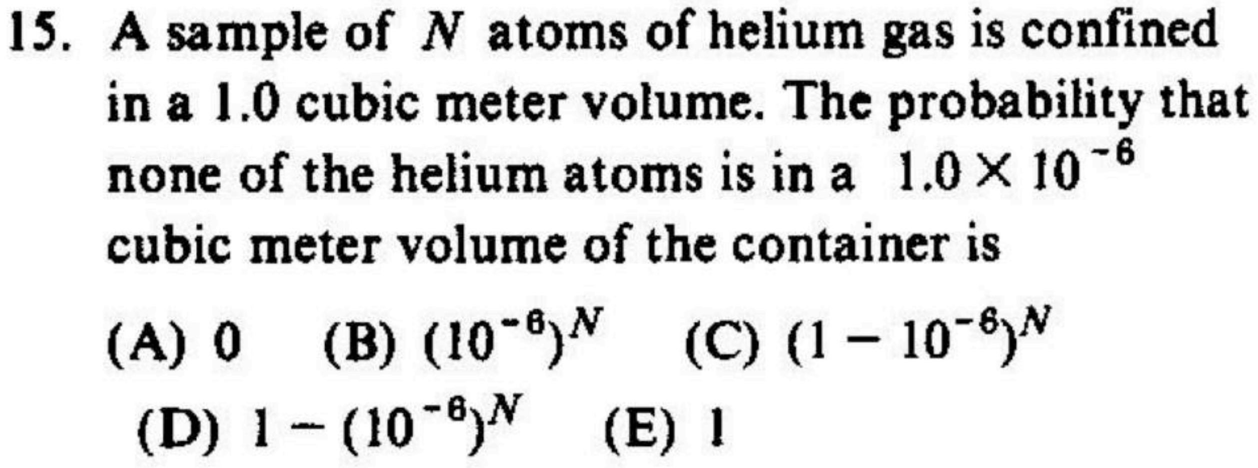
Statistical Mechanics Summary

- Maxwell-Boltzmann probability weights
- Partition Function
- Calculating expectation values using the partition function
  - Equipartition theorem
- Entropy
- Quantum statistical mechanics
  - Bosons, Fermions, classical particles
  - Blackbody radiation
- Additional concepts
  - **Free electron gas**
  - **Diffusion equation**
  - Heat capacity and response functions
  - Blackbody radiation
  - Bose-Einstein condensation

Probabilistic Thinking

- An example problem:



15. A sample of N atoms of helium gas is confined in a 1.0 cubic meter volume. The probability that none of the helium atoms is in a 1.0×10^{-6} cubic meter volume of the container is

(A) 0 (B) $(10^{-6})^N$ (C) $(1 - 10^{-6})^N$

(D) $1 - (10^{-6})^N$ (E) 1

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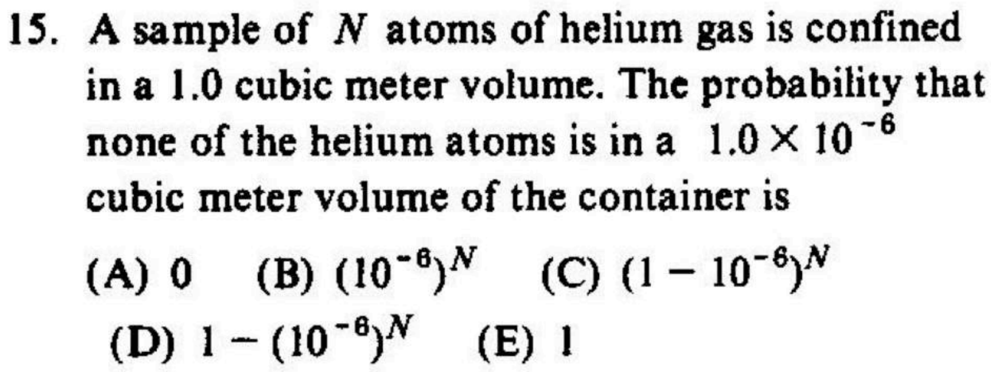

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- Just need to consider the probability of placing all N particles outside the tiny excluded volume
- P(Outside) = 1-P(Inside) = $1\text{-}10^{-6}$
- Placement of each of the N atoms is independent of the placement of the others
- => P(Outside)^{N} = $(1\text{-}10^{-6})^N$
- Alternatively: take limits! Should the probability be big or small as N approaches infinity?

