Advanced Thermodynamics

Assignment - 3

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(Q1) Explain how probability is used to describe the state of a physical system in statistical mechanics. what is the physical meaning of assigning probabilities to microstates?

Ans - In statistical mechanics, the state of a system is described probabilistically because we cannot track every particle.
Each microstates has a probability P_i.
Assigning a probability means:

$$P_i = \frac{e^{-\beta E_i}}{Z}, \quad Z = \sum_i e^{-\beta E_i}$$

This expresses our uncertainity about which microstate the system occupies while keeping macroscopic quantities fixed.

physical Meaning: The probability gives the fraction of time that the system spends in that microstate.

(Q2) Define the expectation value of a random variable. How does it relate to the concept of ensemble average in statistical mechanics?

Ans - The expectation value of a random variable X is:

$$\langle X \rangle = \sum_i X_i P_i$$

In statistical mechanics, this is the ensemble average of a physical quantity A:

$$\langle A \rangle = \sum_i A_i P_i$$

Thus, the expectation value and ensemble average are identical - they represent the average over all possible microstates, weighted by their probabilities.

(Q3) Discuss the difference between time average and ensemble average. Under what condition are they expected to be equal?

Ans - Time Average - Average of a property over a long time for one system

$$\overline{A} = \lim_{T\to\infty} \frac{1}{T}\int_0^T A(t)\,dt$$

Ensemble average - Average of the same property across many identical systems at one instant.

$$\langle A \rangle = \sum_i A_i P_i$$

⇒ They are equal when the system is ergodic: the phase-space trajectory of the system (over long times) visits all accessible microstates consistent with conserved quantities so that time fractions equal ensemble probabilities.

(Q4) What is phase space? Explain what a point in phase space represents for a system of N classical particles.

Ans - Phase space is a multidimensional space in which each possible microstate of a physical system is represented by a single point.

→ The complete microscopic state of a system of N particles is specified by:

The positions of all particles: $(x_1, y_1, z_1, x_2, y_2, z_2, \dots, x_N, y_N, z_N)$ & their momenta: $(p_{x_1}, p_{y_1}, p_{z_1}, p_{x_2}, p_{y_2}, p_{z_2}, \dots, p_{x_N}, p_{y_N}, p_{z_N})$

Together these 6N coordinates, define a point in a 6N-dimensional space called phase space.

(Q5) Give one example each of a physical quantity that can be represented by a discrete probability distribution and by a continuous probability distribution.

Ans ⇒ Discrete probability Distribution.

→ No. of particles occupying a particular energy levels (occupation numbers) $\{0, 1, 2, \dots\}$ — we eg: Binomial / Multinomial or Poisson Distribution.

⇒ Continuous Probability Distribution.

→ Kinetic energy or speed of a gas molecule (Maxwell – Boltzmann speed distribution, continuous PDF).

(Q6) A random variable x can take values $\{0,1,2,3\}$ with corresponding probabilities $P(x) = \{0.1, 0.3, 0.4, 0.2\}$.

(a) Calculate the mean, median & mode.

(b) Interpret the mean in terms of the average occupation number of that state.

(c) Interpretation.

The mean value $\langle x \rangle = 1.7$ represents the average occupation number. In an ensemble of identical systems, on average each state is occupied by 1.7 particles. Although the most probable and median occupations are both 2 the mean is slightly lower due to lower-occupation states.

Ans - Given $X \in \{0,1,2,3\}$ with $P(0) = 0.1$, $P(1) = 0.3$, $P(2) = 0.4$
$P(3) = 0.2$.

(a) Mean: $\sum x P(x) = 0(0.1) + 1(0.3) + 2(0.4) + 3(0.4) = \underline{1.7}$

(b) Median :

Cumulative probabilities.

$F(0) = 0.1$, $F(1) = 0.4$, $F(2) = 0.8$, $F(3) = 1.0$

The median (value where cumulative ≥ 0.5) is $\underline{\underline{2}}$

(c) Mode

Most probable value is the one with largest probability :
$\underline{X = 2}$. (since $P(2) = 0.4$ is largest).

(d) Interpretation.

$\langle x \rangle = 1.7$ means the average occupation number per realization is $\underline{\underline{1.7}}$.

