Partition derivatives, energy fluctuations and heat capacity

GRE undergraduate preparation · local supported objectives

Partition derivatives, energy fluctuations and heat capacity

- Build Z with degeneracies and find level probabilities.
- Get U, F, S and C_V from Z.
- Relate heat capacity to energy **fluctuations** 涨落.
- Analyse the **two-level system** 二能级系统 and its **Schottky peak** 肖特基峰.

The partition function

- Differentiate with the energy levels held fixed.
- For N independent, distinguishable subsystems, $Z_{\text{tot}} = z^N$ and $U_{\text{tot}} = Nu$.

$$Z = \sum_i g_i\, e^{-\beta E_i}, \qquad p_i = \frac{g_i\, e^{-\beta E_i}}{Z}, \qquad U = -\frac{\partial \ln Z}{\partial \beta}$$

Free energy, entropy and heat capacity

- Shifting every level by the same constant shifts U and F by that constant, but leaves the probabilities, S and C_V unchanged.
- Check the conditions before using the result.

$$F = -k_B T \ln Z, \qquad S = k_B(\ln Z + \beta U), \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Energy fluctuations

- So C_V can never be negative.
- For N subsystems, the relative fluctuation $\sqrt{\mathrm{Var}(E)}/U$ shrinks as $1/\sqrt{N}$, which is why large systems have sharp energies.

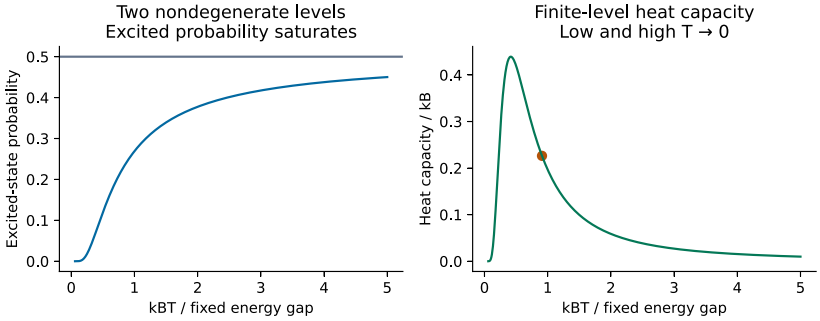
$$C_V = \frac{\mathrm{Var}(E)}{k_B T^2} = \frac{\langle E^2 \rangle - U^2}{k_B T^2}$$

The two-level system

- At low temperature almost nothing is excited, so little heat is absorbed: $C \to 0$.
- At high temperature both levels are almost equally filled: $p_{\text{exc}} \to \frac{1}{2}$, $U \to \Delta/2$, $S \to k_B \ln 2$, and again $C \to 0$.
- In between, C has a single peak near $k_B T \approx 0.42\Delta$: the Schottky peak.

$$p_{\text{exc}} = \frac{1}{1+e^{x}}, \qquad \frac{C}{k_B} = \frac{x^2 e^{x}}{(1+e^{x})^2}$$

Figure: The two-level system



- Identify the axes, units, directions and the stated model.

Worked example: a two-level system at kT = Δ/ln 3

- $z = 1 + \frac{1}{3} = \frac{4}{3}$, so $p_{\text{exc}} = \frac{1}{4}$ and $U = \Delta/4$.
- $\langle E^2 \rangle = \Delta^2/4$, so $\mathrm{Var}(E) = \Delta^2/4 - \Delta^2/16 = \frac{3}{16}\Delta^2$.
- $C/k_B = \mathrm{Var}(E)/(k_B T)^2 = \frac{3}{16}(\ln 3)^2 = 0.23$, the same as the formula above gives.

Worked example: spins in a magnetic field

- The Schottky peak is near $T = 0.42\Delta/k_B = 0.42 \times (1.0 \times 10^{-3})/(8.62 \times 10^{-5}) = 4.9$ K.
- At high temperature the entropy per mole approaches $R \ln 2 = 5.8$ J/K.
- Magnetic cooling works by changing Δ with the field while the entropy stays fixed.

Common errors

- Forgetting the degeneracy g_i in Z.
- Differentiating with respect to T when the formula uses β, without the chain rule.
- Thinking a finite level system's heat capacity grows without limit at high temperature.

Common errors (2)

- Thinking that shifting all levels changes the entropy.
- Allowing a negative heat capacity in the canonical ensemble.

Key terms

- **partition function**: $Z = \sum g_i e^{-E_i/k_B T}$, the sum that normalises the probabilities.
- **free energy**: $F = U - TS = -k_B T \ln Z$.
- **heat capacity**: The heat needed per unit rise in temperature.
- **fluctuation**: Random variation of a quantity about its mean.

Check yourself

- Levels 0 ($g = 1$) and ε ($g = 2$) at $k_B T = \varepsilon / \ln 2$. What is Z?
- Why can the heat capacity in the canonical ensemble never be negative?
- Every level is shifted up by 5 meV. Does the entropy change?