

Statistical Mechanics: Entropy, Order Parameters, and Complexity

James P. Sethna

Substantive corrections to the first printing of the second edition

Throughout: Changed inconsistent convention for floating point numbers, from, for example, $6.02 \cdot 10^{23}$ to 6.02×10^{23} .

Section 5.2, changed figures 5.4 and 5.5 to orange and blue atoms, rewrote section appropriately.

Exercise 2.21, "*Lévy flight*", four lines above eqn 2.39, parenthesis in wrong place

$(1/2\sqrt{\pi}) \exp(-x^2/4)$ should become $1/(2\sqrt{\pi}) \exp(-x^2/4)$

Footnote 55, replaced "Oddly..." with "Sometimes...", since the stable multivariate distribution is apparently mainstream. I'm not sure whether I'm the only one doing it wrong.

Exercise 3.16, "*Taste, smell, and μ* ", section around part (c) rewritten. We now assume no energy is exchanged between fluid and receptor except for the binding energy, and also S_f^U should be S_f^B in part (c). Other changes on same page to match the total space.

Exercise 3.19, "*Ideal gas glass*", part (b) and hints in the preceding paragraph. Removed 'Check that you get the same residual entropy using eqn 3.57 for the ideal gas.' (You don't.) Added hints to the preceding paragraph.

Exercise 4.4, "*Jupiter*", footnote 28 absorbed into text for formatting reasons (new LaTeX version). All succeeding footnotes in this chapter are renumbered.

Chapter 5, footnote 23, p. 106, added

" , and Exercise 5.11 for a more precise interpretation of eqn 5.18."

Chapter 5, page 108,

Error in eqn 5.20: S is not divided by h^{3N} , it is shifted by $-3N k_B \log h$. Also, the restriction on $E < H < E + \delta E$ is not appropriate here.

The nonequilibrium entropy then becomes

$$\begin{aligned} S_{\text{nonequil}} &= -k_B \langle \log \rho \rangle = -k_B \int \rho \log \rho \\ &= -k_B \int dP dQ \rho(P,Q) \log \rho(P,Q) - 3 N k_B \log h \end{aligned} \quad (5.20)$$

where the last term³¹ is zero in natural units where $h=1$.

Added a new footnote 31:

³¹ $dP dQ$ has units of h^{3N} , where h is Planck's constant (Section 3.5). ρ has units of $1/h^{3N}$. So the entropy is shifted by $-k_B \log(1/h^{3N}) = -3N k_B \log(h)$ from its value in natural units.

Page 109: Removed footnote 32. Changed the sentence referring to the footnote to ... entropy should increase (Exercises 5.7 and 7.4).

Exercise 5.8, “*The Arnol’d cat map*”, first sentence part (c), reworded to “Calculate the momentum h at which the thin strip, pointing along the expanding eigenvector from part (b), first crosses the line $x = 0$.”

Exercise 5.24, “*Nucleosynthesis and the arrow of time*”, just above part (a), we need to specify the number of ideal gas atoms N .

Exercise 6.18, “*Langevin dynamics*”, fifth line on page 170, ... $F = -p / (m \gamma)$. Added some parentheses after this around $(m \gamma)$ for clarity.

Exercise 6.22, “*FIM for Gibbs*”, fourth line below eqn 6.94, minus sign error in two formulas
 $G(p, \beta) = -k_B T \log(\Gamma) = -(1/\beta) \log(\Gamma(p, \beta))$, so $\log(\Gamma) = -\beta G(p, \beta)$.

Section 7.5, p. 189, eqn 7.50, last subscript below first summation sign (big Sigma) should be k_N not k_n . This is the wrong version:

$$Z_N^{\text{NI, dist}} = \sum_{k_1, k_2, \dots, k_n} e^{-\beta(\varepsilon_{k_1} + \varepsilon_{k_2} + \dots + \varepsilon_{k_N})} = \prod_{j=1}^N \left(\sum_{k_j} e^{-\beta \varepsilon_{k_j}} \right) = Z_1^N. \quad (7.50)$$

Exercise 7.11, “*Phonons on a string*”, last line: $k \rightarrow 0$ not $k \rightarrow \text{infinity}$.

Exercise 7.3, “*Phase-space units and the zero of entropy*”, removed the question about δE ,

(a) Arbitrary zero of the classical entropy. Show that the choice of units in phase space affects the classical entropy per particle.

and added a concluding paragraph:

Quantum statistical mechanics, especially for bound systems (with discrete eigenstates) is intellectually simpler than the classical theory: every eigenstate at a given energy is occupied with equal likelihood. We use the classical theory both because classical chaos naturally motivates ergodicity, and because it is not obvious (but true⁴²) that volume in phase space (divided by h^{3N}) gives the number of quantum eigenstates for large systems.

