lecture 8 - classical statistics

- microcanonical - fixed energy E

$$S = k_B \ln \frac{\Delta p \Delta q}{(h^3)^N}$$
$$\Delta p = \Delta p_{1x}\Delta p_{1y}\Delta p_{1z}...\Delta p_{Nx}\Delta p_{Ny}\Delta p_{Nz}$$
$$\Delta q = \Delta q_{1x}\Delta q_{1y}\Delta q_{1z}...\Delta q_{Nx}\Delta q_{Ny}\Delta q_{Nz}$$

- Boltzmann distribution- (p,q)

$$dw = \frac{e^{-\epsilon(p,q)/k_BT}}{Z} dpdq$$
$$Z = \frac{1}{h}\int dpdq e^{-\epsilon(p,q)/k_BT}$$
$$\bar{f} = \frac{\int dpdq f(p,q) e^{-\beta\epsilon(p,q)}}{\int dpdq e^{-\beta\epsilon(p,q)}}$$

- $\epsilon(p,q) = p^2/2m$

$$\bar{\epsilon} = \frac{\int dpdq \frac{p^2}{2m} e^{-p^2/2mk_BT}}{\int dpdq e^{-p^2/2mk_BT}} \tag{1}$$

  factorize q-integral
  Gaussian p-integral $(\int_{-\infty}^{+\infty} dx e^{-ax^2} = \sqrt{\frac{\pi}{a}})$
  $\bar{\epsilon} = \frac{1}{2}k_BT$

- harmonic oscillator $\epsilon(p,q) = p^2/2m + (1/2)kq^2$

$$\bar{\epsilon} = \frac{\int dpdq (\frac{p^2}{2m} + \frac{1}{2}kq^2) e^{-\beta\epsilon(p,q)}}{\int dpdq e^{-\beta\epsilon(p,q)}} \tag{2}$$

  kinetic + potential energy - Gaussian integrals
  $\bar{\epsilon} = \frac{1}{2}k_BT + \frac{1}{2}k_BT$
  N-harmonic oscillators, $\bar{E} = Nk_BT$, $c = C/N = k_B$ (Dulong-Petit)

- at $T \to +\infty$ quantum = classical
- particle in a potential $\epsilon(p,q) = p^2/2m + v(q)$

$$\begin{aligned} \bar{\epsilon} &= \frac{1}{2}k_B T + \bar{v}(q) \\ \bar{v} &= \frac{\int dq v(q) e^{-\beta v(q)}}{\int dq e^{-\beta v(q)}} \end{aligned}$$

- general equipartition theorem

$$\overline{q_i \frac{\partial \epsilon}{\partial q_i}} = \overline{p_j \frac{\partial \epsilon}{\partial p_j}} = k_B T \tag{3}$$

- Maxwell distribution - $\epsilon = p_x^2/2m + p_y^2/2m + p_z^2/2m$
q-integrals factorize, p-integrals add up
$\bar{\epsilon} = 3\frac{1}{2}k_B T$
- Maxwell distribution
$dw_v = (\frac{m}{2\pi k_B T})^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2k_B T} dv_x dv_y dv_z$
$= (\frac{m}{2\pi k_B T})^{3/2} e^{-mv^2/2k_B T} 4\pi v^2 dv$
- many interacting particles - $(p,q) = \{p_1, ..., p_N, q_1, ... q_N\}$
$E(p,q) = \sum_i p_i^2/2m + V(q_1, ..., q_N)$
often $V(q_1, ..., q_N) = \sum_{i,j} v(q_i, q_j)$

$$\begin{aligned} \overline{F} &= \frac{\int dp_1 ... dp_N dq_1 ... dq_N F(p_1, ..., p_N, q_1, ..., q_N) e^{-\beta E}}{\int dp_1 ... dp_N dq_1 ... dq_N e^{-\beta E}} \\ \overline{E} &= \frac{\int dp_1 ... dp_N dq_1 ... dq_N E(p_1, ..., p_N, q_1, ..., q_N) e^{-\beta E}}{\int dp_1 ... dp_N dq_1 ... dq_N e^{-\beta E}} \end{aligned}$$

p-integrals separate
$\overline{E} = N\frac{1}{2}k_B T + \frac{\int dq_1 ... dq_N V(q_1, ..., q_N) e^{-\beta V}}{\int dq_1 ... dq_N e^{-\beta V}}$

- how to evaluate
$\overline{V} = \frac{\int dq_1 ... dq_N V(q_1, ..., q_N) e^{-\beta V}}{\int dq_1 ... dq_N e^{-\beta V}}$?
- Monte Carlo, Molecular Dynamics -

- ergodic theorem
  $\overline{F} = lim_{\tau \to 0} \frac{1}{\tau} \int_0^\tau dt F(p_1(t), ..., p_N(t), q_1(t), ..., q_N(t))$
  initial conditions
  $\{p_i(t=0), q_i(t=0)\}$, fixed - E
- free energy of ideal Boltzmann gas

$$
\begin{aligned}
F &= -k_B T \ln Z = -k_B T \ln \sum_n e^{-\beta E_n} \\
F &\simeq -k_B T \ln \frac{1}{N!} (\sum_k e^{-\beta \epsilon_k})^N \\
F &= -N k_B T \ln (\frac{e}{N} \sum_k e^{-\beta \epsilon_k}) \\
F &= -N k_B T \ln \frac{e}{N} \int e^{-\epsilon(p,q)/k_B T} \frac{dp dq}{h^3} \\
& \quad \epsilon_k(p_x, p_y, p_z) = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + \epsilon_k' \\
F &= -N k_B T \ln (\frac{eV}{N}) - N k_B T \ln (\frac{2\pi m T}{h^2})^{3/2} (\sum_k e^{-\beta \epsilon_k'}) \\
&= -N k_B T \ln (\frac{eV}{N}) + N f(T) \\
P &= -\frac{\partial F}{\partial V}|_T \to PV = N k_B T \\
S &= -\frac{\partial F}{\partial T}|_V \to S = N k_B \ln \frac{eV}{N} - N f'(T) \\
U &= \frac{3}{2} N k_B T (monoatomic)
\end{aligned}
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