

35.1 Partition derivatives, energy fluctuations and heat capacity

Name: _____ Class: _____ Date: _____

Total: 11 marks

KEY WORDS energy fluctuation • Helmholtz free energy

Objective

Obtain canonical mean energy and free energy from a fixed energy spectrum; Relate energy variance to constant-volume heat capacity with fixed-spectrum conditions; Evaluate entropy and low/high-temperature limits for an original finite-level model. Original public practice; not an ETS paper.

1 Key knowledge and worked examples

Canonical $\beta=1/(k_B T)$, $Z=\sum_i g_i e^{(-\beta E_i)}$, $U=-\partial \ln Z / \partial \beta$. Hold the energy spectrum fixed during derivatives; independent distinguishable subsystems have $Z_{\text{total}}=z^N$.

$F=-k_B T \ln Z$ and $S=k_B(\ln Z + \beta U)$. A constant common energy offset shifts U/F but preserves probabilities, S and C . Mean energy and heat capacity have different units.

$\text{Var}(E)=\partial^2 \ln Z / \partial \beta^2$. With fixed spectrum at fixed N, V , $C_V = \text{Var}(E)/(k_B T^2)$, or $C_V/k_B = \beta^2 \text{Var}(E)$. Independent variances add; relative fluctuations decrease for large N .

For nondegenerate levels $0, \Delta$, $x=\Delta/(k_B T)$: $p_{\text{exc}}=1/(1+e^x)$, $u=\Delta p_{\text{exc}}$, $C/k_B=x^2 e^x/(1+e^x)^2$. C vanishes at both temperature extremes; S tends from zero to $k_B \ln 2$.

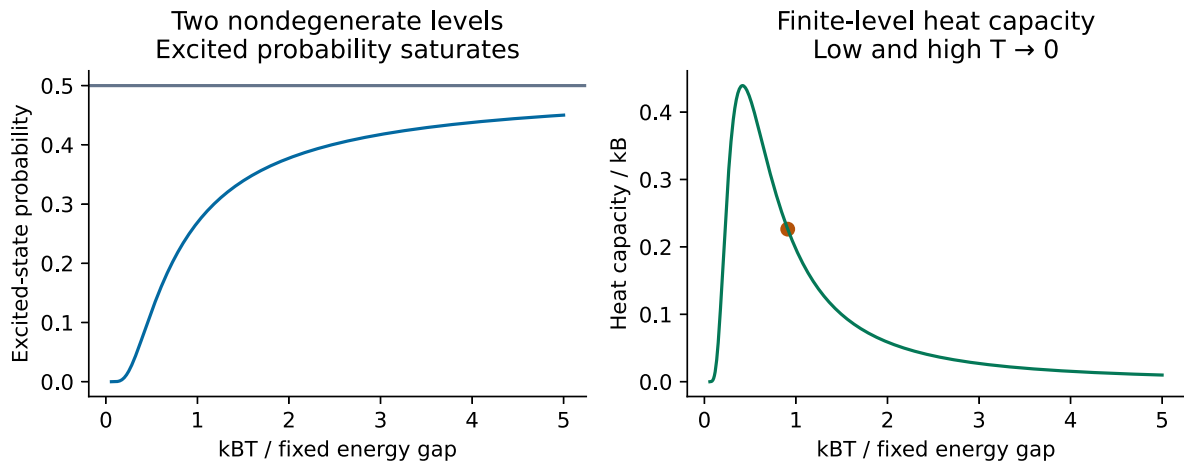
■ Worked method

Hold the two energy levels 0 and Δ fixed when differentiating the partition function

$$Z = 1 + e^{-\beta \Delta}, \quad U = -\partial_{\beta} \ln Z = \frac{\Delta}{1 + e^{\beta \Delta}}.$$

$$\text{Var}(E) = \partial_{\beta}^2 \ln Z = \frac{\Delta^2 e^{\beta \Delta}}{(1 + e^{\beta \Delta})^2}, \quad C_V = \text{Var}(E)/(k_B T^2).$$

At $\beta \Delta = \ln 3$, excited probability is $1/4$, mean energy $\Delta/4$, variance $3\Delta^2/16$ and $C_V/k_B = 3(\ln 3)^2/16 = 0.2263$. Degeneracy, if present, belongs in Z before differentiation.



2 Practice

2.1 Two nondegenerate levels have energies 0 and fixed Δ . At $\Delta/(kBT)=\ln 4$, excited probability is: [1]

- A. $1/4$
- B. $1/5$
- C. $4/5$
- D. $\ln 4$
- E. $1/2$

2.2 A constant temperature-independent energy ε is added to every state. Which quantity stays unchanged? [1]

- A. Mean energy U
- B. Free energy F
- C. Entropy S
- D. Every energy eigenvalue
- E. Z itself

2.3 For equally probable energies 0 J and 2 J, energy variance is _____ J^2 . Show your relation and units. [2]

