

Statistical Mechanics 2026.2
Referee exercise — practice (Modules I–II)

Not graded. Allow yourself 40 minutes and work without the notes.

A key will be posted separately.

Why this exists. Part A of Assessment 1 is worth 40 of 100 points and asks you to do something you have not yet been asked to do in writing. This sheet is that task, at full scale, on material from the same two modules but with different content. Nothing here is collected.

Instructions. A colleague has asked you to comment on the draft section below before it is submitted. It is competently written and most of it is correct, but it contains **exactly four substantive defects**: statements that are wrong, or that are presented as having a stronger status than they actually possess.

For each defect you find:

- (a) **Locate** it — quote the sentence or equation number;
- (b) **Diagnose** it — say precisely what is wrong, and name the assumption, limit, or approximation that has been misused or hidden;
- (c) **Repair** it — give the corrected statement together with its status: *exact, thermodynamic-limit, controlled approximation, mean field, model-specific exact result, or heuristic*.

Not everything that looks unusual is wrong. Flagging a correct statement costs points on the real paper, so justify what you flag.

Draft: Engines, extensivity, and the thermodynamic limit

1. Carnot's theorem and the absolute scale. Let an engine work in a cycle between reservoirs at temperatures $T_h > T_c$, absorbing heat Q_h from the hot one and rejecting Q_c to the cold one. Carnot's analysis shows that the efficiency of any engine operating between these two reservoirs is

$$\eta = 1 - \frac{T_c}{T_h}. \quad (1)$$

The argument nowhere mentions the working substance. That independence is what allows Eq. (1) to be used in reverse, as the *definition* of the absolute temperature scale, with no reference to any particular thermometric material.

2. Entropy and the third law. Applying Eq. (1) to a reversible cycle decomposed into infinitesimal Carnot cycles gives $\oint \delta Q_{\text{rev}}/T = 0$, so that

$$S(B) - S(A) = \int_A^B \frac{\delta Q_{\text{rev}}}{T} \quad (2)$$

is path-independent and defines a state function. As the temperature is lowered, the accessible region of phase space shrinks, and 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.

3. The fundamental relation. Write the fundamental relation as $E(S, V, N)$, with $dE = T dS - P dV + \mu dN$. Since E , S , V and N are all extensive, Euler's theorem gives

$$E = TS - PV + \mu N, \quad (3)$$

and differentiating Eq. (3) and subtracting the first law yields the Gibbs–Duhem relation $S dT - V dP + N d\mu = 0$. Both relations follow from the first law together with the definitions of the conjugate variables, and so hold for any thermodynamic system whatever.

4. Counting microstates. For an isolated system we count the microstates with energy in a shell $[E, E + \Delta E]$. The result is insensitive to the width: changing ΔE shifts $\ln \Omega$ by a term of order $\ln N$, which is negligible beside the extensive part. For a system with a bounded spectrum — N two-level units, say — the density of states rises and then falls, so $\partial S / \partial E$ turns negative once more than half the units are excited, and the microcanonical temperature is negative there.

5. Thermodynamic potentials. A laboratory usually fixes T rather than S , and the Legendre transform $F = E - TS$ trades the inconvenient natural variable for its conjugate. At fixed (T, V, N) , equilibrium minimises F . 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 . The same reasoning applied to $G = E - TS + PV$ gives the minimum principle for G at fixed (T, P, N) , and the argument goes through for any system placed in contact with a reservoir.

A note on what is being asked. The hard part is not spotting that something is false. It is saying *what kind* of thing has gone wrong: a missing hypothesis, a limit taken outside its range of validity, a theorem mistaken for a definition, or a result that is exact for one model quoted as though it were general. A repair that gives the right formula but the wrong status earns only part of the marks.