

Statistical Mechanics 2026.2

Referee exercise — practice (Modules I–II): key

Attempt the practice sheet before reading this.

How to use this key. Each of the four defects is quoted below in the order in which it appears in the draft, then diagnosed and repaired. When you compare with your own answer, start with the diagnosis. Locating the sentence is the easy step, and the largest share of the credit for each defect goes to naming what went wrong: the hypothesis that was dropped, the limit that was left unstated, or the kind of statement that was misidentified. A repair with the right formula and the wrong status earns only part of the credit. Flagging a correct statement costs points, so each entry also says which nearby statements are correct, and the last section explains the two statements in §4 that were placed there because they look wrong.

	In the draft	Defect	In the notes
1	§1, Eq. (1)	Carnot’s efficiency claimed for every engine	Secs. 1.2.3, 1.3.3
2	§2, last two sentences	Vanishing entropy claimed for every system	Sec. 1.7, Ex. 1.7
3	§3, last sentence	Euler and Gibbs–Duhem credited to the first law	Sec. 1.4.2, Ex. 1.4
4	§5, third sentence	The minimum of F derived from its definition	Sec. 1.5
—	§4	Two correct statements	Sec. 3.2, Ex. 3.1

1. Carnot’s efficiency claimed for every engine

Locate. Draft §1, Eq. (1): “Carnot’s analysis shows that the efficiency of any engine operating between these two reservoirs is” $\eta = 1 - T_c/T_h$.

Diagnose. Carnot’s theorem, as we proved it in Sec. 1.2.3, is a statement about reversible engines: all of them, working between the same two reservoirs, share one efficiency, and that common value is the one in Eq. (1). The draft has dropped the word *reversible*. This is a missing hypothesis in its plainest form, and without it the claim is false. For an arbitrary engine, the Clausius inequality of Sec. 1.3.3 applied to a single cycle gives

$$\frac{Q_h}{T_h} - \frac{Q_c}{T_c} \leq 0,$$

with equality only when the cycle produces no entropy. Since $\eta = 1 - Q_c/Q_h$, this is the bound $\eta \leq 1 - T_c/T_h$, and every irreversible engine falls strictly below the Carnot value. Note that the two-engine argument of Sec. 1.2.3 leads to the same bound, because only the engine that is run backward needs to be reversible.

Repair. Every engine operating between two reservoirs satisfies $\eta \leq 1 - T_c/T_h$, with equality if and only if it is reversible. *Status: exact.*

Correct nearby. The rest of §1 is right. The argument never refers to the working substance, and that independence is precisely what allows the reversible efficiency to define the absolute temperature scale.

2. Vanishing entropy claimed for every system

Locate. Draft §2, last two sentences: “in the limit $T \rightarrow 0$ the entropy of any system tends to zero. The third law therefore fixes the zero of entropy absolutely, which is what makes tabulated absolute entropies meaningful.”

Diagnose. In the form stated in Sec. 1.7, the third law says that the entropy of a system in equilibrium approaches a constant as $T \rightarrow 0$. Statistical mechanics identifies that constant: for a ground state of degeneracy g_0 ,

$$S(0) = k_B \ln g_0,$$

which vanishes only when the ground state is unique. The draft has taken a result that holds in one case, $g_0 = 1$, and stated it for every system. Exercise 1.7 shows how $S(T)$ approaches this value when the first excited level lies a gap Δ above the ground state.

What survives in general is a statement about the entropy density. If g_0 grows more slowly than exponentially with N , the residual term is subextensive and $S/N \rightarrow 0$ in the thermodynamic limit. If the number of ground states grows exponentially with N , the residual entropy is extensive and the density survives as well. Ice is the classic instance. Pauling counted the ways the protons can be arranged in the ice lattice and obtained a residual entropy of $R \ln(3/2)$ per mole, close to the discrepancy Giauque and Stout found between the calorimetric and spectroscopic entropies of water. In ice the proton disorder is also frozen in, which is why the equilibrium condition in the statement of the third law matters. The same example settles the draft's final clause: an entropy obtained by integrating C_P/T upward from low temperature is an absolute entropy only when the residual term is zero or has been accounted for.

Repair. As $T \rightarrow 0$ the equilibrium entropy tends to $k_B \ln g_0$, where g_0 is the ground-state degeneracy. *Status: exact.* The entropy density vanishes, $S/N \rightarrow 0$, when g_0 grows subexponentially with N . *Status: thermodynamic-limit.*

Correct nearby. The clause “the accessible region of phase space shrinks” is a fair description of cooling. The error lies in the conclusion drawn from it.

3. Euler and Gibbs–Duhem credited to the first law

Locate. Draft §3, last sentence: “Both relations follow from the first law together with the definitions of the conjugate variables, and so hold for any thermodynamic system whatever.”