Probabilistic Thinking

- Classical mechanics is purely deterministic
- Laplace: can perfectly describe everything given enough time
- For many O(10^{23}) degrees of freedom, phase space becomes too complicated to describe exactly
- If we can't describe the system exactly, let's describe it probabilistically
- So we posit:
  - System is constantly exploring phase space, moving from state to state
  - Given that the system has fixed energy, all states with that energy are available to the system
  - The system spends an equal amount of time in each of these states (probabilities of each of these states are identical)

Maxwell-Boltzmann Probability Weights

- What is the probability that the system will be found in a state with energy E?
- Boltzmann weights: $P(E) \propto e^{-E/kT} = e^{-\beta E}$
- Can use Boltzmann weights to find the relative probabilities of being found in two states
- Think of temperature as a parameter that controls the frequency at which the system jumps from a lower energy state to a higher energy state

Maxwell-Boltzmann Probability Weights

- Example problem:

77. An ensemble of systems is in thermal equilibrium with a reservoir for which $kT = 0.025$ eV. State A has an energy that is 0.1 eV above that of state B. If it is assumed the systems obey Maxwell-Boltzmann statistics and that the degeneracies of the two states are the same, then the ratio of the number of systems in state A to the number in state B is

(A) e^{+4}

(B) $e^{+0.25}$

(C) 1

(D) $e^{-0.25}$

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$$P(A) \propto e^{-\beta(E+.1eV)}$$

$$P(B) \propto e^{-\beta(E)}$$

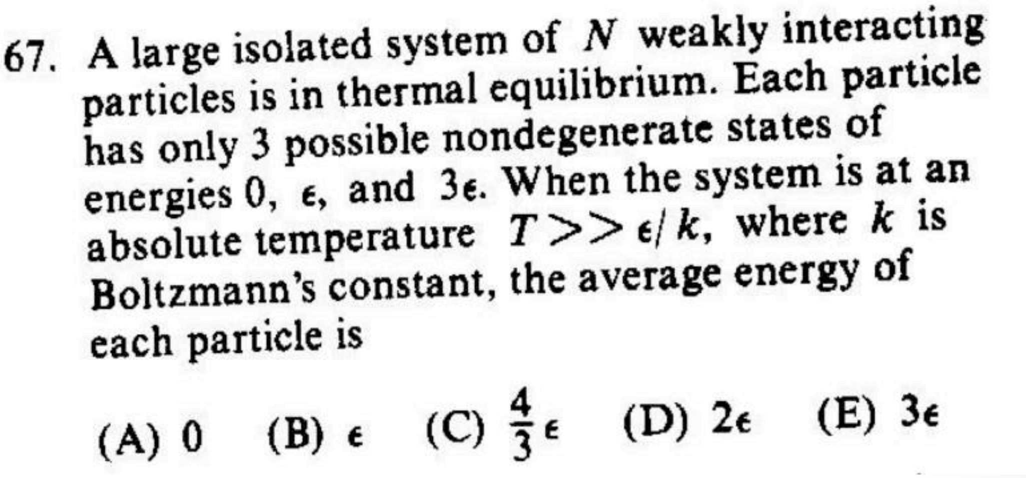
$$P(A)/P(B) = e^{-.1eV/(.025eV)} = e^{-4}$$

Partition Function

- Suppose we know the energy E for each system configuration σ
- Sum MB factors over all possible system configurations {σ}

$$z = \sum_{\{\sigma\}} e^{-\beta E(\sigma)}$$

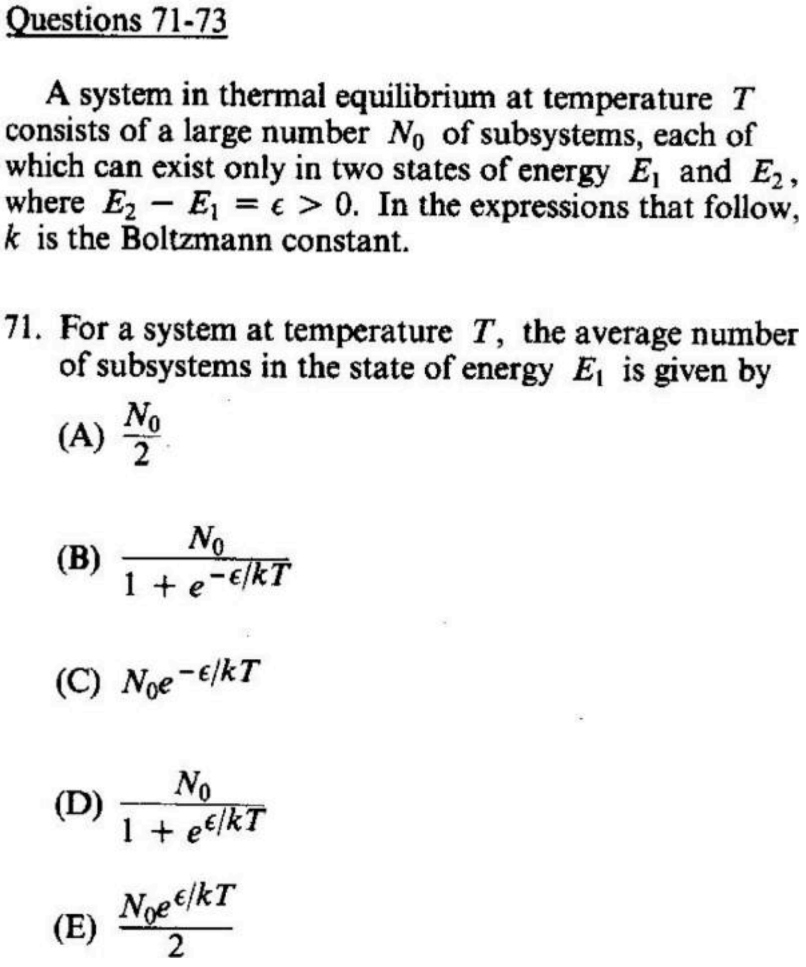
- (Note possibility of degeneracy, where many σ's produce same E)
- Observations: Take limits!
  - kT-> 0
  - kT >> E