Even though the most probable value is 2, lower-probability smaller values reduce the average to $\underline{\underline{1.7}}$.

(Q7) A system has $N = 4$ independent particles, each of which can be in one of two states : 0 (ground) or 1 (excited), with equal probability:

(a) write the probability of finding K particles in excited states.

(b) compute the probabilities for $K = 0, 1, 2, 3, 4$.

(c) calculate the mean number of excited particles.

Sol.^{n} System: $N = 4$ independent particles, each can be 0 or 1, with $P(1) = P(0) = \frac{1}{2}$.

(a) Probability of K excited particles:

$$P(K) = \binom{4}{K} p^K (1-p)^{4-K} = \underline{\binom{4}{K}\left(\frac{1}{2}\right)^4}$$

(b) Values;

$P(0) = \frac{1}{16} = \underline{0.0625}$, $P(1) = \frac{4}{16} = \underline{0.25}$.

$P(2) = \frac{6}{16} = \underline{0.375}$, $P(3) = \underline{0.25}$, $P(4) = \underline{0.0625}$

(c) Mean

$$\langle K \rangle = Np = 4 \times \frac{1}{2} = \underline{\underline{2}}$$

(Q8) For $N = 6$ distinguishable particles that can occupy 3 states (A, B, C) with equal probability, derive the probability of finding 3 in A, 2 in B & 1 in C.

Sol.^{n} $N = 6$ distinguishable particles, states A, B, C with equal probability $P_A = P_B = P_C = \frac{1}{3}$. Probability to find $n_A = 3$, $n_B = 2$ & $n_C = 1$ is

$$P(3,2,1) = \frac{6!}{3!\,2!\,1!}\left(\frac{1}{3}\right)^3\left(\frac{1}{3}\right)^2\left(\frac{1}{3}\right)^1 = \frac{6!}{3!\,2!\,1!}\left(\frac{1}{3}\right)^6$$

computing, we get:

$$\frac{6!}{3!\,2!\,1!} = \frac{720}{12} = \underline{\underline{60}} \quad \& \quad P = \frac{60}{3^6} = \frac{60}{729}$$

$$\therefore \boxed{P = 0.0823}$$

(Q9) The kinetic energy E of a particle is distributed according to $P(E) = \alpha e^{-\alpha E}$, where $\alpha > 0$.

(a) Normalize the distribution.

(b) Find the expectation value of energy $\langle E \rangle$.

(c) Find the most probable energy.

Sol.ⁿ Given: $P(E) = \alpha e^{-\alpha E}$ for $E \geq 0$ & $\alpha > 0$.

(a) Normalization:

Checking:

$$\int_0^\infty \alpha e^{-\alpha E} = \left[-e^{-\alpha E}\right]_0^\infty = \underline{\underline{1}}$$

so, distribution is normalized.

(b) Expectation value:

$$\langle E \rangle = \int_0^\infty E \alpha e^{-\alpha E} \, dE .$$

using $\int_0^\infty x e^{-ax} \, dx = \frac{1}{a^2}$, Thus.

$$\underline{\langle E \rangle = \frac{1}{\alpha}}$$

(c) Most probable Energy

we have to maximize $P(E)$. since $P(E) = \alpha e^{-\alpha E}$ is decreasing for $E \geq 0$, max. occurs at $E = 0$. so $\underline{\underline{E_{mp} = 0}}$.

(Q10) For the same distribution $P(E) = \alpha e^{-\alpha E}$, derive the cumulative probability function $F(E)$. what is the probability that the energy lies between 0 & $2/\alpha$?

Sol.ⁿ For $P(E) = \alpha e^{-\alpha E}$

$$F(E) = \int_0^E \alpha e^{-\alpha E'} \, dE' = \underline{\underline{1 - e^{-\alpha E}}}$$

probability that $0 < E < 2/\alpha$.

$$P(0 < E < 2/\alpha) = F\left(\frac{2}{\alpha}\right) - F(0) = \underline{\underline{1 - e^{-2}}}$$

(Q11) Consider a system of 3 distinguishable ... can occupy energy levels 0 or ε.

(a) List all possible microstates.

