Advanced Thermodynamics

Assignment - 4

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(Q1) The Kinetic Energy E of the molecule in an equilibrium system is described by :

$$P(E) = \frac{1}{KT} e^{-E/(KT)} \quad , \quad E \geq 0$$

(a) verify that the distribution is normalized.
(b) compute the mean energy $\langle E \rangle$ & the variance σ^2.
(c) Discuss the physical significance of the variance in the context of thermal energy fluctuations.

Sol.n

$$P(E) = \frac{1}{KT} e^{-E/(KT)} \quad , \quad E \geq 0$$

(a) Normalization

$$\int_0^\infty P(E)\, dE = \frac{1}{KT} \int_0^\infty e^{-E/(KT)}\, dE = 1$$

(b) Mean & Variance.

$$\langle E \rangle = \int_0^\infty E\, p(E)\, dE = KT$$

$$\langle E^2 \rangle = \int_0^\infty E^2 P(E)\, dE = 2(KT)^2$$

$$\sigma^2 = \langle E^2 \rangle - \langle E \rangle^2 = (KT)^2$$

(c) Significance

Variance shows the fluctuation in molecular energy. Higher $T \Rightarrow$ larger fluctuations. In equilibrium, $\sigma/\langle E \rangle = 1$, meaning fluctuation are comparable to mean energy for a single molecule, but become negligible for macroscopic systems.

(Q2) The velocity component of a gas molecule along the x-axis follows:

$$p(V_x) = \sqrt{\frac{m}{2\pi KT}}\, e^{-mV_x^2/(2KT)}$$

(a) Verify that $p(V_x)$ is normalized.

(b) Calculate $\langle V_x^2 \rangle$ and the root mean-square velocity V_{rms}.

(c) Explain how this results connects to the mean kinetic energy per DOF in an ideal gas.

Sol.^{n}

$$p(V_x) = \sqrt{\frac{m}{2\pi KT}}\, e^{-mV_x^2/(2KT)}$$

(a) Normalization

$$\int_{-\infty}^{\infty} p(V_x)\, dV_x = 1$$

we have used Gaussian integral $\int e^{-ax^2} dx = \sqrt{\pi/a}$.

(b) $$\langle V_x^2 \rangle = \frac{KT}{m}, \quad V_{max} = \sqrt{\langle V_x^2 \rangle} = \sqrt{\frac{KT}{m}}.$$

(c) Mean kinetic energy per DoF

$$\frac{1}{2} m \langle V_x^2 \rangle = \frac{1}{2} KT$$

(Q3) Consider a probability density,

$$p(E) = A E^2 e^{-\alpha E}, \quad E \geq 0$$

where A & α are positive constants.

(a) Determine the normalization constant A.

(b) Compute the mean energy $\langle E \rangle$ and variance σ^2.

(c) Discuss which kind of system this distribution may represent and why the factor E^2 appears.

Sol.^{n}

$$P(E) = A E^2 e^{-\alpha E}, \quad E \geq 0$$

(a) Normalization

$$1 = A \int_0^{\infty} E^2 e^{-\alpha E} dE = A \frac{2!}{\alpha^3} \Rightarrow A = \frac{\alpha^3}{2}$$

(b) $$\langle E \rangle = \frac{3}{\alpha}, \quad \langle E^2 \rangle = \frac{12}{\alpha^2}; \quad \sigma^2 = \langle E^2 \rangle - \langle E \rangle^2 = 3/\alpha^2$$

(c) Represents a 3D system (three translational DOF). The E^2 factor arises from the density of states proportional to $E^{(f/2-1)}$ with $f = 6$ phase variables.

(Q4) Suppose the probability of a system being in microstate i is given by:

$$P(i) = \frac{1}{Z} e^{-\beta \varepsilon_i^2},$$

where ε_i is the energy of the i^{th} microstate and Z is a normalization factor.

(a) Derive an expression of the partition function Z for a continuous energy distribution.

(b) Compute the expectation value $\langle \varepsilon \rangle$.

(c) Discuss physically how this differs the standard Boltzmann distribution and what kind of system could show such quadratic dependence in the exponent.

Sol.ⁿ

$$P(i) = \frac{1}{Z} e^{-\beta \varepsilon_i^2}$$

(a) Continuous Partition function.

$$Z = \int_0^\infty e^{-\beta \varepsilon_i^2} \, d\varepsilon = \frac{1}{2} \sqrt{\frac{\pi}{\beta}}.$$

(b) Expectation

$$\langle \varepsilon \rangle = \frac{1}{Z} \int_0^\infty \varepsilon e^{-\beta \varepsilon_i^2} \, d\varepsilon = \frac{1}{\sqrt{\pi \beta^3}}.$$

(C) Discussion.

Unlike Boltzmann ($e^{-\beta \varepsilon}$), this shows stronger suppression of high energies. May represent systems with quadratic energy bias.

(Q5) A small system in thermal contact with a reservoir has energy fluctuation described by:

$$P(\Delta E) = \frac{1}{\sqrt{2\pi \sigma^2}} e^{-(\Delta E)^2/(2\sigma^2)}$$

(a) show that $\langle \Delta E \rangle = 0$ and compute the variance.

(b) Relate σ^2 to the heat capacity C_V in the canonical ensemble.

(c) What does a small σ^2 imply about the system's thermodynamic stability?

