Quantum Statistical Mechanics

In this chapter we will look at a formulation of Statistical Mechanics based on a Quantum Mechanical description of Physical Systems.

Basics

In QM, a system is described by a wave equation that obeys the Time dependent Schrodinger Equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$$ where $\hat{H}$ is the Hamiltonian Operator

$\hat{p} = -i\hbar \frac{\partial}{\partial x}$ is the momentum operator.

The SE becomes:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2 \Psi}{\partial x^2} + V(x)$$

More generally, for a system with no. degrees of freedom described by coordinates q, the solution is:

$$\Psi(q,t) = \sum_n c_n u_n(q) e^{-iE_n t/\hbar}$$ where $u_n(q)$ are eigenstates of Hamiltonian.

E_n are eigenvalues and c_n can be written as $c_n = |c_n| e^{i\phi_n}$ where ϕ_n are associated phases

Phase Space and Probabilities

The probability that a measurement finds a system in eigenstate c_n:

$$P_n = |c_n|^2$$

Postulate of a priori probabilities is now: "For an isolated system, all accessible eigenstates have equal a-priori probability"

Partition Function

The Partition function is calculated as a sum over all eigenstates u_n:

$$Z = \sum_n e^{-\beta E_n}$$

We can perform the semiclassical limit in the case of the ideal gas, but we will do this later in the course.

Quantum Harmonic Oscillator

This is a good approximation of many systems which is why we study it so much!

Suppose a general potential $V(r)$ has a minimum at $r = r_0$.

$\left(\frac{\partial V}{\partial r}\right)_{r=r_0} = 0$ Taylor expand around $r = r_0$!

$$V(r) \approx \underbrace{V(r_0) + \frac{1}{2}\left(\frac{\partial^2 V}{\partial r^2}\right)_{r=r_0}(r-r_0)^2}_{\text{Harmonic Oscillator Potential}} + \text{higher order terms}$$

The mean energy $\langle \varepsilon \rangle$ of a single 1D harmonic oscillator, from equipartition theorem, is $\langle \varepsilon \rangle = 2 \times \frac{\tau}{2} = \tau$ $\quad \therefore C_v = \frac{\partial \langle \varepsilon \rangle}{\partial T} = k_B$

This is in the classical case. Let's do it in QM now:

From QM last semester:

$$\varepsilon_n = \hbar\omega\left(n + \frac{1}{2}\right)$$ sub into Z to give:

$$Z = \sum_n e^{-\beta E_n} = e^{-\frac{\beta\hbar\omega}{2}} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

in the last step we used geometric series:

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-r}$$

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

We can now calculate mean energy

$$\langle \varepsilon \rangle = -\frac{\partial \ln Z}{\partial \beta} = \hbar\omega\left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right]$$

And specific heat capacity C_V is:

$$C_V = \frac{\partial \langle \varepsilon \rangle}{\partial T} = -K_B \beta^2 \frac{\partial \langle \varepsilon \rangle}{\partial \beta} = K_B(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

where we used

$$\frac{\partial}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial}{\partial \beta}$$

$$\uparrow$$

$$\frac{\partial}{\partial T}\left(\frac{1}{\tau}\right)$$

$$\frac{\partial}{\partial T}\left(\frac{1}{K_B T}\right)$$

$$= -\frac{1}{K_B T^2}$$

$$= \frac{-K_B}{K_B^2 T^2} = -K_B \beta$$

consider a high temperature limit $\tau \to \infty$ or $\beta \to 0$

$$\langle \varepsilon \rangle \overset{\beta \to 0}{=} \hbar\omega\left[\frac{1}{2} + \frac{1}{\beta\hbar\omega}\right]$$ since $e^{\beta\hbar\omega} = 1 + \beta\hbar\omega + \ldots$ when expanded

$$\text{so } \langle \varepsilon \rangle = \frac{\hbar\omega}{2} + \frac{1}{\beta} = \underbrace{\frac{\hbar\omega}{2}}_{\text{negligible at high } \tau} + \tau$$

so $\langle \varepsilon \rangle = \tau$ our classical result. So we obtain classical result at high temperature!

$C_V = K_B$ as $\beta \to 0$ and $\langle \varepsilon \rangle \to \tau$. Which also agrees with classical result.

What about $\tau \to 0$ or $\beta \to \infty$?

In this case we have $\langle \varepsilon \rangle = \frac{\hbar\omega}{2}$ and $C_V = 0$. Disagrees with classical result from equipartition theorem.

For low τ ($K_B T \ll \hbar\omega$), a small change in temperature cannot change the oscillator energy from groundstate $\frac{\hbar\omega}{2}$ to first excited state. So $\Delta U = 0$ for $\Delta T \neq 0$

$$\Delta U = C_V\, \Delta T$$

reservoir/heatbath

$= 0$ for system; C_V: $= 0$; ΔT: $\Delta T \neq 0$

A Quantised SHO has the properties we need to agree with the observation that $\sigma \to 0$ and $C_V \to 0$ for real physical systems.