9/26

- Test: next class 9/28!!!
- Bring a calculator!!! (Not your phone)
- You can use handwritten notes.
- You cannot use books nor electronic devices.

- Includes everything up to Hw #4.
  - Microcanonical formalism.
  - Canonical formalism.
  - Know the meaning and how to obtain physical properties.

Last time:

$$P(E) = g(E)\, e^{-\beta E}$$

Let's find E^* which is the maximum of $P(E)$:

$$0 = \frac{\partial P(E)}{\partial E}\Big|_{E=E^*} = \frac{\partial}{\partial E}\left(e^{-\beta E} g(E)\right)\Big|_{E=E^*} =$$

$$= -\beta\, e^{-\beta E^*} g(E^*) + e^{-\beta E^*} \frac{\partial g(E)}{\partial E}\Big|_{E=E^*}$$

$$\therefore\ \beta = \frac{1}{g(E)} \frac{\partial g(E)}{\partial E}\Big|_{E=E^*} = \frac{\partial \ln g(E)}{\partial E}\Big|_{E=E^*}$$

But

$$Z_N(\beta) = \int g(E)\, e^{-\beta E}\, dE$$

For fix E $g(E)$ is the number of microstates accessible to the system.

$$S(E) = k \ln \Omega \equiv k \ln g(E)$$

and

$$\left.\frac{\partial S(E)}{\partial E}\right|_{E=U} = \frac{1}{T} = k\beta$$

$$dU = TdS - PdV$$

Then

$$\beta = \frac{1}{k} \frac{\partial S}{\partial E}\Big|_{E=E^*} \qquad \text{if} \quad E^* = U$$

because $\beta = \frac{\partial \ln g}{\partial E}\Big|_{E=E^*}$ $\qquad S = k \ln g$

$$\frac{\partial S}{\partial E} = \frac{1}{T} = k\beta$$

Then β, the Lagrange multiplier, results to be $1/kT$.

Now let's expand $P(\epsilon)$ about $\epsilon = \epsilon^* \equiv U$:

$$\ln P(\epsilon) = \ln\left(e^{-\beta\epsilon} g(\epsilon)\right) \simeq \Big(-\beta U + \underbrace{\ln g(U)}_{S/k}\Big) +$$

$$+ \frac{1}{2}\frac{\partial^2}{\partial\epsilon^2}\ln\left(e^{-\beta\epsilon}g(\epsilon)\right)\Big|_{\epsilon=U}(\epsilon-U)^2 =$$

$$\frac{\partial \ln P}{\partial \epsilon}\Big|_{\epsilon=U} = 0$$

$$= \underbrace{\Big(-\beta U + \frac{S}{k}\Big)}_{-\beta(U-ST)} + \frac{1}{2}\frac{1}{kT^2 C_V}(\epsilon-U)^2 + \cdots$$

$$\beta\frac{SkT}{k}$$

$$\frac{S}{k} \Rightarrow \frac{1}{k}\frac{\partial S}{\partial \epsilon} = \left(\frac{1}{kT} = \beta\right)$$

$$\frac{\partial^2}{\partial\epsilon^2}\ln\left(e^{-\beta\epsilon}g(\epsilon)\right)\Big|_{\epsilon=U} = \frac{\partial^2}{\partial\epsilon^2}\Big[-\beta\epsilon + \ln g(\epsilon)\Big]_{\epsilon=U}$$

$$\frac{\partial \epsilon}{\partial\beta} = \frac{\partial\epsilon}{\partial T}\frac{\partial T}{\partial \beta} = -C_V kT^2$$

$$= \frac{\partial}{\partial\epsilon}\Big[\cancel{-\beta} + (-\epsilon)\frac{\partial\beta}{\partial\epsilon} + \cancel{\beta}\Big] = -\frac{\partial}{\partial\epsilon}\left(\frac{\partial\beta}{\partial\epsilon}\right) = \frac{1}{C_V kT^2}$$

We see that $P(\epsilon)$ looks like a gaussian since exponentiating we obtain:

$$P(\epsilon) \propto e^{-\beta\epsilon} g(\epsilon) \simeq e^{-\beta(U-TS)} e^{-\frac{(\epsilon-U)^2}{2kT^2 C_V}}$$

the dispersion about U of the gaussian is

$\sqrt{kT^2 C_V} = \sqrt{\langle(\Delta\epsilon)^2\rangle}$ which $\to 0$ as $N \to \infty$.

This distribution is a very sharp gaussian, almost like a δ.

Ideal gas:

$$g(\epsilon) \propto \epsilon^{\frac{3N}{2}-1} \quad \text{(saw last time)}$$

$$P(\epsilon) \propto g(\epsilon)e^{-\beta\epsilon} \propto \epsilon^{\frac{3N}{2}-1} e^{-\beta\epsilon}$$

here β is a fixed parameter

$$\left.\frac{\partial P}{\partial \epsilon}\right|_{\epsilon=\epsilon^*} = 0 = \left.\left(\frac{3N}{2}-1\right)\epsilon^{\frac{3N}{2}-2}e^{-\beta\epsilon} - \beta\epsilon^{\frac{3N}{2}-1}e^{-\beta\epsilon}\right|_{\epsilon=\epsilon^*}$$

$$\left(\frac{3N}{2}-1\right)\epsilon^{*\,\frac{3N}{2}-2}e^{-\beta\epsilon^*} = \beta\epsilon^{*\,\frac{3N}{2}-1}e^{-\beta\epsilon^*}$$

$$\beta = \frac{\left(\frac{3N}{2}-1\right)}{\epsilon^*}$$

$$\therefore \epsilon^* \simeq \left(\frac{3N}{2}-1\right)\frac{1}{\beta} \simeq \frac{3N}{2}kT = U$$