67. A large isolated system of N weakly interacting particles is in thermal equilibrium. Each particle has only 3 possible nondegenerate states of energies 0, ϵ, and 3ϵ. When the system is at an absolute temperature $T >> \epsilon/k$, where k is Boltzmann's constant, the average energy of each particle is

(A) 0 (B) ϵ (C) $\frac{4}{3}\epsilon$ (D) 2ϵ (E) 3ϵ

Partition Function



Questions 71-73

A system in thermal equilibrium at temperature T consists of a large number N_0 of subsystems, each of which can exist only in two states of energy E_1 and E_2, where $E_2 - E_1 = \epsilon > 0$. In the expressions that follow, k is the Boltzmann constant.

71. For a system at temperature T, the average number of subsystems in the state of energy E_1 is given by

(A) $\frac{N_0}{2}$

(B) $\frac{N_0}{1 + e^{-\epsilon/kT}}$

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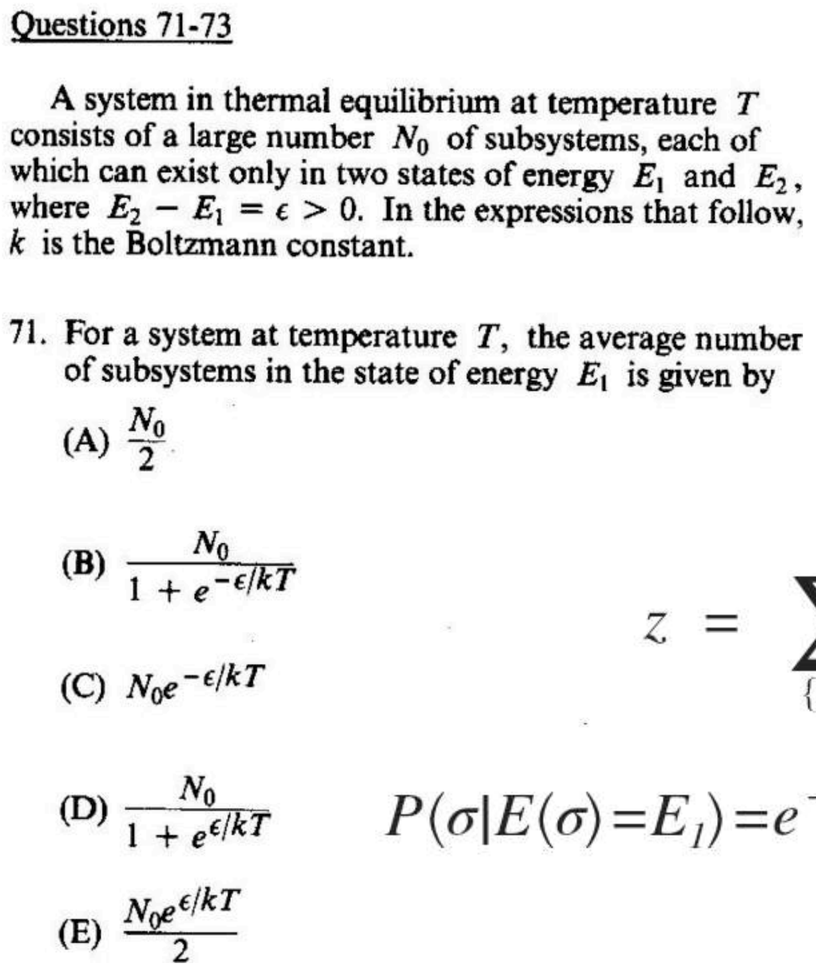
Partition Function



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$$z = \sum_{\{\sigma\}} e^{-\beta E(\sigma)} = e^{-\beta E_1} + e^{-\beta E_2}$$

$$P(\sigma | E(\sigma) = E_1) = e^{-\beta E_1}/z = \frac{e^{-\beta E_1}}{e^{-\beta E_1} + e^{-\beta E_2}} = \frac{1}{1 + e^{-\beta(E_2 - E_1)}}$$

Partition Function

- Contains an incredible amount of information
- We don’t measure z, we measure its moments:
  - Average system energy is found:

$$\langle E\rangle = \sum_{\{\sigma\}} E(\sigma)\, e^{-\beta E(\sigma)}/z \qquad z = \sum_{\{\sigma\}} e^{-\beta E(\sigma)}$$

$$-\frac{\partial}{\partial\beta}\sum_{\{\sigma\}} e^{-\beta E(\sigma)} = \sum_{\{\sigma\}} E(\sigma)\, e^{-\beta E(\sigma)}$$

$$\Rightarrow\ \langle E\rangle = -\frac{\partial}{\partial\beta}\log\sum_{\{\sigma\}} e^{-\beta E(\sigma)} = -\frac{\partial}{\partial\beta}\log z$$

- Question:
  - What is the average height of a single molecule of air with mass m?
  - (Note: Can also answer with dimensional analysis only)

