrm{d}\mu}{\int \mathrm{e}^{-\beta h} \, \mathrm{d}\mu} \,;$$

for $h = U 1\!\!1_A$ we have

$$u = \frac{U \mathrm{e}^{-\beta U} \Delta V}{\mathrm{e}^{-\beta U} \Delta V + V - \Delta V} \to 0$$

as $U \to 0+$, but also as $U \to +\infty$.

The entropy $S = \beta u + \Lambda(-\beta h)$ is constant in an adiabatic process. Starting at $h_0 = U_0 1\!\!1_A$ with a small U_0 we have $S_0 = \beta_0 u_0 + \Lambda(-\beta_0 U_0 1\!\!1_A) \approx 0 + \ln V$. Finishes at $h_1 = U_1 1\!\!1_A$ with a high U_1 we have $S_1 = \beta_1 u_1 + \Lambda(-\beta_1 U_1 1\!\!1_A) \approx 0 + \ln(V - \Delta V)$; a contradiction!

Well, the contradiction appears if β_1 is assumed to be positive. In fact, β converges to zero, and the temperature — to infinity. The reason is simple: in

[1] See "Kinetic theory" in Wikipedia.

the absence of kinetic energy the system cannot absorb the incoming energy without infinite heating.

We must include the three one-dimensional momenta. The entropy of the coordinate subsystem decreases from $\ln V$ to $\ln(V - \Delta V)$, therefore the entropy of each momentum system must increase by $\frac{1}{3} \ln \frac{V}{V-\Delta V}$. By 3a5 and 3c4 the entropy of a momentum system is $\frac{1}{2} \ln x + \text{const}$ where $x = 1/(2\beta)$; that is, the entropy is $-\frac{1}{2} \ln \beta + \text{const}$. Thus, $-\frac{1}{2}(\ln \beta_1 - \ln \beta_0) = \frac{1}{3} \ln \frac{V}{V-\Delta V}$;

$$\frac{\beta_1}{\beta_0} = \Big(\frac{V - \Delta V}{V} \Big)^{2/3} ;$$

a fact well-known in physics. Interestingly, '3' in '2/3' is the dimension of the momentum space, while '2' appears because the kinetic energy is quadratic in the momentum.

The energy of the coordinate subsystem returns to its original value. For each momentum subsystem the energy is $1/(2\beta)$ by 3a5. Thus, the work is

$$\frac{1}{2\beta_1} - \frac{1}{2\beta_0} = \frac{1}{2\beta_0} \bigg(\Big(\frac{V}{V - \Delta V} \Big)^{2/3} - 1 \bigg) .$$

For small ΔV the work per particle is close to $\frac{1}{3\beta_0} \frac{\Delta V}{V}$, the whole work to $n \frac{1}{\beta_0} \frac{\Delta V}{V}$ as before (in the isothermal case), and we get the pressure (4a2) again.

So, the temperature is inversely proportional to β. In physics the temperature T, defined via the ideal gas law

$$PV = n k_{\mathrm{B}} T ,$$

is

$$T = \frac{1}{k_{\mathrm{B}} \beta} .$$

4b Differentials of energy and entropy

Given $h \in K$ we have a strictly convex, infinitely differentiable function $\lambda \mapsto \Lambda(\lambda h)$ defined on $\mathbb{R}$ if $\mu(\Omega) < \infty$, otherwise on $(-\infty, 0)$. Its derivative is the energy (assuming $\beta = -\lambda$, as before):

$$u = \langle h, \operatorname{grad} \Lambda(\lambda h) \rangle = \frac{\mathrm{d}}{\mathrm{d}\lambda} \Lambda(\lambda h) .$$

Its Fenchel-Legendre transform is the rate function (recall 3d3): if $x = \operatorname{grad} \Lambda(\lambda h)$ and $u = \langle h, x \rangle$ then

$$\sup_{\lambda_1} \big(\lambda_1 u - \Lambda(\lambda_1 h) \big) = \lambda u - \Lambda(\lambda h) = \Lambda^*(x) = -S(x) .$$

