

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

$F=-kBT \ln Z$ and $S=kB(\ln Z+\beta U)$. 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 , $C_V=\text{Var}(E)/(kBT^2)$, or $C_V/kB=\beta^2 \text{Var}(E)$. Independent variances add; relative fluctuations decrease for large N .

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

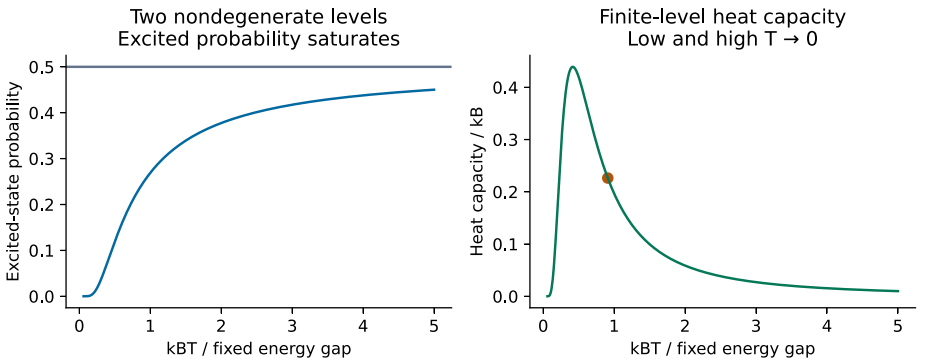
■ Worked method

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]

Solutions

2.1 Answer: B. $p_{\text{exc}} = 1/(1 + e^x) = 1/(1 + 4) = 1/5$.

Compare the rejected options: $1/4$; $4/5$; $\ln 4$; $1/2$. Use the stated model and conditions.

2.2 Answer: C. All probabilities are unchanged. U and F shift by ε and Z gains $e^{-\beta\varepsilon}$, but entropy and heat capacity remain the same.

Compare the rejected options: Mean energy U; Free energy F; Every energy eigenvalue; Z itself. Use the stated model and conditions.

2.3 1. Mean = 1 J and second moment = $2 J^2$, so variance = $2 - 1^2 = 1 J^2$.

2.4 True. Energy approaches $\Delta/2$ and its temperature derivative tends to zero; a finite spectrum saturates.

3.1 Write $x = \beta\Delta$, $w = ge^{-x}$, $z = 1 + w$ and $Z = z^N$. $U = N\Delta w/(1 + w)$; $\text{Var}(E) = N\Delta^2 w/(1 + w)^2$. $C = Nk_B x^2 w/(1 + w)^2$. At high T every complete state is equally likely, so $S \rightarrow Nk_B \ln(1 + g)$. C tends to zero at low T and at high T. Award Z, U, variance/C, entropy and limits. This is not a quantum-gas state-counting model.