we see that $\epsilon^* = U$ average energy of the ideal gas

Due to the sharpness of the gaussian we see that for the ideal gas

$$P(E) = 0 \quad \text{if} \quad E \neq U.$$

Partition function (for ideal gas):-

$$Z_N(V,T) = \int_0^\infty e^{-\beta E} g(E)\, dE \underset{\substack{\text{using} \\ \text{gaussian} \\ \text{expansion} \\ \text{of } P(E)}}{\simeq} e^{-\beta(U-TS)} \int_0^\infty e^{-\frac{(E-U)^2}{2kT^2c_V}} dE =$$

$$= e^{-\beta(U-TS)} \sqrt{2\pi k T^2 c_V}$$

Since $F = -kT \ln Z_N$

$$-kT \ln Z_N = F \simeq kT\beta\,(\underbrace{U-TS}_{\propto N}) - kT \ln \underbrace{\sqrt{2\pi k T^2 c_V}}_{\propto \ln N^{1/2}} \simeq$$

since $c_V \propto N$

$$\simeq U - TS \quad \text{(as expected for } F\text{)}$$

All these statistical identities are "exact" when $N \sim 10^{23}$.

Theorems that can be demonstrated in the canonical formalism:

Let's find

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle$$

$H(q, p)$ Hamiltonian (classical)

x_i, x_j 2 of the 6N generalized coordinates (q, p).

In the canonical formalism:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} \, d\omega}{\int e^{-\beta H} \, d\omega}$$

↳ integral over all phase space.

Notice that

$$\frac{\partial}{\partial x_j}\left(x_i e^{-\beta H}\right) = \frac{\partial x_i}{\partial x_j} e^{-\beta H} + x_i (-\beta)\frac{\partial H}{\partial x_j} e^{-\beta H}$$

$$\therefore \quad x_i \frac{\partial H}{\partial x_j}(+\beta) e^{-\beta H} = -\frac{\partial}{\partial x_j}\left(x_i e^{-\beta H}\right) + \frac{\partial x_i}{\partial x_j} e^{-\beta H}$$

$$x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = +\frac{1}{\beta}\frac{\partial x_i}{\partial x_j} e^{-\beta H} - \frac{1}{\beta}\frac{\partial}{\partial x_j}\left(x_i e^{-\beta H}\right)$$

$$\therefore \int x_i \frac{\partial H}{\partial x_j} e^{-\beta H}\, dx_j \underbrace{d\omega(j)}_{\text{all } d^3q\, d^3p \text{ except } x_j} = \int \frac{1}{\beta}\underbrace{\frac{\partial x_i}{\partial x_j}}_{\delta_{ij}} e^{-\beta H}\, dx_j\, d\omega(j) -$$

$$- \int \underbrace{\frac{1}{\beta}\frac{\partial}{\partial x_j}\left(x_i e^{-\beta H}\right) dx_j}_{\frac{1}{\beta} x_i e^{-\beta H}\Big|_{(x_j)_1}^{(x_j)_2}} d\omega(j)$$

$\rightarrow$ extreme values of x_j so that $H(x_{j1}) \to \infty$, $H(x_{j2}) \to \infty$

$$\therefore \int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega = \int \frac{1}{\beta} \delta_{ij} e^{-\beta H} d\omega =$$

$$= \frac{1}{\beta} \delta_{ij} \int e^{-\beta H} d\omega$$

Then

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{1}{\beta} \delta_{ij} \frac{\int e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega} = \frac{1}{\beta} \delta_{ij} = \boxed{kT \delta_{ij}} \quad (*)$$

Then if $x_i = x_j = p_i$

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle \equiv \langle p_i \dot{q}_i \rangle \overset{(*)}{=} kT$$

If $x_i = x_j = q_i \Rightarrow \left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle = -\langle q_i \dot{p}_i \rangle \overset{(*)}{=} -kT$

Then:

$$\left\langle \sum_{i=1}^{3N} p_i \frac{\partial H}{\partial p_i} \right\rangle = \left\langle \sum_{i=1}^{3N} p_i \dot{q}_i \right\rangle = 3NkT$$

Also

$$\left\langle \sum_{i=1}^{3N} q_i \frac{\partial H}{\partial q_i} \right\rangle = - \left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3NkT$$

What happens if H is a quadratic function of its coordinates?

$$H = \sum_j \left(A_j P_j^2 + B_j Q_j^2 \right) \qquad (1)$$

Quadratic form ① can also be obtained from a canonical transformation of the coordinates when H is quadratic in p_i and q_i. P_i and Q_i are canonical transforms of q_i and p_i.

Hamilton equations are valid for $H(P,Q)$.

$$\therefore \sum_j \Big(P_j \underbrace{\frac{\partial H}{\partial P_j}}_{2A_j P_j} + Q_j \underbrace{\frac{\partial H}{\partial Q_j}}_{2B_j Q_j} \Big) = 2\sum_j \left(A_j P_j^2 + B_j Q_j^2 \right)$$

$$= 2H$$

$$\therefore \langle H \rangle = \frac{1}{2} \Big\langle \sum_j P_j \frac{\partial H}{\partial P_j} + Q_j \frac{\partial H}{\partial Q_j} \Big\rangle = \frac{1}{2} f kT$$

# of nonvanishing coefficients.

f is the number of active degrees of freedom.

$f = 3N$ for ideal gas.

Then we see that there is $\frac{1}{2}kT$ energy associated to any active (quadratic) degree of freedom – Principle of equipartition of energy.

Each harmonic (quadratic) term in H contributes $\frac{1}{2}kT$ to the energy if the degree is active.

(always true in classical mechanics; true at certain temperatures in quantum).