Treating them all as functions of β,

$$\Lambda(\beta) = \Lambda(-\beta h)\,, \quad u(\beta) = \langle h, \operatorname{grad}\Lambda(-\beta h)\rangle\,, \quad S(\beta) = S\big(\operatorname{grad}\Lambda(-\beta h)\big)\,,$$

we have

$$\begin{gathered} u(\beta) = -\Lambda'(\beta)\,, \\ S(\beta) = \beta u(\beta) + \Lambda(\beta) = \min_{\beta_1}\big(\beta_1 u(\beta) + \Lambda(\beta_1)\big)\,, \\ S(\beta) = \Lambda(\beta) - \beta\Lambda'(\beta)\,. \end{gathered}$$

4b1 Remark. These relations are in fact a special case (for $\dim L_1 = 1$) of more general relations between two spaces $L_1 \subset L_2$ satisfying $L_1 \cap K_2 \ne \emptyset$. However, we do not need it.

4b2 Example. One-dimensional momentum, see 3a5:

$$\begin{gathered} \beta \in (0,\infty)\,, \\ \Lambda(\beta) = -\frac{1}{2}\ln\beta + \text{const}\,, \\ u(\beta) = \frac{1}{2\beta}\,, \\ S(\beta) = -\frac{1}{2}\ln\beta + \text{const}\,. \end{gathered}$$

4b3 Example. Spin 1/2, see 3a3 and 3c4. We take $h(\omega) = h\omega$ for $\omega \in \{-1,1\}$, assuming that some $h > 0$ is given. Then

$$\begin{gathered} \beta \in (-\infty,\infty)\,, \\ \Lambda(\beta) = \ln(\mathrm{e}^{-\beta h} + \mathrm{e}^{\beta h})\,, \\ u(\beta) = -h\tanh\beta h\,, \\ S(\beta) = -\frac{1-x}{2}\ln\frac{1-x}{2} - \frac{1+x}{2}\ln\frac{1+x}{2} \quad \text{where } x = -\tanh\beta h\,. \end{gathered}$$

Generally, $u'(\beta) = -\Lambda''(\beta)$ and $S'(\beta) = \Lambda'(\beta) - \big(\Lambda'(\beta) + \beta\Lambda''(\beta)\big) = -\beta\Lambda''(\beta)$, thus,

$$S'(\beta) = \beta u'(\beta)\,,$$

which is often written as

$$\beta = \frac{\mathrm{d}S}{\mathrm{d}u} \tag{4b4}$$

or

$$k_{\mathrm{B}}T = \frac{\mathrm{d}u}{\mathrm{d}S}\,, \tag{4b5}$$

treating u and S as two functionally related variables.

Compare it with 3d5.

Equilibrium between two subsystems maximizes the total entropy S_1+S_2 (that is, minimizes the rate function) given the total energy u_1+u_2. Clearly, the corresponding differential condition is

$$\frac{\mathrm{d}S_1}{\mathrm{d}u_1}=\frac{\mathrm{d}S_2}{\mathrm{d}u_2}\,,\quad \text{that is,}\quad \beta_1=\beta_2\,;$$

temperatures are equal in equilibrium.

4c Negative temperature, really?

If $\mu(\Omega)=\infty$ then $\beta\in(0,\infty)$, thus $T\in(0,\infty)$; the temperature is always positive. In particular, this is the case for the ideal gas (see 4b2). However, if $\mu(\Omega)<\infty$ then $\beta\in(-\infty,\infty)$, thus the temperature, if still defined by $k_{\mathrm{B}}T=1/\beta$, can be positive, infinite and negative. In particular, this is the case for spin systems (see 4b3). What could it mean?