Sol.ⁿ

$$P(\Delta E) = \frac{1}{\sqrt{2\pi \sigma^2}} e^{-(\Delta E)^2/(2\sigma^2)}$$

(a) $$\langle \Delta E \rangle = \int_{-\infty}^{\infty} \Delta E \, P(\Delta E) \, d(\Delta E)$$

Because $P(\Delta E)$ is symmetric about $\Delta E = 0$, the positive and negative parts of the integral cancel out.

$$\langle \Delta E \rangle = 0$$

$$\langle (\Delta E)^2 \rangle = \int_{-\infty}^{\infty} (\Delta E)^2 P(\Delta E) \, d(\Delta E) \Rightarrow \boxed{\langle (\Delta E)^2 \rangle = \sigma^2}$$

(b) $P(E) = \frac{1}{Z} e^{-\beta E}$, $\beta = \frac{1}{KT}$

$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$, $\langle (\Delta E)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2}$

Now differentiating $\langle E \rangle$ w.r.t T

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

Using $\beta = 1/(KT)$, we get $\frac{\partial}{\partial \beta} = -KT^2 \frac{\partial}{\partial T}$

$\therefore \langle (\Delta E)^2 \rangle = KT^2 C_V \Rightarrow \boxed{\sigma^2 = KT^2 C_V}$.

(c) Small $\sigma^2 \rightarrow$ Small fluctuations $\longrightarrow$ thermodynamic stability.
Large C_V enhances fluctuations.

(Q6) A system of particles is subject to an external potential, and the probability of finding a particle at position x is given by:

$$P(x) = Be^{-\lambda x^4} , \quad x \in (-\infty, \infty),$$

where B is the normalization constant and $\lambda > 0$.

(a) Determine B in terms of λ.
(b) Compute the mean $\langle x \rangle$ and discuss its symmetry.
(c) Qualitatively discuss how this quadratic dependence might arise in real physical systems.

Sol.n

$$P(x) = Be^{-\lambda x^4} , \quad x \in (-\infty, \infty)$$

(a) Using,

$$\int_{-\infty}^{\infty} e^{-\lambda x^4} dx = \frac{1}{2} \lambda^{-1/4} \lambda\left(\frac{1}{4}\right)$$

$$\boxed{B = \frac{2\lambda^{1/4}}{\lambda(1/4)}}$$

(b) Symmetric $\rightarrow$ $\langle x \rangle = 0$

(c) Quartic dependence arises in anharmonic oscillators, Landau potentials or polymer stretching models.

(Q7) For a normalized probability density $p(x)$, define the shannon entropy.

$$S = -k \int p(x) \ln p(x)\, dx.$$

(a) compute S for the exponential distribution $p(x) = \lambda e^{-\lambda x}$, $x \geq 0$.

(b) compare qualitatively the entropy of this distribution with that of a Gaussian having same mean.

(c) what does higher entropy imply about the uncertainity or disorder in the thermodynamic system?

Sol.^{n}

$$S = -K \int p(x) \ln p(x)\, dx$$

(a) Given: $p(x) = \lambda e^{-\lambda x}$, $x \geq 0$

and $\int_0^\infty p(x)\, dx = 1$

$$S = -K \int_0^\infty \lambda e^{-\lambda x} [\ln (\lambda e^{-\lambda x})]\, dx$$

$$\ln (\lambda e^{-\lambda x}) = \ln \lambda - \lambda x$$

$$S = -K \Big[\ln \lambda \underbrace{\int_0^\infty \lambda e^{-\lambda x} dx}_{1} - \lambda \underbrace{\int_0^\infty x \lambda e^{-\lambda x} dx}_{1/\lambda} \Big]$$

$$\therefore S = -K (\ln \lambda - 1) \Rightarrow \boxed{S = K (1 - \ln \lambda)}.$$

(b) $\langle x \rangle = 1/\lambda$

For a Gaussian distibution with the same mean and an equivalent wrdth, the probability is spread out more symmetrically.

$$S_{Gaussian} > S_{Exponential}$$

(c) Higher entropy $\rightarrow$ Greater disorder or uncertainity.

In thermodynamics, this corresponds to a system with more accessible microstates.

Lower entropy distributions mean more certainity or constraints on the system.

(Q8) You record the instantaneous kinetic energy of a Brownian particle suspended in water at different ~~rate~~ times. The measured distribution appears slightly broader than the ideal Maxwell-Boltzmann form.

(a) Suggest possible physical reasons for this brodening.

(b) How would this affect the inferred temp.^{r} if you used $\langle E \rangle = \frac{1}{2}KT$?

(c) Discuss how finite sampling, noise, and fluctuations bridge the gap between theoretical probability distributions and experimental observations.

Sol.^{n} (a) Possible Reason.

(i) Temp.^{r} fluctuations in surrounding fluid.

(ii) Measurement noise or limited precision of instruments.

(iii) Finite sampling - only a small number of observations, not enough for perfect statistics.

(iv) Non-equilibrium effects - if the particles is distributed or not fully equilibrated.

(v) viscous drag variations or local microflows of the fluid.

(b) Effect on inferred temp.^{r}.

$$\langle E \rangle = \frac{1}{2}KT$$

and our measured distribution is broader, it means your $\langle E \rangle$ is larger than expected.

Broader Distribution $\longrightarrow$ Higher Apparent Temp.^{r}.

(c) Experimental vs Theoretical Distributions.

Aspect	Theoretical Expectation	Experimental observation
Distribution shape	Maxwell - Boltzmann	slightly Broader
Mean Energy (E)	$\frac{1}{2}KT$	slightly higher
Implication	True Equilibrium	small deviation from equilibrium