0.1 Ensemble Theory

0.1.1 Space

描述 gas model 的方法: 列出所有气体粒子的 (q,p).

0.1.1.1 μ-space by Ehrenfest

(x,y,z,v_x,v_y,v_z) 6-dim space. 其中的一个点描述的是一个粒子的状态. 共需 $N\sim N_A$ 个点进行描述.

$$\sum_i \delta(x-x_i)\delta(y-y_i)\delta(z-z_i)\delta(v_x-v_{xi})\delta(v_y-v_{yi})\delta(v_z-v_{zi})$$
$$\text{Distribution function:}\quad f(\vec{x},\vec{v},t)\mathrm{d}^3\vec{x}\mathrm{d}^3\vec{v}$$

随着时间推移, $H=\int f\ln f$ 总是趋向于减小. 在达成最小/细致平衡时: $\vec{x}$: 均匀; $\vec{v}$: Maxwell 分布.

[Discussion] 质疑: 令某一时刻 t 下 $\vec{v}\to-\vec{v}$, 难道不会使 H 回升吗?

0.1.1.2 Γ-space

$\{q_1,q_2,q_3,p_1,p_2,p_3,q_4,q_5,q_6,p_4,p_5,p_6,\cdots\}$, $6N$-dim. 空间中的一个点描述的是整团气体某时刻下的状态. 系统的演化即点的运动.

在 μ-空间中的通过 course-graining 分割的一个 $|k\rangle$ 状态格子中, 有着 n_k 个粒子. 该格子的体积为 6-dim phase volume $\omega_k=\Delta\vec{q}_k\Delta\vec{p}_k$. 相应地, 在 Γ 空间中由这 n_k 个粒子所占据的空间体积为 $\prod_{\alpha=1}^{n_k}\Delta\vec{q}_\alpha\Delta\vec{p}_\alpha=\prod_{\alpha=1}^{n_k}\omega_k=\omega_k^{n_k}$. 因此所有粒子所占据的空间为 $\prod_k\omega_k^{n_k}$

在给定的 $\{n_k\}$ 中, 同状态 $|k\rangle$ 的粒子间交换不会产生新的状态数, 因此修正: $W'=\dfrac{N!}{\prod_k n_k!}\prod_k\omega_k^{n_k}$. 该体积和状态数成正比, 那么寻找在 $\sum_k n_k=N,\quad \sum_k\varepsilon_k n_k=E$ 约束下使得空间体积/状态数极大的 $n_k^*=A\omega_k e^{-\beta\varepsilon_k}$.

0.1.1.3 Geomatry of High-Dimensional Space

0.1.1.3.1 An Illustrative Example: Sphere in n-dim Space 3-dim space: S^2,B^3; n-dim space: S^{n-1},B^n.

在 n-dim 欧式空间中的一个点 $x=(x_1,x_2,\cdots,x_n)$. $\vec{x}$ 的长度为 $|x|=\sqrt{\sum_{i=1}^n x_i^2}$.

体积: $V\left(B_R^n\right)=C_nR^n,\quad C_n=\dfrac{\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}+1\right)},\quad \Gamma(z+1)\equiv\int_0^\infty t^{-z}e^{-t}\mathrm{d}t\overset{z\in\mathbb{Z}}{=}z!\approx\sqrt{2\pi z}\left(\dfrac{z}{e}\right)^z$

$$C_n\overset{n\text{ even}}{=}\frac{\pi^{n/2}}{\left(\frac{n}{2}\right)!}\Rightarrow V\left(B_R^n\right)\simeq\frac{1}{\sqrt{n\pi}}\left(\sqrt{\frac{2\pi e}{n}}\right)^nR^n,\quad\text{unit sphere: }V\left(B_R^n\right)=1\Leftrightarrow R=\sqrt{\frac{n}{2\pi e}}$$

设两共心球半径分别为 R, $R(1+\varepsilon)$. 求夹层(Shell)体积为 $V_{\text{shell}}=V(R)[(1+\varepsilon)^n-1^n]$. 即使 ε 很小, 也会随着 $n\uparrow$ 使得 $V[R(1+\varepsilon)]$ 急剧上升. 即高维空间中体积集中在 "边缘".