Imagine two subsystems with the total energy $u=u_1+u_2$, total entropy S_1+S_2 and different temperatures (thus, out of equilibrium):

$$\frac{\mathrm{d}S_1}{\mathrm{d}u_1}=\beta_1<\beta_2=\frac{\mathrm{d}S_2}{\mathrm{d}u_2}\,.$$

Recall that generally the energy $u(\beta)=-\Lambda'(\beta)$ decreases in β (be β positive or negative), and moreover, $u'(\beta)<0$. Imagine a move from (β_1,β_2) to $(\beta_1+\mathrm{d}\beta_1,\beta_2+\mathrm{d}\beta_2)$ such that $\mathrm{d}u=u_1'(\beta_1)\mathrm{d}\beta_1+u_2'(\beta_2)\mathrm{d}\beta_2=0$. Then $\mathrm{d}S=S_1'(\beta_1)\mathrm{d}\beta_1+S_2'(\beta_2)\mathrm{d}\beta_2=\beta_1u_1'(\beta_1)\mathrm{d}\beta_1+\beta_2u_2'(\beta_2)\mathrm{d}\beta_2=(\beta_2-\beta_1)u_2'(\beta_2)\mathrm{d}\beta_2$. If $\mathrm{d}\beta_1>0$ and $\mathrm{d}\beta_2<0$ then $\mathrm{d}S>0$; if $\mathrm{d}\beta_1<0$ and $\mathrm{d}\beta_2>0$ then $\mathrm{d}S<0$. Thus, in the process of relaxation β_1 increases and β_2 decreases; u_1 decreases and u_2 increases; the energy flows from the system with smaller β to the system with higher β.

If $\beta_1>0$, $\beta_2>0$ then the energy flows from the system with higher temperature to the system with lower temperature. (Yes, rather!) If $\beta_1<0$, $\beta_2>0$ then the energy flows from the system with negative temperature to the system with positive temperature. In this sense negative temperatures are not colder than the absolute zero temperature. Just the opposite: they are hotter than infinite temperature!

Needless to say, a negative temperature cannot be measured by a gas thermometer. Thus, the definition $k_{\mathrm{B}}T=1/\beta$ for negative β is just a groundless extrapolation. (However, see the end of Sect. 4d.)

A spin system can have a negative temperature as long as it is isolated from its positive-temperature environment. It never is completely isolated,

but it can be approximately isolated for a short time. The same holds for two-state systems that physically are not spins but mathematically are isomorphic to spins. Especially, in a laser: the two states of an atom are the ground state and the relevant excited state. Pumping this system to a negative temperature ("population inversion": most atoms are excited) is necessary for the laser to work.[1]

4d Heat engine, heat pump

Quasistatic process, defined in Sect. 3a, is called a *cycle* if $h_1 = h_0$ and $\beta_1 = \beta_0$. It follows that $x_1 = x_0$ (recall that $x = \operatorname{grad} \Lambda(-\beta h)$), $u_1 = u_0$ (recall that $u = \langle h, x \rangle$) and therefore

$$\underbrace{\int_0^1 \langle h_t', x_t \rangle \, \mathrm{d}t}_{\text{work}} + \underbrace{\int_0^1 \langle h_t, x_t' \rangle \, \mathrm{d}t}_{\text{heat}} = 0 \, .$$

The case work < 0, heat > 0 corresponds to a *heat engine.* The case work > 0, heat < 0 corresponds to a *heat pump.* A heat engine converts heat to work. A heat pump converts work to heat.

For an adiabatic cycle heat $= 0$ trivially, and therefore also work $= 0$.

For an isothermal process, by 3d5,

$$S(x_1) - S(x_0) = \beta \cdot \text{heat} \, ,$$

therefore for an isothermal cycle heat $= 0$ and work $= 0$. It means that energy conversion is impossible[2] when only a single heat reservoir is available.

