

Partition derivatives, energy fluctuations and heat capacity

GRE · GRE Subject Test · GRE Physics

A thermal energy gap can keep heat capacity small at both low and high temperatures, even while the excited-state probability keeps increasing.

Prerequisites: 20.

- 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

Differentiate a fixed spectrum

For a system exchanging energy with a bath at T while N and V remain fixed, let $\beta = 1/(kBT)$. Sum $Z = \sum_i g_i \exp(-\beta E_i)$ over energy levels with their degeneracies. Level probability is $g_i \exp(-\beta E_i)/Z$; mean energy U is the probability-weighted energy sum. Differentiating a temperature-independent spectrum gives $U = -\partial \ln Z / \partial \beta$. Keep the energy gap and degeneracies fixed during the derivative. Writing $\Delta = kBT \ln 3$ to describe one evaluation temperature must not be read as making Δ change with T . For N independent distinguishable identical two-level subsystems, $Z_{\text{total}} = z^N$ and $U_{\text{total}} = N u$. Indistinguishable particles and interactions need their own state counting rather than this product assumption.

Identify the thermodynamic quantity

The Helmholtz free energy is $F = -kBT \ln Z$. Canonical entropy follows from $S = kB(\ln Z + \beta U)$, equivalently $-kB \sum_j p_j \ln p_j$ over individual microstates. Constant-volume heat capacity is $C_V = (\partial U / \partial T)_{V,N}$. These quantities carry different units and describe different derivatives. Adding a constant energy offset ε to every state multiplies Z by $\exp(-\beta \varepsilon)$, increases U and F by ε , and leaves probabilities, entropy and heat capacity unchanged when ε is independent of T . A negative chosen mean energy is therefore not evidence of a negative heat capacity. Use the same energy reference in the probabilities and thermodynamic expressions.

Relate fluctuations and response

The second β derivative of $\ln Z$ gives variance $\text{Var}(E) = \langle E^2 \rangle - U^2$. For the same fixed-spectrum canonical model, $C_V = \text{Var}(E)/(kBT^2)$, so $C_V/kB = \beta^2 \text{Var}(E)$. Nonnegative variance implies nonnegative C_V within these conditions. The denominator includes kB , not kB^2 , when heat capacity retains its ordinary J/K units. This fluctuation formula concerns the canonical energy distribution; it does not say each particle

has exactly the mean energy. For independent subsystems variances add, while means add too. Relative energy fluctuations typically shrink like $1/\sqrt{N}$ when the mean and per-subsystem variance remain finite and nonzero.

Test finite-level temperature limits

For one ground state at $E=0$ and one excited state at fixed $E=\Delta>0$, put $x=\Delta/(kBT)$. Then $z=1+\hat{e}(-x)$, $p_{\text{exc}}=1/(1+\hat{e}x)$, $u=\Delta p_{\text{exc}}$ and $C/k_B=x^2\hat{e}x/(1+\hat{e}x)^2$. At low T , excitation and heat capacity vanish exponentially. At high T , p_{exc} tends to one half and energy saturates, so heat capacity tends to zero again. Entropy rises from zero for the unique ground state toward $k_B \ln 2$ as the two states become equiprobable. The resulting finite-temperature heat-capacity peak is specific to the finite-level model; it is not the constant classical oscillator value. Ground-state degeneracy or additional levels would change the limiting entropy and temperature response.

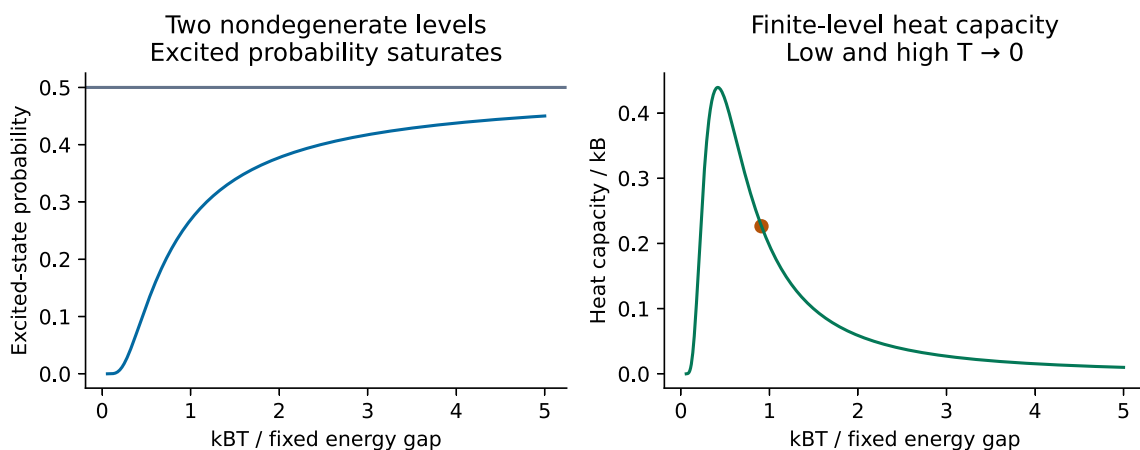
Worked method

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.



Partition derivatives, energy fluctuations and heat capacity: original GRE teaching diagram.

Check conditions and vocabulary

Hold Δ fixed when differentiating, include degeneracies in Z , and use energy variance rather than the square of mean energy in the heat-capacity formula.

energy fluctuation : Canonical spread of energy about its ensemble mean, quantified by the energy variance.

Helmholtz free energy: Thermodynamic potential $F=U-TS$, equal to $-kBT \ln Z$ for the canonical ensemble.