[Example] 高维酒杯. 要求填满圆锥形酒杯的一半, 随着维度升高, 酒面高度也会升高, 趋近于酒杯边缘.

[Example] 密度均匀, n-dim, 半径为 R 的高维球 B_R^n. 只取单个轴 x, 另一个轴作为垂直 x 分量的 B_R^n 球切片 $B_{R'}^{n-1}$, 其中 $R'=R\sqrt{1-\dfrac{x^2}{R^2}}$. 存在 $\int_{-R}^R\rho(x)\mathrm{d}x=\int_{-R}^RV\left(B_{R'}^{n-1}\right)\mathrm{d}x=V\left(B_R^n\right)$, 求 $\rho(x)$ 表达式.

$\dfrac{V\left(B_{R'}^{n-1}\right)}{V\left(B_R^{n-1}\right)}=\left(\dfrac{R'}{R}\right)^{n-1}=\left(1-\dfrac{x^2}{R^2}\right)^{\frac{n-1}{2}}\simeq e^{-(n-1)x^2/2R^2}$; For a unit ball, $R=\sqrt{\dfrac{n}{e}}\Rightarrow\rho(x)\simeq e^{-ex^2/2}V(B_1^{n-1})$

0.1.1.3.2 The Geometric Deviation Principle Minkowski 求和. 点集 $A+B$ 对应于 $\vec{a}+\vec{b}$. A, B 本身具有一定的形状.

Brunn-Minkowski inequality: $[V(A+B)]^{1/n} \geq [V(A)]^{1/n} + [V(B)]^{1/n}$. A 和 B 为齐形凸体, 即 $A=\alpha B+x$ 时取等.

Isoperimetric principle: 等面积, 求周长最小; 等体积, 求表面积最小.

设 n-dim 无定形点集 C 和 n-dim 球点集 B, 两者体积相同 $V(C)=V(B)=V(B_R^n)$. 设 $\epsilon \to 0$, $C+\epsilon B$ 使得在 C 表面增加薄壳. 那么 C 的 $(n-1)$-dim 表面积(Area)可借该薄壳体积除以厚度 ϵ 得到: Area $= \lim_{\epsilon\to 0} \dfrac{V(C+\epsilon B)-V(C)}{\epsilon}$. 不等式: $V(C+\epsilon B)^{1/n} \geq V(C)^{1/n} + V(\epsilon B)^{1/n} = V(B)^{1/n} + (\epsilon^n V(B))^{1/n} \Rightarrow$ Area $\geq \lim_{\epsilon\to 0} \dfrac{[(1+\epsilon)^n - 1]}{\epsilon} V(B) \approx n \cdot V(B)$, C 为球时取等. 于是 "等体积, 表面积最小时为球" 得证.

[Example] 取两铁环沾肥皂水, 铁环间由肥皂水薄膜相连. 几何: curvature; 物理: surface tension. Laplace preessure: $p \propto \sigma \overline{H}$. [Example] 悬链线(Catenary Curve).

类比不等式 $\dfrac{x+y}{2} \geq \sqrt{xy}$, 那么 $\sqrt{[V(C)V(D)]} \leq V\left[\dfrac{C+D}{2}\right] \leq \left(1-\dfrac{\epsilon^2}{8}\right)^n V(B)$. ϵ 为不对齐程度.

设单位体积球点集 B, 而 C 占据 B 体积的 $\dfrac{1}{2}$, 剩下的 $\dfrac{1}{2}$ 体积为 D. 即有 $V(C)=\dfrac{1}{2}V(B)$. 那么 $M=\dfrac{C+D}{2}$ 所能占据的体积是有限的. 代入 $V(B)=1$ 得 $V(D) \leq 2(1-\dfrac{1}{8}\epsilon^2)^{2n} \times V(B) = 2e^{-n\epsilon^2/4}V(B)$.

