Lecture #6. - Physics 418

$\therefore$ We can identify

$$g(E) = \int \frac{d^D q \, d^D p}{h^D} \, \delta(E - H(p,q))$$ as the

average number of states per unit energy, with h as planck's constant. Why?

Recall from Quantum mechanics $H \to \hat{H}$ operator

~~g(E)~~ Schrödinger Equation $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

$$\Rightarrow g(E) = \sum_n \delta(E - E_n) = \mathrm{Tr}\, \delta(E - \hat{H})$$

$$\pi\, \delta(E - \hat{H}) = \mathrm{Im}\left(\frac{1}{E - \hat{H} + i\varepsilon}\right) = \mathrm{Im} \int_0^\infty \frac{dt}{\hbar}\, e^{+it(E-\hat{H})/\hbar}$$

$$\therefore g(E) = \frac{1}{\pi}\mathrm{Im} \int_0^\infty \frac{dt}{\hbar}\, e^{+iEt/\hbar}\, \mathrm{Tr}\, e^{-it\hat{H}/\hbar}$$, but $e^{-it\hat{H}/\hbar}$ is the evolution operator

$$i\hbar\, \partial_t|\psi\rangle = H|\psi\rangle \Rightarrow |\psi(t)\rangle = e^{-it\hat{H}/\hbar}|\psi(0)\rangle$$

$$\therefore g(E) = \frac{1}{\pi}\mathrm{Im} \int_0^\infty \frac{dt}{\hbar}\, e^{iEt/\hbar} \int d^D q\, \langle q| e^{-it\hat{H}/\hbar} |q\rangle$$

$$\mathrm{Tr}\,\{\ \} = \int dq\, \langle q|\{\ \}|q\rangle$$

$$g(E) = \frac{1}{\pi} \mathrm{Im} \int_0^\infty \frac{dt}{\hbar} e^{\frac{iEt}{\hbar}} \int d^D q \, \langle q | e^{-i\hat{H}t/\hbar} | q \rangle$$

$$\mathbb{1} = \int \frac{d^D p}{h^D} |p\rangle\langle p|$$

$$g(E) = \frac{1}{\pi} \mathrm{Im} \int_0^\infty \frac{dt}{\hbar} e^{\frac{iEt}{\hbar}} \int \frac{d^D q \, d^D p}{h^D} \langle q | p \rangle \langle p | e^{-i\hat{H}t} | q \rangle$$

$$= \frac{1}{\pi} \mathrm{Im} \int \frac{d^D q \, d^D p}{h^D} \int_0^\infty \frac{dt}{\hbar} e^{\frac{iEt}{\hbar}} e^{i\vec{p}\cdot\vec{q}/\hbar} \langle p | e^{-i\hat{H}t} | q \rangle$$

Approximation: small time $\langle p | e^{-i\hat{H}t} | q \rangle \simeq$ free propagator

$$\langle p | e^{\frac{-i\hat{H}\delta t}{\hbar}} | q \rangle \simeq \langle p | 1 - \frac{i\delta t}{\hbar} \left[\hat{p}^2 + V(\hat{q}) \right] + \cdots | q \rangle$$

$$= \langle p | 1 - \frac{i\delta t}{\hbar} (p^2 + V(q)) + \cdots | q \rangle$$

eigenvalues, not operators

$$\simeq \langle p | e^{\frac{-i\delta t}{\hbar} H(p,q)} | q \rangle = e^{-i\frac{\delta t}{\hbar} H(p,q)} e^{-ip\cdot q/\hbar}$$

$$\therefore g(E) \simeq \frac{1}{\pi} \mathrm{Im} \int \frac{d^D q \, d^D p}{h^D} \int_0^\infty \frac{dt}{\hbar} e^{i\frac{Et}{\hbar}} e^{\frac{-i\delta t}{\hbar} H(p,q)}$$

$$g(E) = \int \frac{d^D q \, d^D p}{h^D} \delta(E - H(p,q))$$

Weyl formula for density of states

For Chaotic systems we can do a better job.

Recall

$$g(E) = \sum_n \delta(E - E_n) = \text{sum of delta functions}$$

Not $\int \frac{d^Dp\, d^Dq}{h^D} \delta(E-H)$ (smooth)

treat system semi-classically: do integrals in path integral semi-classically: $\hbar \ll A_{\text{classical}}$

$$g(E) = g^{\text{weyl}} \pm \sum_{\text{periodic orbits}} D_p(E)\, e^{iS_p(E)/\hbar}$$

Smooth, (average) contribution to DOS

(stability matrix determinant)

action of periodic orbit.

oscillatory (in principle) part that leads to δ-function train

Nevertheless, $g(E)^{\text{weyl}}$ is the Microcanonical Ensemble

If $g(E)$ is density of states,
the # of states $\Omega(E,V,N)$ within an energy shell of width Δ is

$$\Omega(E,V,N) = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} dE' \, g(E') \quad , \quad \frac{E}{N} < \Delta \ll E$$

(arbitrary smoothing energy)

Example #1: Ideal Gas. (3D)

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(x_i)$$

(Volume V)

$$V = \begin{cases} 0 & \text{inside Box} \\ \infty & \text{outside Box} \end{cases}$$

$$g = \prod_i \int \left[\frac{d^3 q_i \, d^3 p_i}{h^3} \right] \delta(E - H) = \frac{V^N}{h^{3N}} \int \prod_i d^3 p_i \, \delta\left(E - \sum_i \frac{p_i^2}{2m}\right)$$