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$$z = \sum_{h} e^{-\beta mgh} \propto \int_{0}^{\infty} e^{-\beta mgh} = \frac{1}{\beta mg}$$

$$\langle E\rangle = mg\langle h\rangle = -\frac{\partial}{\partial(\beta mg)}\log\frac{1}{\beta mg} = \beta mg = \frac{mg}{kT}$$

Heat Capacity and Response Functions

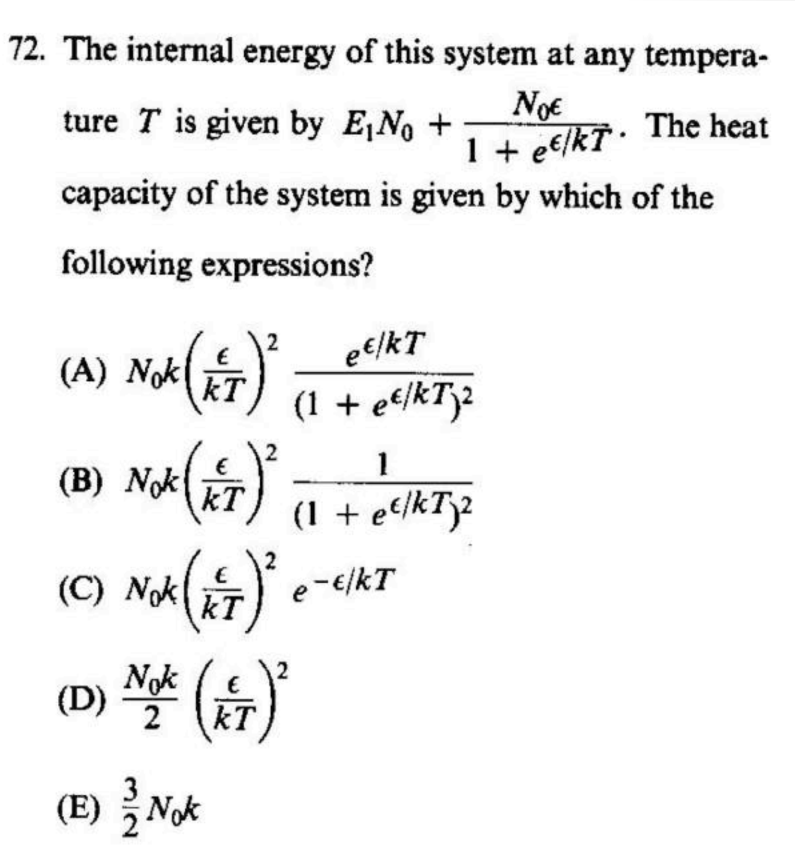
- Response functions measure how a macroscopic property of the system changes when a control parameter is varied
- Calculated using derivatives of the partition function
- Heat capacity: How much energy does it take to raise the temperature of an object?
  - [C] = Joule/Kelvin

$$C = \frac{\partial}{\partial T}\langle E\rangle = k\beta^2\frac{\partial^2}{\partial\beta^2}\log z$$

- Magnetic susceptibility
  - How much does the magnetization change given an applied field?

$$\chi = \frac{\partial}{\partial B}\langle M\rangle = -\frac{\partial^2}{\partial B^2}\log z$$

- Thermal expansion (V vs. T)
- Isothermal compressibility (V vs P)



72. The internal energy of this system at any temperature T is given by $E_1N_0 + \frac{N_0\epsilon}{1+e^{\epsilon/kT}}$. The heat capacity of the system is given by which of the following expressions?

(A) $N_0k\left(\frac{\epsilon}{kT}\right)^2\frac{e^{\epsilon/kT}}{(1+e^{\epsilon/kT})^2}$

(B) $N_0k\left(\frac{\epsilon}{kT}\right)^2\frac{1}{(1+e^{\epsilon/kT})^2}$

(C) $N_0k\left(\frac{\epsilon}{kT}\right)^2 e^{-\epsilon/kT}$

(D) $\frac{N_0k}{2}\left(\frac{\epsilon}{kT}\right)^2$

(E) $\frac{3}{2}N_0k$

Equipartition Theorem

- Each degree of freedom that contributes **quadratically** to the Hamiltonian (momentum, rotation, oscillation) contributes ½ $k_B T$ to the internal energy of the particle (and ½ k_B to the specific heat)
- Derived from Gaussian integral form of expectation values