[Example] 考虑 n-dim 球的球面 S^{n-1}, 在球面上有一分布函数 f 且随球面坐标缓慢变化. 找到 f 的中位数 M, 分界为 $S_1(f<M)$ 和 $S_2(f>M)$. 令 S_1 向 S_2 方向膨胀微薄一层, 得到 $f=M+\epsilon$ 界线; 同样地, S_2 向 S_1 方向膨胀后, 得到 $f=M-\epsilon$ 界线. 因为 $V(S_1) \ll V(S^{n-1})$ 且 $V(S_2) \ll V(S^{n-1})$, 说明球面上大部分数值都集中在中值 M 附近.

0.1.1.3.3 Probability Perspective @ Levy, 1980 Uniform distribution of dots $\to$ volume interpretted as the probability.

[Example] Probability theory of large deviation. Toss coin(抛掷硬币): $X_i=0,1$; 均值 $M_N = \dfrac{1}{N}\sum_{i=1}^{N} X_i$. 令 $x \in \left(\dfrac{1}{2}, 1\right)$, $P(M_N > x) < e^{-NI(x)}$,, 其中 $I(x) = x\ln x + (1-x)\ln(1-x) + \ln 2$. 令 $x=\dfrac{1}{2}+\epsilon$, 则 $P(M_N > \dfrac{1}{2}+\epsilon) < e^{-2N\epsilon^2}$.
M_N, "macrostate". microstates: $C_N^{NM_N} = C_N^k$.
$C_N^k = \dfrac{N!}{k!(N-k)!} \Rightarrow \ln C_k = \ln\left[\dfrac{N!}{k!(N-k)!}\right] \simeq -N\ln x \ln x - N(1-x)\ln(1-x) = -N[I(x)-\ln 2]$
$S = k_B \ln C_N^k$

[Example] $[-1,1]\otimes[-1,1]$ 空间内随机撒点. 设 $x+y=0$ 分割线, 该线上的点有 $\lim_{n\to\infty}\sum_i^n x_i = 0$; 相应地, 若 $\lim_{n\to\infty} x+y=\epsilon$ 描述了偏离中心线的程度.

0.1.2 From Dynamics to Probability Description

Measurement: time-avarage. Phase space with macroscopic constraint: ensemble-avarage. Poincare recurrence theorem(庞加莱回归定理)

时间平均: $\langle f\rangle_t = \dfrac{\sum_i f_i\tau_i}{\sum_i \tau_i}$

Course-grained description of phase space: $f_i = f_\alpha, \quad \forall i \in \alpha$.

$$\begin{aligned}\langle f\rangle_t &= \frac{1}{T}\sum_\alpha f_\alpha t_\alpha, \quad t_\alpha = \sum_{i\in\alpha}\tau_\alpha \\ &= \sum_\alpha f_\alpha \times \left(\frac{t_\alpha}{T}\right) = \sum_\alpha f_\alpha p_\alpha, \quad \text{prob description: } p_\alpha = \frac{t_\alpha}{T}\end{aligned}$$

Formal presentation: in equilibrium,

$$\begin{aligned}
\overset{\text{ensemble avarage}}{\langle f\rangle_e} &= \langle\langle f\rangle_e\rangle_t = \langle\langle f\rangle_t\rangle_e \\
\left\langle \lim_{T\to\infty}\langle f\rangle_t \right\rangle_e &= \lim_{T\to\infty}\langle f\rangle_t : \quad \text{ergodic(各态历经), 初态无关} \\
\langle f\rangle_e &= \lim_{T\to\infty}\langle f\rangle_t
\end{aligned}$$

不同情况下的 microstate: 1. In Γ-space($6N$-dim), (q,p); 2. $|n\rangle$; 3. $\sigma=\pm1$; 4. $\sigma=\{0,1\}$...