Diagnose. Euler's relation, Eq. (3) of the draft, comes from Euler's theorem on homogeneous functions, so it requires

$$E(\lambda S, \lambda V, \lambda N) = \lambda E(S, V, N)$$

for every $\lambda > 0$. That is the precise content of extensivity, and it is an independent assumption about the system. The first law records energy conservation as $dE = T dS - P dV + \mu dN$ and places no constraint on how E scales when the system is enlarged. Note that the draft states the assumption correctly two sentences earlier, where it says that E , S , V and N are all extensive, so its last sentence contradicts the paragraph it closes. Pointing out that contradiction is already a full diagnosis. The assumption fails when the interactions are long-ranged: the gravitational energy of a self-gravitating body at fixed density scales as $N^{5/3}$, and Eq. (3) no longer holds. Exercise 1.4 asks you to locate the step that fails in that case.

Repair. For an additive system with short-range interactions, $E(S, V, N)$ is homogeneous of degree one, and then $E = TS - PV + \mu N$ and $S dT - V dP + N d\mu = 0$. *Status: exact, conditional on extensivity.*

Correct nearby. The derivation in §3 is right, and so is the clause asserting extensivity. Differentiating Eq. (3) and subtracting the first law does give the Gibbs–Duhem relation.

4. The minimum of F derived from its definition

Locate. Draft §5, third sentence: “This is immediate from the definition: equilibrium maximises the entropy, and F carries S with a minus sign, so whatever maximises S must minimise F .”

Diagnose. This is the hardest of the four, because the argument fails at three levels and a complete diagnosis names all of them. The first is elementary. At fixed (T, V, N) the system exchanges energy with the bath, so E changes along with S , and maximising S alone says nothing about $E - TS$. The second concerns which entropy is maximised. The entropy principle applies to an isolated system, and here the isolated system is the system together with its reservoir. The entropy of the system by itself would keep growing as it drew energy from the bath, and it is the loss of reservoir entropy that stops this.

The third is the content of the minimum principle itself. In Sec. 1.5 we derived it from the entropy of system plus reservoir, expanding the reservoir entropy to second order in the energy ΔE that the system takes from it,

$$\Delta S_{\text{tot}} = -\frac{\Delta F}{T} - \frac{(\Delta E)^2}{2T^2 C_R} + \dots,$$

where T and C_R are the temperature and heat capacity of the reservoir. Maximising the total entropy therefore coincides with minimising F in the limit $C_R \rightarrow \infty$ of an ideal reservoir, and at finite C_R the quadratic term corrects it. Thus the minimum principle is a theorem about the composite system, and it rests on a limit that the draft never mentions.

Repair. For a system in contact with an ideal reservoir at temperature $T > 0$, equilibrium at fixed (T, V, N) minimises $F = E - TS$, with T the temperature of the reservoir; the system itself need not possess a temperature away from equilibrium. *Status: exact in the ideal-reservoir limit, and a controlled approximation for a large finite reservoir, with the leading correction shown above. The same reservoir accounting gives the minimum of G at fixed (T, P, N) .*

Reading the draft as a whole. Note that the condition $T > 0$ in the repair carries weight. It enters through the factor $-1/T$ in the entropy accounting, and the draft’s own §4 has just reminded the reader that a bounded spectrum admits negative temperatures. For a normalisable negative-temperature Gibbs state the extremum of the free energy is a maximum, as Sec. 1.5 points out, so the draft’s closing claim that the argument “goes through for any system placed in contact with a reservoir” also needs this qualification. An answer that connects §5 back to §4 has read the draft the way a referee reads a paper.

The two correct statements in §4

Both statements in §4 are correct as written. They were placed there because each looks wrong at first reading, and flagging either one would have cost points.

The width of the energy shell. The draft says that changing ΔE “shifts $\ln \Omega$ by a term of order $\ln N$, which is negligible beside the extensive part.” As noted in Sec. 3.2, when the density of states varies slowly across the shell the width enters only through an additive term, so that replacing ΔE by $c \Delta E$ shifts $\ln \Omega$ by $\ln c$. Moving the width anywhere between a microscopic energy scale and the total energy of the system therefore changes $\ln \Omega$ by at most a term of order $\ln N$, while the extensive part is of order N . *Status: thermodynamic-limit.*

Negative temperature. The draft says that for N two-level units $\partial S / \partial E$ “turns negative once more than half the units are excited”. With m units excited and $E = m\epsilon$, the shell count is the binomial coefficient $\binom{N}{m}$, and Stirling’s approximation gives

$$\frac{1}{T} = \frac{k_B}{\epsilon} \frac{\partial}{\partial m} \ln \binom{N}{m} \simeq \frac{k_B}{\epsilon} \ln \frac{N-m}{m},$$

which is negative for $m > N/2$. The sign change survives without Stirling’s approximation, since $\ln \binom{N}{m+1} - \ln \binom{N}{m} = \ln[(N-m)/(m+1)]$ is negative as soon as $m > (N-1)/2$. This is Exercise 3.1, and it is a genuine consequence of a bounded spectrum. *Status: model-specific exact result.*

Note that the statement relies on the shell entropy, which is the one the draft uses. Sec. 3.2 points out that the shell count and the cumulative volume $\Sigma(E)$ can give different entropies for bounded spectra near an entropy maximum, and with $k_B \ln \Sigma$ the temperature of this system stays positive at every filling. Raising that point is good refereeing, and the draft’s statement remains correct as written.