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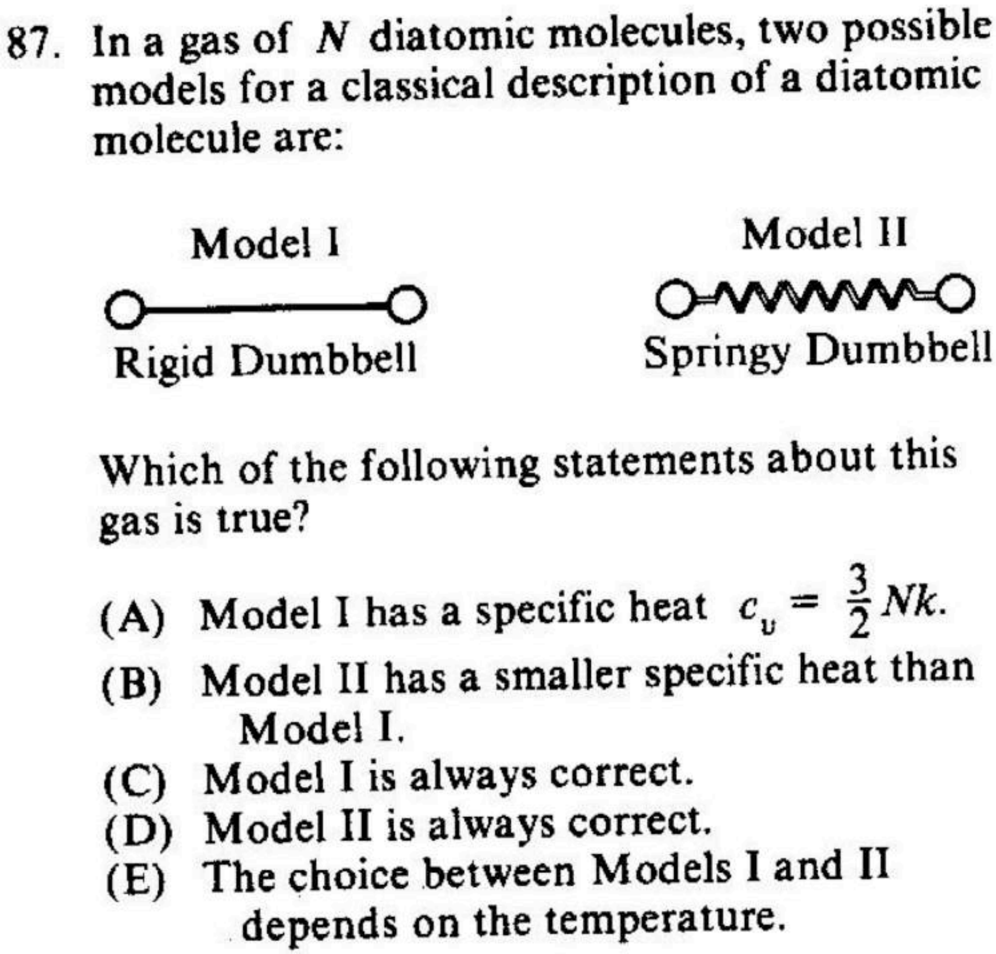
- Consider monatomic (ideal) gas:
    - Molecule may translate only
- Consider diatomic gas:
    - Molecule may translate (3), rotate (2), oscillate (1)
    - Different modes relevant at different temperatures

Equipartition Theorem



87. In a gas of N diatomic molecules, two possible models for a classical description of a diatomic molecule are:

Model I
Rigid Dumbbell

Model II
Springy Dumbbell

Which of the following statements about this gas is true?

(A) Model I has a specific heat $c_v = \frac{3}{2}Nk$.
(B) Model II has a smaller specific heat than Model I.
(C) Model I is always correct.
(D) Model II is always correct.
(E) The choice between Models I and II depends on the temperature.

Equipartition Theorem

A diatomic ideal gas of N particles is trapped on a layer of material, such that the gas molecules are free to move only in two dimensions. What is the C_V of this gas? Assume temperature is too low for the molecule's chemical bond to vibrate.

A. $1/2\ N\ k_B$

B. $N\ k_B$

C. $3/2\ N\ k_B$

D. $2\ N\ k_B$

E. $5/2\ N\ k_B$

Entropy

- Microscopic:
  - Entropy measures disorder and ignorance: How difficult is it to make a prediction?
  - More available states makes it difficult to predict the specific state

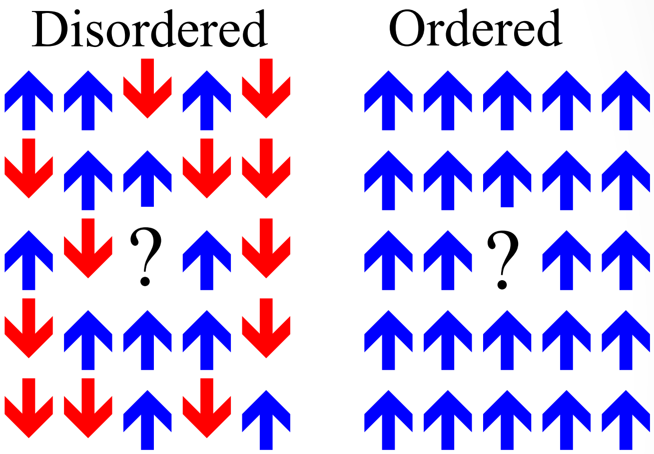
$$S \sim \log \Omega_{\#states}$$

- Macroscopic

$$F = E - TS$$

  - In real world systems, we minimize free energy
  - Maximize entropy as energy is minimized