Imagine now that two heat reservoirs are available, hot and cold, of temperatures

$$\frac{1}{\beta_{\text{cold}}} = k_{\text{B}} T_{\text{cold}} < k_{\text{B}} T_{\text{hot}} = \frac{1}{\beta_{\text{hot}}} \, .$$

Reservoirs are so large that their temperatures may be treated as constant.[3] We compose a cycle, well-known as *Carnot cycle,* out of four processes: one isothermal at T_{cold}, one isothermal at T_{hot}, and two adiabatic. On the plane of entropy and temperature we get a rectangle (compare it with Sect. 1f):

	(S_1, T_{cold}) $\mapsto$	(S_1, T_{hot}) $\mapsto$	(S_2, T_{hot}) $\mapsto$	(S_2, T_{cold}) $\mapsto$	(S_1, T_{cold})
type	adiabatic	isothermal	adiabatic	isothermal	
heat	0	$\frac{S_2 - S_1}{\beta_{\text{hot}}}$	0	$\frac{S_1 - S_2}{\beta_{\text{cold}}}$	

[1] How to pump it? See "Population inversion" in Wikipedia.

[2] For quasistatic processes. Dissipation of mechanical energy (say, friction) is possible and quite usual, but not quasistatic.

[3] See also Sect. 4e.

Thus,

$$\text{heat} = (S_2 - S_1)\Big(\frac{1}{\beta_{\text{hot}}} - \frac{1}{\beta_{\text{cold}}}\Big) = (S_2 - S_1)k_{\text{B}}(T_{\text{hot}} - T_{\text{cold}})$$

and work = −heat, of course.

Case 1 (usual): $0 < T_{\text{cold}} < T_{\text{hot}}$.

If $S_2 > S_1$ we have a heat engine; if $S_2 < S_1$ we have a heat pump.

Consider first a heat engine; converted energy = |heat| = |work|. The heat received from the hot reservoir (spent) is

$$\text{spent heat} = \frac{S_2 - S_1}{\beta_{\text{hot}}} = (S_2 - S_1)k_{\text{B}}T_{\text{hot}}\,;$$

the heat sent to the cold reservoir (lost) is

$$\text{lost heat} = \frac{S_2 - S_1}{\beta_{\text{cold}}} = (S_2 - S_1)k_{\text{B}}T_{\text{cold}}\,.$$

Introducing

$$\text{efficiency} = \frac{\text{converted energy}}{\text{spent heat}}$$

we have

$$\text{efficiency} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} = \frac{\beta_{\text{cold}} - \beta_{\text{hot}}}{\beta_{\text{cold}}}\,.$$

An important implication: it is possible to establish the scale of temperature without the gas thermometer (or anything like that). An even more important implication: it is very ineffective to use a small difference in temperature (say, ocean water on different depths).

Consider now a heat pump: $S_2 < S_1$. Mechanical energy $(S_1 - S_2)k_{\text{B}}(T_{\text{hot}} - T_{\text{cold}})$ is spent; the heat $(S_1 - S_2)k_{\text{B}}T_{\text{hot}}$ is pumped into the hot reservoir; and the heat $(S_1 - S_2)k_{\text{B}}T_{\text{cold}}$ is pumped from the cold reservoir.

Case 2 (unusual): $T_{\text{cold}} < T_{\text{hot}} < 0$.

If $S_2 > S_1$ we have a heat engine and a heat pump simultaneously in this wonderland! The cycle releases mechanical energy $(S_2 - S_1)k_{\text{B}}(T_{\text{hot}} - T_{\text{cold}})$, pumps the heat $(S_2 - S_1)k_{\text{B}}|T_{\text{hot}}|$ into the hot reservoir, and pumps the heat $(S_2 - S_1)k_{\text{B}}|T_{\text{cold}}|$ out of the cold reservoir. The case $S_2 < S_1$ leads to the opposite.

Case 3 (strange): $T_{\text{cold}} < 0 < T_{\text{hot}}$.