$\Rightarrow$ find the surface area of a $D \equiv 3N$ sphere of Radius $\sqrt{2mE}$. Go to Polar Coordinates

$$\prod_i d^3 p_i = dP \, P^{3N-1} \, d\Omega_{3N} \longleftarrow \text{diff. solid angle}$$

$$g = \frac{V^N}{h^{3N}} \int d\Omega_{3N} \int dP \, P^{3N-1} \, \delta\left(E - \frac{P^2}{2m}\right)$$

$$g(E) = \frac{V^N}{h^{3N}} \Omega_{3N} \int dP \left|\frac{1}{P/m}\right| P^{3N-1} \delta(P - \sqrt{2mE})$$

because $\int dx\, \delta(f(x)) = \int dx \frac{1}{|f'(x)|} \delta(x)$

$$g(E) = \frac{V^N}{h^{3N}} \Omega_{3N} \cdot m \,(2mE)^{\frac{3N-2}{2}}$$

Ω_{3N} = area of unit sphere in 3N dimensions

Similar Exercise as H.W. #2. problem $\longrightarrow$ $\Omega_{3N} = \dfrac{2(\pi)^{3N/2}}{\left(\frac{3N}{2}-1\right)!}$ (see Appendix C of Pathria), C.76

$$\therefore g(E) = \frac{V^N}{h^{3N}} \frac{2(\pi)^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!} m \frac{(2mE)^{\frac{3N}{2}}}{2mE}$$

$$g(E) = \frac{V^N}{h^{3N}} \frac{(2\pi m E)^{\frac{3N}{2}}}{\left(\frac{3N}{2}-1\right)!} \frac{1}{E} \Rightarrow \Omega(E) \simeq \Delta \cdot g(E)$$

$\Rightarrow$ for large N, Ω is a very rapidly increasing function of E. $\sim E^{\frac{3N}{2}-1}$

Again, use Stirling's formula.

$S(E, V, N) = k_B \ln \Omega$

Stirling's Approximation: $n! \equiv I(n) = \int_0^\infty e^{-x} x^n \, dx = \int_0^\infty e^{-x} n x^{n-1} dx = n I(n-1) \dots = n!$ (16.5)

Integrate by parts

Define Γ function, $\Gamma(z+1) = \int_0^\infty e^{-x} x^z dx$; $z \in \mathbb{C}$

find saddle-point of exponent: $\Gamma = \int_0 e^S dx$;

$$S(x) = z \log x - x \; ; \; S'(x) = \frac{z}{x} - 1$$

$$S'(x) = 0 \Rightarrow x_{sp} = z$$

$$S(x) = S(x_{sp}) + S'(x_{sp}) \cdot (x - x_{sp}) + S''(x_{sp}) \frac{(x - x_{sp})^2}{2} + \dots$$

$$= (z \log z - z) + 0 + \left. -\frac{z}{x^2} \right|_{x=z} \frac{(x-z)^2}{2}$$

$$= z \log z - z - \frac{1}{z} \frac{(x-z)^2}{2} + \dots$$

$$\Gamma(z+1) = \int_0^\infty dx \; \exp[z \log z - z] \; \exp\left[-\frac{1}{2z} (x-z)^2 \right] + \dots$$

$$\simeq \exp[z \log z - z] \int_{-\infty}^\infty dx \; \exp\left[-\frac{1}{2z} (x^2) \right]$$

$$\simeq \exp[z \log z - z] \sqrt{2\pi z} + \text{corrections.}$$

$$\therefore n! \simeq e^{n \ln n - n} \sqrt{2\pi n}$$

This is an asymptotic expansion, valid as $n \to \infty$ for fixed # of terms. The expansion actually diverges for fixed n w/ # of terms increasing.

$$S = k_B N \ln\left[V \frac{(2\pi m E)^{3/2}}{h^3} \right] - k_B\left(\frac{3N}{2}-1\right)\ln\left[\frac{3N}{2}-1\right]$$

$$+ k_B \left(\frac{3N}{2}-1\right) + \ln\frac{\Delta}{E}$$

Neglect the 1 compared to $\frac{3N}{2} \gg 1$

$$\therefore S = k_B N \ln\left[\frac{V}{h^3}(2\pi m E)^{3/2}\right] + k_B N \ln\left[\left(\frac{3N}{2}\right)^{-\frac{3}{2}}\right]$$

$$+ \frac{3Nk_B}{2} + \mathcal{O}(\ln N)$$

$$S = k_B N \ln\left[\frac{V}{h^3}\left(\frac{2\pi m E}{N}\right)^{3/2}\right] + \frac{3}{2}N k_B + \mathcal{O}(\ln N)$$

N.B. $\rightarrow$ No Δ dependence

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_{V,N} = k_B N \cdot \left(\frac{3}{2}\right)\frac{1}{E} \Rightarrow \boxed{E = \frac{3}{2}k_B T}$$

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_{E,N} = \frac{k_B N}{V} \Rightarrow \boxed{PV = N k_B T}$$

Good! We recover Eqns. of state.

Problem! S as written above is NOT extensive. Return to this later!