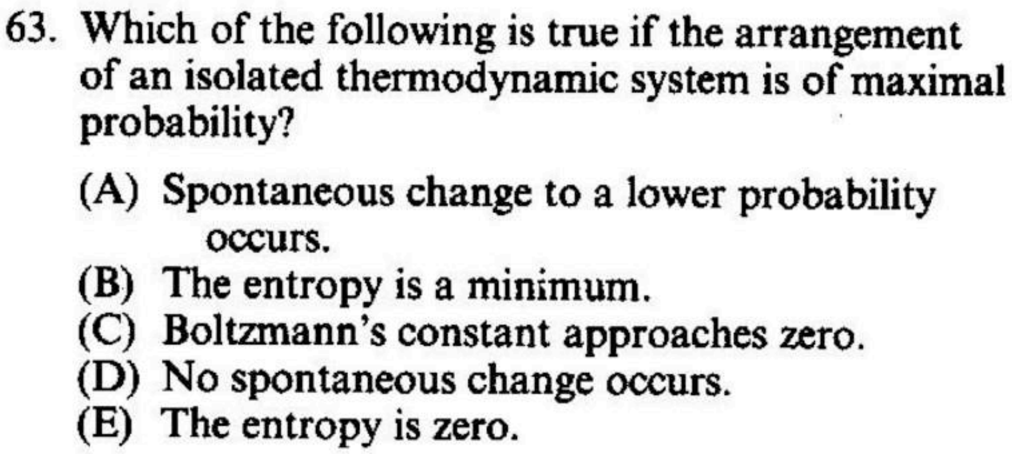
Ising Model Phases:



In which case is the missing spin's state easier to predict?

Entropy: Probabilistic Interpretation

- Entropy is maximized when there is maximal ignorance about the state of the system
  - Macroscopically, the system reaches equilibrium is in the most probable state, which has the largest number of available microstates
  - For systems with many, many degrees of freedom, it becomes vanishingly unlikely that the system will spontaneously switch to a lower-probability, lower-entropy state
- Shannon entropy: $S = -k \sum_{\sigma} p_{\sigma} \log p_{\sigma}$



63. Which of the following is true if the arrangement of an isolated thermodynamic system is of maximal probability?

(A) Spontaneous change to a lower probability occurs.
(B) The entropy is a minimum.
(C) Boltzmann's constant approaches zero.
(D) No spontaneous change occurs.
(E) The entropy is zero.

Entropy: counting states

The three-dimensional harmonic oscillator transitions from the n=1 state to the n=2 state. What is the change in entropy?

A. 0
B. hw
C. k_B
D. k_B log(2)
E. k_B log(3)

Relating Entropy to Partition Function

- Try: plug MB weights into the probabilistic interpretation of entropy
- Results in familiar expression for free energy

$$S = -k \sum_{\sigma} p_{\sigma} \log p_{\sigma}$$

$$S = -k \sum_{\sigma} e^{-\beta E} (\log e^{-\beta E} - \log z)/z$$

$$S = -k(\beta \langle E \rangle + \log z)$$

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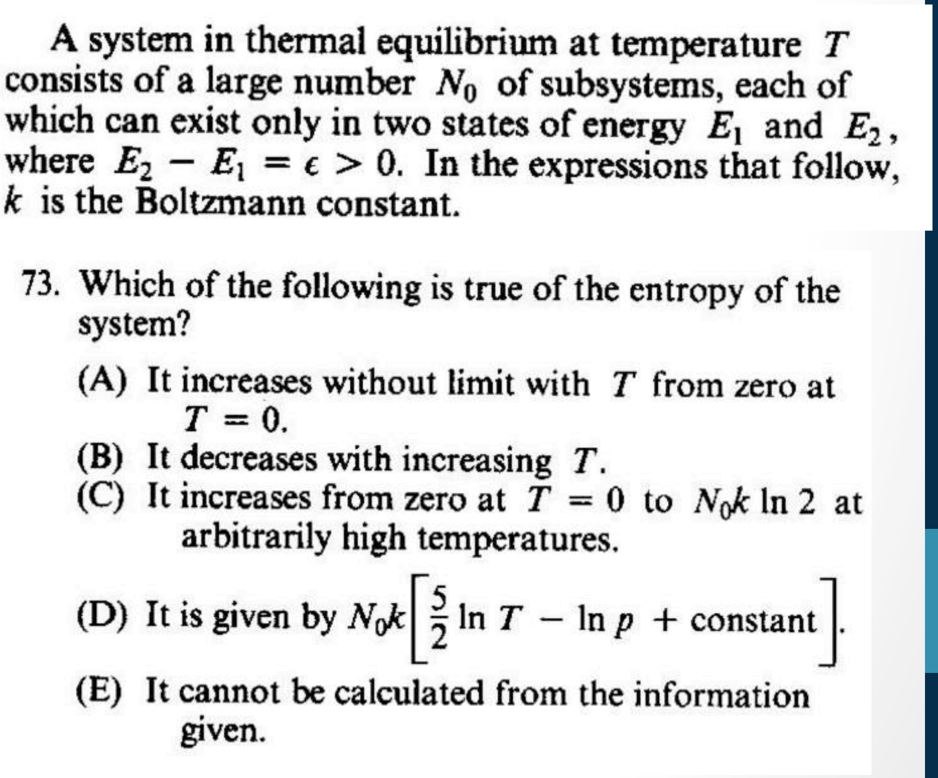

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73. Which of the following is true of the entropy of the system?