Representative point $\leftrightarrow$ one gas. Density function(continuum description) $\sum_i \delta(x-x_i)\to\rho(x)$.

$$\langle f\rangle = \frac{\sum_\alpha f_\alpha p_{\alpha,t}}{\sum_\alpha p_{\alpha,t}} \Longrightarrow \frac{\int f(q,p)\rho(q,p,t)\mathrm{d}^{3N}q\mathrm{d}^{3N}p}{\int \rho(q,p,t)\mathrm{d}^{3N}q\mathrm{d}^{3N}p}$$

equilibrium condition: $\langle f\rangle$ time-invariant $\to \dfrac{\partial\rho}{\partial t}=0$

[Discussion] 若 $\rho(q,p,t)=q(q,p)f(t)$, $\langle f\rangle$ 在数学上也是平衡的. 这种情况下需要考虑到

$$\int g(q,p)f(t)\mathrm{d}^{3N}q\mathrm{d}^{3N}p = N \Rightarrow f(t)=\text{const.} \Rightarrow \frac{\partial\rho}{\partial t}=0.$$

0.1.2.1 Dynamics

0.1.2.1.1 A Single Representative Point in Γ-Space .

Hamiltonian 力学: $\dot{q}_i=\dfrac{\partial H}{\partial p_i}, \quad \dot{p}_i=-\dfrac{\partial H}{\partial q_i}$. 特征: 1. 轨迹不可能自相交; 2. 回归定理.

0.1.2.1.2 Multiple Representative Points

在 Γ-空间中选取一个体积 ω, 将会有 $\int_\omega \rho(q,p,t)\mathrm{d}\omega$ 个代表点. 其表面为 $\partial\omega$. 代表点在 Γ-空间中的运动速度为 $\vec{v}_i=\{\dot{q}_i,\dot{p}_i\}$. 那么存在关系

$$\begin{aligned}
&\frac{\partial}{\partial t}\int_\omega \rho(q,p,t)\mathrm{d}\omega = -\int_{\partial\omega}\rho\vec{v}\cdot\hat{n}\mathrm{d}\sigma = -\int_\omega \nabla\cdot(\rho\vec{v})\mathrm{d}\omega, \quad \nabla=\left(\frac{\partial}{\partial\mathbf{q}},\frac{\partial}{\partial\mathbf{p}}\right) \\
&\Rightarrow \frac{\partial\rho}{\partial t}+\nabla\cdot(\rho\vec{v})=0, \quad \text{Continuity Equation}
\end{aligned}$$

Material deriavtive. 设 $g(\vec{x},t)$, flow field: $\vec{v}(\vec{x},t)$.

$$g(\vec{x}+\delta\vec{x},t+\delta t)-g(\vec{x},t) = g(\vec{x},t)+\delta\vec{x}\frac{\partial g}{\partial\vec{x}}+\delta t\frac{\partial g}{\partial t}-g(\vec{x},t) = \delta\vec{x}\frac{\partial g}{\partial\vec{x}}+\delta t\frac{\partial g}{\partial t} = \delta t\left(\vec{v}\cdot\frac{\partial g}{\partial\vec{x}}+\frac{\partial g}{\partial t}\right)$$

$$\frac{\mathrm{D}g}{\mathrm{D}t} \equiv \frac{g(\vec{x}+\delta\vec{x},t+\delta t)-g(\vec{x},t)}{\delta t} = \vec{v}\cdot\frac{\partial g}{\partial\vec{x}}+\frac{\partial g}{\partial t}$$

Liouville's theorem:
$$\begin{aligned}
\frac{\mathrm{D}\rho(q,p,t)}{\mathrm{D}t} &= \frac{\partial\rho}{\partial t}+\vec{v}\cdot\nabla\rho = \frac{\partial\rho}{\partial t}+\sum_i\left(\dot{q}_i\frac{\partial\rho}{\partial\rho_i}+\dot{p}_i\frac{\partial\rho}{\partial p_i}\right) \\
&= \frac{\partial\rho}{\partial t}+\sum_i\left(\frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial\rho_i}-\frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial p_i}\right) = \boxed{\frac{\partial\rho}{\partial t}+\{\rho,H\}=0}
\end{aligned}$$