Exercise 7.11, “*Phonons on a string*”, clarifications and simplifications. We now discuss the total potential and kinetic energy, rather than their densities, and give the mass of the decoupled harmonic oscillators $m = \mu L/2$.

Exercise 7.25, “*Quantum measurement and entropy*”, hint in part (g), we integrate out only \mathbf{x} , since \mathbf{x}' is not there in the trace.

Just before the final paragraph, added a summary:

As ChatGPT summarized for me:

- * The decohered joint state (from Schrödinger evolution and macroscopic amplification) gives rise, when the object is integrated out, to an effective photon density matrix that exactly matches the Born-rule prediction.
- * This derivation requires no stochastic collapse, only unitary entanglement and the inaccessibility of the macroscopic object's microstates.
- * Just as in statistical mechanics, where we integrate over unobservable degrees of freedom to get a free energy or reduced distribution, here we trace out the measuring device to obtain the reduced quantum state.

Exercise 7.27, "*Heisenberg entanglement*", added acknowledgement to Chao-Ming Jian.

Chapter 8, p. 226, first paragraph "thus the equilibrium probability density" changed to "thus the steady-state probability density"

Chapter 8, p. 227, third paragraph "converge to equilibrium" changed to "converge to a unique steady state"

Exercise 9.6, "*Symmetries of waves*", below eqn 9.20, the in-line equation for $g(y)$ is missing a close parenthesis.

Exercise 9.14, "*Sound and Goldstone's theorem*", end of part (c), "about how much will the sound..."

Chapter 10, section 10.3, p. 291:

- Last sentence p. 291: changed
"The correlation function of an uncorrelated system is white noise" (wrong)
to
The correlation function of white noise is a delta function.
- Just after eqn 10.14, changed
The density fluctuations in different boxes are uncorrelated.
to
The density fluctuations in different boxes are uncorrelated (white noise).⁹
- Shifted footnote 11 to new footnote 9, footnote 9 renumbered to 10, footnote 10 renumbered to 11
- This will change six footnote entries, moving 11 to 9 for
\Index{White noise}}
\Index{White noise!ideal gas equal-time correlation function}
\Index{Correlation function!equal-time!ideal gas is white noise}
\Index{Ideal gas!uncorrelated at equal times}
and 9 to 10 for
\Index{White noise!zero correlation length}
\Index{Correlation length!zero for white noise}

Exercise 10.5, “Telegraph noise in nanojunctions”, part (e): The transition matrix P to lowest order is $P_{\mu\nu} \approx \Gamma_{\mu\nu} \Delta t$ for $\mu \neq \nu$. The diagonal elements are what is needed to make the columns sum to one, hence $P_{\mu\mu} = 1 - \sum_{\nu \neq \mu} \Gamma_{\nu\mu} \Delta t$. It is the ratio, not the difference, of the two unmeasured rates that can be determined.

Exercise 10.12, “Liquid Free energy”, part (b): $C(k_m) = \langle |\tilde{\rho}(k_m)|^2 \rangle / L = \dots$

Exercise 10.13, “Quasiparticle poles and Goldstone’s theorem”, part (a): added need to calculate Γ_k .

Exercise 10.19, “Critical Point Response”, part (b), first sentence, removed ?

Chapter 11: “undercool” changed to “supercool” a few times

p. 326:

The critical droplet radius $R_c \propto 1/\Delta T$. If you supercool
It can be tiny for small supercoolings.

Also in index:

\Index{Nucleation!driving force from supercooling}

\Index{Critical droplet!balances surface tension vs. supercooling force}

Exercise 11.1, “Maxwell and van der Waals”, removed the 500 K black curve (which cuts through zero and thus cannot be used for equal area constructions).

Exercise 11.3, “Interfaces and van der Waals”, fixed units for density axis (not molecules/cm³, but moles/cm³), and fixed calculational error in computing curve (used $T=300$ for calculating thermal de Broglie length λ , rather than 373).

Exercise 11.9, “Snowflakes and linear stability”, “undercool” changed to “supercool” XXX times
Hence Δ represents the effects of supercooling (favoring crystal over vapor)
Footnote 38: too large to be absorbed by the supercooling;

Fig. 12.6, caption, “effective magnetization for the liquid-gas critical point” should be $(\rho - \rho_c) + 0.75(1-T/T_c)$.

Exercise 12.29, “The onset of chaos: lowest order RG”, second column line 35, forgot epsilon

$$T[g^* + \epsilon \psi](x) - g^*(x) = \delta \epsilon \psi(x)$$

Section A.2, just above eqn A.15 should read:

$$\text{Because } (d/dt)e^{-i\omega t} = -i\omega e^{-i\omega t}$$

(wrong version had missing minus sign in last exponent).