(b) Assuming all microstates are equally probable, calculate the probability of the systems having total energy 2ε.

Sol.^{n} (a) All microstates (ordered triple notation (s_1, s_2, s_3) where $s_i \in \{0, \varepsilon\}$):

$(0,0,0)$, $(\varepsilon,0,0)$, $(0,\varepsilon,0)$, $(0,0,\varepsilon)$,

$(\varepsilon,\varepsilon,0)$, $(\varepsilon,0,\varepsilon)$, $(0,\varepsilon,\varepsilon)$, $(\varepsilon,\varepsilon,\varepsilon)$.

(b) Probability total energy $= 2\varepsilon$.

Microstates with two particles excited: $(\varepsilon,\varepsilon,0)$, $(\varepsilon,0,\varepsilon)$, $(0,\varepsilon,\varepsilon)$ — there are 3 such microstates. If all microstates are equal likely.

$$P(E_{tot} = 2\varepsilon) = \frac{3}{8}$$

(Q12) Explain the ergodic hypothesis. Using the idea of phase space trajectories, discuss ~~which~~ why it allows replacement of time averages with ensemble averages in equilibrium system.

Sol.^{n} Ergodic hypothesis - For an isolated system, a single trajectory in phase space (with constant energy) will pass arbitrarily close to every point on the energy surface given sufficiently long time. Therefore, the long-time average of any observable along the trajectory equals the ensemble average over the microcanonical ensemble.

Reasoning (sketch) — If the trajectory is dense on the accessible energy surface, the fraction of the time spent in any small phase-space region equals the fraction of the energy surface volume that region occupies; hence time averages equal phase-space (ensemble) averages.

(Q13) A single particle moves freely in a 1D box of length L. Using the idea of phase space, calculate the phase space volume accessible to the particle if its total energy is less than E. Express your answer in terms of L, m & E.

Sol.^{n} Single particle of mass m in 1D box of length L. The K.E is $E = \frac{p^2}{2m}$. Allowed positions $x \in [0, L]$. For total energy strictly less than E, momentum satisfies $|p| < \sqrt{2mE}$. Thus phase-space region (position x Momentum) has volume.

$$\Omega(E) = \int_{x=0}^{L} \int_{-\sqrt{2mE}}^{\sqrt{2mE}} dp\, dx = \underline{L \cdot 2\sqrt{2mE}}$$

So, $\boxed{\Omega(E) = 2L\sqrt{2mE}}$.

(Q14) In Classical mechanics, a system's trajectory is completely determined by its initial conditions. Yet, in statistical mechanics, we use probability distributions to describe its behaviour. Why is probability necessary in a theory that is, in principle, deterministic

Sol.^{n} Although classical mechanics is deterministic, we cannot know or control microscopic initial conditions to the precision needed for 10^{23} particles. Probability arises because:

=> we only have incomplete information about initial conditions.

=> Macroscopic observables depend on averages over many DoF.

(Q15) If two microstates have the same energy but differ in microscopic configuration, does averaging over them have any physical meaning? Discuss with an example from molecular systems or gases.

Sol.^{n} Averaging over microstates that shares the same energy but differ microscopically has physical meaning: Microscopic observables that depend only on conserved quantities will be same, while observables depending on micro-configuration may differ.

Eg: Two microstates of a gas ~~which~~ with identical total energy but different spatial distributions produce same total energy and temp.^{r}, but different local densities; averaging over these microstates yields macroscopic equilibrium values (pressure & temp.^{r}) while smoothing out microscopic differences.

(Q15) Consider a fair coin tossed 100 times. The outcome "50 heads and 50 tails" has the highest multiplicity but is not the only possible result. Discuss how this idea connects to the most probable macrostate of an ideal gas and why equilibrium is associated with maximum multiplicity rather than certainty.

Sol.^{n} The macrostate "50 heads, 50 tails" has the largest multiplicity but other outcomes are possible. In an ideal gas, the macrostate with maximum multiplicity (max. entropy) is more probable than other microstates because the number of corresponding microstate is astronomically larger. Equilibrium corresponds to that macrostate of maximal multiplicity (most probable), not absolutely certain; fluctuations are possible but extremely unlikely for macroscopic systems

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