(A) It increases without limit with T from zero at $T = 0$.

(B) It decreases with increasing T.

(C) It increases from zero at $T = 0$ to $N_0 k \ln 2$ at arbitrarily high temperatures.

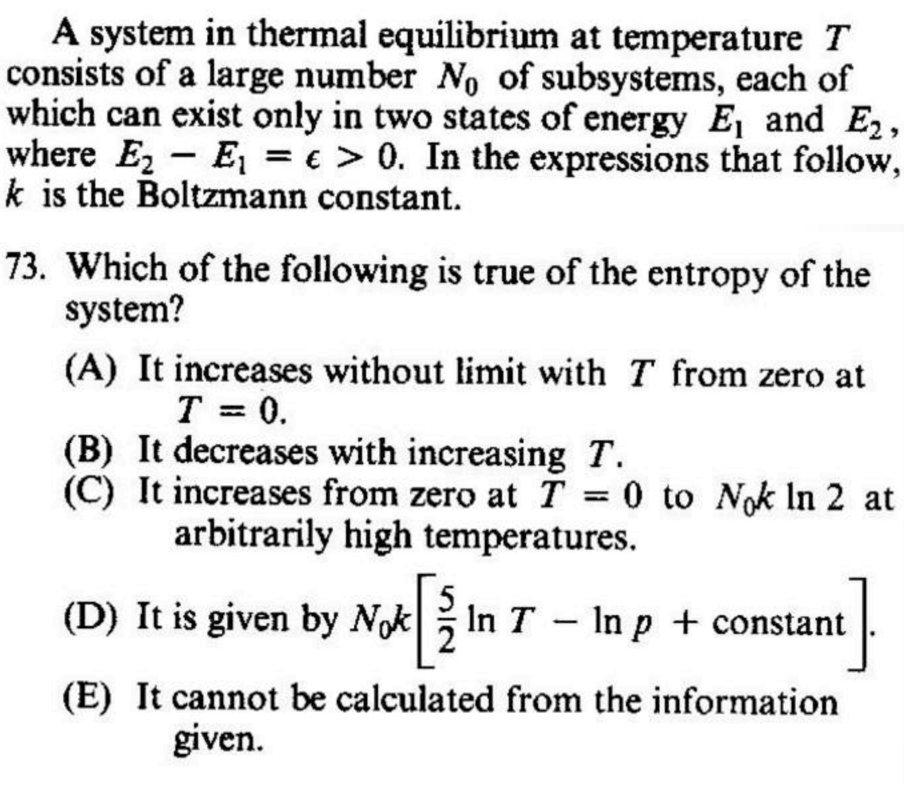
(D) It is given by $N_0 k \left[\frac{5}{2} \ln T - \ln p + \text{constant} \right]$.

(E) It cannot be calculated from the information given.

Relating Entropy to Partition Function

- Calculation:
  - Use: $S = -k(\beta\langle E\rangle + \log z)$
  - As T->∞, β->0
  - Need to calculate z:

$$z=e^{-\beta E_1}+e^{-\beta E_2}\longrightarrow e^0+e^0=2$$



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- Intuition:

(D): is for ideal gases

(B): Higher temperature means higher probability of jumping between states => more disorder and entropy

(A) & (C): For high temperatures, we know all energy states approach equal probability, so there probably a finite cutoff instead of a boundless increase

Quantum Statistical Mechanics

72. Which of the following statements about bosons and/or fermions is true?

(A) Bosons have symmetric wave functions and obey the Pauli exclusion principle.
(B) Bosons have antisymmetric wave functions and do not obey the Pauli exclusion principle.
(C) Fermions have symmetric wave functions and obey the Pauli exclusion principle.
(D) Fermions have antisymmetric wave functions and obey the Pauli exclusion principle.
(E) Bosons and fermions obey the Pauli exclusion principle.