[Discussion]How to understand $\dfrac{\mathrm{D}\rho}{\mathrm{D}t}=0$? 1. canonical transform; 2. incompressibility ($\nabla\cdot\vec{v}=0$)

$$\frac{\partial\rho}{\partial t}+\nabla(\rho\vec{v})=0 \Rightarrow \overset{\frac{\mathrm{D}\rho}{\mathrm{D}t}=0}{\underline{\frac{\partial\rho}{\partial t}+\vec{v}\cdot\nabla\rho}}+\rho\nabla\cdot\vec{v}=0 \Rightarrow \nabla\cdot\vec{v}=0$$

check: $\quad \nabla\cdot\vec{v}=\sum_i\left(\dfrac{\partial}{\partial q_i}\dot{q}_i+\dfrac{\partial}{\partial p_i}\dot{p}_i\right)=\sum_i\left(\dfrac{\partial}{\partial q_i}\dfrac{\partial H}{\partial p_i}-\dfrac{\partial}{\partial p_i}\dfrac{\partial H}{\partial q_i}\right)=0$

H-dynamics $\Leftrightarrow$ incompressibility of representative points.

若ρ为H函数$\rho(H)$, 则$\{\rho,H\}=0\Rightarrow\dfrac{\partial\rho}{\partial t}=0$, 即达成 equilibrium; 两种可能: 1. $\rho=$ const.; 2. @Gibbs: canonical $\Rightarrow \ln\rho\propto H$

0.1.3 Microcanonical Ensemble

气体模型 macrostate: (E, N, V), to construct an ensemble of microstates. surface of $(6N-1)$-dim.

[Discussion] 可能总动量 $\vec{P} \neq \vec{0}$, 总角动量 $\vec{L} \neq \vec{0}$. 以动量为例子:

$\underbrace{p_{1x}^2 + p_{1y}^2 + p_{1z}^2}^{\text{1st particle}} + p_{2x}^2 + \cdots + p_{Nz}^2 \overset{\text{ideal gas}}{=} 2mE, \quad P_z = \sum_{i=1}^{N} p_{1z} \to 0$, due to high dimension.

[Example] 2-state system. $|1\rangle : N_1, |2\rangle : N_2. \quad P_1 = \dfrac{N_1}{N_1+N_2}, P_2 = \dfrac{N_2}{N_1+N_2} \Rightarrow \langle f \rangle = f_1 P_1 + f_2 P_2.$

Equilibrium density function? $\rho(q,p) = \begin{cases} \text{const.} & H(q,p) \in \lim\limits_{\Delta \to 0} \left[E - \dfrac{\Delta}{2}, E + \dfrac{\Delta}{2}\right] \\ 0, & \text{others} \end{cases}$

Foudation of equilibrium: 等概率假设, 且为 ergodicity(各态历经).

Closed system: $S = k_B \ln \Omega, \quad \Omega = \dfrac{\omega}{\omega_0}, \quad \omega:$ allowed region of motion, $\omega_0:$ some constant

$$\delta q \delta p \sim h \Rightarrow (\delta \mathbf{q} \delta \mathbf{p}) \sim h^{3N} \Rightarrow \omega_0 = h^{3N}$$

$$\Omega = \frac{1}{N! h^{3N}} \int_\omega \mathrm{d}^3\vec{q}_1 \mathrm{d}^3\vec{q}_2 \cdots \mathrm{d}^3\vec{q}_N \mathrm{d}^3\vec{p}_1 \mathrm{d}^3\vec{p}_2 \cdots \mathrm{d}^3\vec{p}_N, \quad N! \text{ to make } S \text{ is extensive}$$

$\Rightarrow$ indisdinguishability of microscopic particles

0.1.3.1 Equation of State for Ideal Gas

Derive the equation of state by microcanonical ensemble method.