If $S_2 > S_1$, the cycle receives heat from both reservoirs, $(S_2 - S_1)k_{\text{B}}T_{\text{hot}}$ from the hot one and $(S_2 - S_1)k_{\text{B}}|T_{\text{cold}}|$ from the cold one, and releases mechanical energy $(S_2 - S_1)k_{\text{B}}(T_{\text{hot}} - T_{\text{cold}}) = (S_2 - S_1)k_{\text{B}}(T_{\text{hot}} + |T_{\text{cold}}|)$. The case $S_2 < S_1$ leads to the opposite.

However, can an adiabatic process cross the border $\beta = \infty$, or not?

4d1 Example. $(\Omega, \mu) = (\mathbb{R}, \gamma^1)$ as in Sect. 1f (see also 3a2); $x = -\beta h$, $u = hx = -\beta h^2$, $S = -\frac{1}{2}x^2 = -\frac{1}{2}\beta^2 h^2$. An adiabatic process at $S = \text{const} \neq 0$ cannot cross $\beta = \infty$.

4d2 Example. $(\Omega, \mu) = (\mathbb{R}, \gamma^1)$ again; x_t must be constant in any adiabatic process. Let $x_t = -1$ and $h_t = 2t - 1$ for all $t \in [0, 1]$. Then $\beta_t = 1/h_t = 1/(2t - 1)$ is infinite at $t = 0.5$. Does it make any sense physically?

We know that this system is a high-temperature approximation to a spin system (recall 3a3). Thus, we turn to spin 1/2 (see 3a3, 3c4, 4b3). Again, x_t must be constant in any adiabatic process; but now $x_t = -\tanh \beta_t h_t \in (-1, 1)$. We choose some $\beta_0 \in (0, \infty)$, let $x_0 = -\tanh \beta_0$, $x_t = x_0$ for all t, $h_t = 2t - 1$ again, and $\beta_t = \beta_0/h_t = \beta_0/(2t - 1)$. It is quite feasible: magnetic field changes its sign, while spins do not change. The temperature crosses 0, and β_t crosses infinity. Why not, really?

We reconsider the definition of quasistatic process given in Sect. 3a, as follows. Functions $t \mapsto h_t$ and $t \mapsto \beta_t h_t$ are assumed to be piecewise smooth, but $t \mapsto \beta_t$ may go to infinity at finitely many points; at every such point we assume that $h_t = 0$ but $\frac{\mathrm{d}}{\mathrm{d}t} h_t \neq 0$, and $\beta_t h_t$ has a nonzero limit.

Now "Case 3" is possible.

Strangely enough, in this situation negative temperatures are treated as colder than zero. "Never say never"...

4e Finite reservoirs

In Sect. 4d the temperature of a reservoir was constant. Now we treat a reservoir as another system that fits into our general framework. The original system will be called "small".

An isothermal process in the small system is now replaced with an adiabatic process in the combined system: the small system plus a reservoir (either cold or hot).

We restrict ourselves to positive temperatures and a heat engine.

The small system receives from the hot reservoir some heat and some entropy. Then it sends this entropy to the cold reservoir, with a part of the heat. And so on. In the end, both reservoirs are of the same, intermediate temperature; their total entropy is unchanged; and their total energy is decreased by the converted energy.

4e1 Exercise. Let the hot reservoir be an ideal gas in a finite-volume container, with no potential, initially at a temperature T_{hot}, and the cold reservoir — also an ideal gas, of the same number of particles and the same

container volume, also with no potential, initially at a temperature T_{cold}. Show that

$$\text{converted energy} = \frac{3}{2} k_{\text{B}} \big(\sqrt{T_{\text{hot}}} - \sqrt{T_{\text{cold}}}\big)^2 n \,,$$
$$\text{efficiency} = \frac{\sqrt{T_{\text{hot}}} - \sqrt{T_{\text{cold}}}}{\sqrt{T_{\text{hot}}}} \,.$$

4f Hints to exercises

4a1: recall 3d5 and the formula for $S(x)$ given after (3c3).

4e1: the intermediate temperature is $\sqrt{T_{\text{hot}} T_{\text{cold}}}$, since the entropy is linear in the logarithm of the temperature.

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