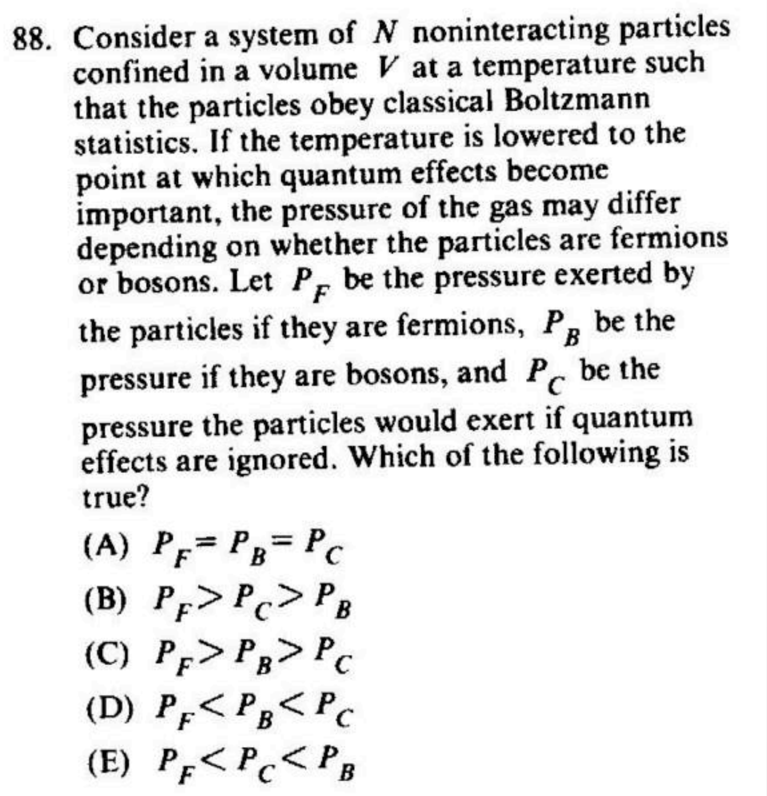
Quantum Statistical Mechanics

- Fermions obey the Pauli Exclusion Principle:
  - No two can occupy the same state at the same time
  - Occupation numbers $n_f = 0$ or 1
  - Creates "degeneracy pressure" in a Fermionic gas
- No restriction on Boson occupation numbers:
  - $n_b = 0, 1,2 ,3,$ etc.
- Average occupation number of states by Bosons and Fermions with energy E:

$$\langle n_E \rangle_{Bosons} = \frac{1}{e^{\beta(E-\mu)} - 1}$$

$$\langle n_E \rangle_{Fermions} = \frac{1}{e^{\beta(E-\mu)} + 1}$$

$$\langle n_E \rangle_{Classical} = \frac{1}{e^{\beta(E-\mu)} + 0} = e^{-\beta(E-\mu)}$$



88. Consider a system of N noninteracting particles confined in a volume V at a temperature such that the particles obey classical Boltzmann statistics. If the temperature is lowered to the point at which quantum effects become important, the pressure of the gas may differ depending on whether the particles are fermions or bosons. Let P_F be the pressure exerted by the particles if they are fermions, P_B be the pressure if they are bosons, and P_C be the pressure the particles would exert if quantum effects are ignored. Which of the following is true?

(A) $P_F = P_B = P_C$

(B) $P_F > P_C > P_B$

(C) $P_F > P_B > P_C$

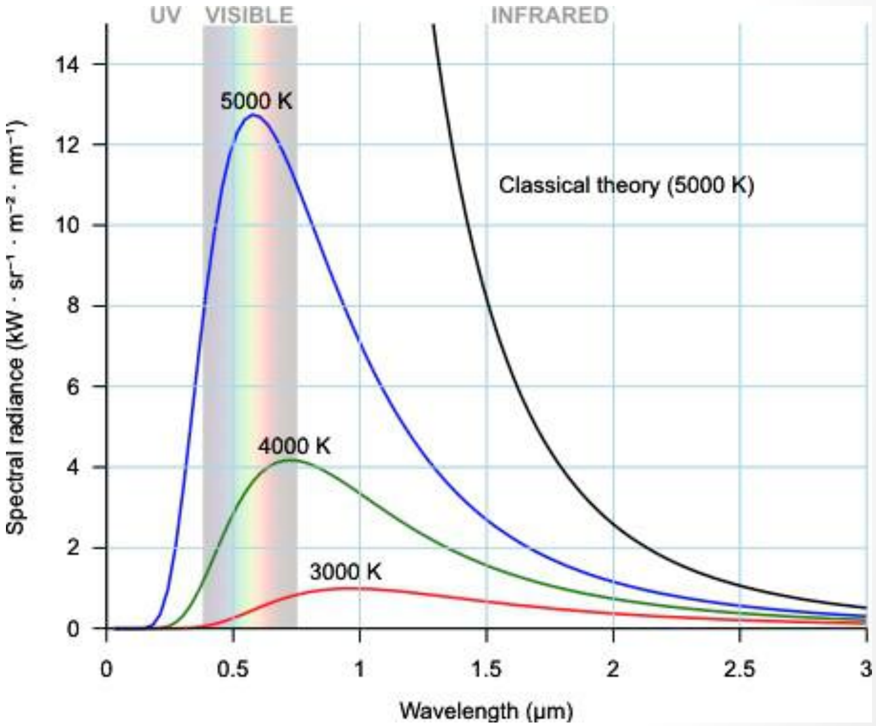
(D) $P_F < P_B < P_C$

(E) $P_F < P_C < P_B$

Blackbody Radiation

- Radiation from a body at thermodynamic equilibrium with its surroundings
- Treats object as a gas of discrete bosonic photons
- Absorbs all incoming photons, emits photons on continuous spectrum
- Examples
  - The Sun
  - Your body in outer space
- Characteristic spectrum (W/m^2/s/steradian)

$$B(\lambda,T)=\frac{2h\nu^3}{c^2}\,\frac{1}{e^{(h\nu/k_BT)}-1}$$



http://en.wikipedia.org/wiki/Black-body_radiation

Rules to Remember

- Scaling of total energy flux (J/m^2/s) vs temperature
  (Stefan-Boltzmann Law)

$$J=\sigma T^4, \qquad \sigma=5.67\times10^{-8}\ Wm^{-2}K^{-4}$$

- Scaling of spectrum peak wavelength vs temperature
  (Wien's Law)

$$\lambda_{max}=bT^{-1}$$