理想气体的内能表达式: $\sum_{i=1}^{N} |\vec{p}_i|^2 = 2mE$. 等能面为 $(3N-1)$ 维球面, 且球面半径约为 $\sqrt{E}$. 那么相空间体积/微观态数 $\Omega \sim (\sqrt{E})^{3N-1} \sim E^{3N/2}$. 克劳修斯熵 $S = k_B \ln \Omega = \dfrac{3}{2} k_B N \ln E + \text{const.}$; 1st law: $\dfrac{1}{T} = \left(\dfrac{\partial S}{\partial E}\right)_V \Rightarrow E = \dfrac{3}{2} N k_B T.$

在 1D 下存在关系 $p \cdot L \sim \pi \Rightarrow p \sim \dfrac{1}{L} \Rightarrow \delta p \sim \dfrac{1}{L}$ ，则更良的微观态数表达式为 $\Omega \sim \dfrac{(\sqrt{E})^{3N-1}}{(\delta p)^{3N}} \overset{V \sim L^3}{\longrightarrow} \left(E^{3/2} V\right)^N$,

$S = k_B \ln \Omega = N k_B \left(\dfrac{3}{2} \ln E + \ln V + \text{const.}\right) \Rightarrow \left(\dfrac{\partial S}{\partial V}\right)_E = \dfrac{N k_B}{V} \Rightarrow \mathrm{d}S = \dfrac{3}{2} N k_B \dfrac{\mathrm{d}E}{E} + N k_B \dfrac{\mathrm{d}V}{V} = \dfrac{\mathrm{d}E}{T} + \dfrac{P\mathrm{d}V}{T},$

观察比较得到 $N k_B \dfrac{\cancel{\mathrm{d}V}}{V} = \dfrac{P \cancel{\mathrm{d}V}}{T} \Rightarrow P = \dfrac{N}{V} k_B T.$

0.1.3.2 Dilute Hard Sphere System

各小球可占体积为因各自体积而相互减少. 设小球半径为 a, 体积为 $\omega_e = \dfrac{4}{3}\pi(2a)^3$. 接触距离至少为球心间距所以是 $2a$.

微观态数为 $\Omega = \dfrac{1}{N! h^N} \displaystyle\int \mathrm{d}^3\vec{q}_1 \mathrm{d}^3\vec{q}_2 \cdots \mathrm{d}^3\vec{q}_N \mathrm{d}^3\vec{p}_1 \mathrm{d}^3\vec{p}_2 \cdots \mathrm{d}^3\vec{p}_N$, 其中

$$\int \mathrm{d}^3\vec{q}_1 \cdots \mathrm{d}^3\vec{q}_N = V(V-\omega_e)(V-2\omega_e)\cdots[V-(N-1)\omega_e] = \prod_{i=0}^{N-1}(V - i\omega_e) \overset{\ln}{\Rightarrow} \ln \prod_{i=0}^{N-1}(V - i\omega_e) = \sum_{i=0}^{N-1} \ln(V - i\omega_e).$$

使用极限 $\ln(x + \delta x) \Leftrightarrow \ln x + \dfrac{1}{x}\delta x$, 则 $\sum_{i=0}^{N-1} \ln(V - i\omega_e) = \sum_{i=0}^{N-1} \left(\ln V - \dfrac{i\omega_e}{V}\right) = N \ln V - \dfrac{\omega_e}{V} \dfrac{(N-1)N}{2}$

$$\simeq N\left(\ln V - \frac{\omega_e N}{2V}\right) \simeq N \ln\left(V - \frac{\omega_e N}{2}\right) \Rightarrow \int \mathrm{d}^{3N} q = \left(V - \frac{\omega_e N}{2}\right)^N$$

[Exercise]设有 N 个硬球, 半径 a, 约定 $\omega_e = \dfrac{4}{3}\pi(2a)^3$, 体系能量为 E, 总体积为 V, 温度为 T. 尝试计算 S(E,V), 状态方程.

[Hint:$\text{Area}(S^{n-1}) = \dfrac{2\pi^{\frac{n}{2}}}{\Gamma\left(\frac{n}{2}\right)} R^{n-1}$]

0.1.3.3 Einstein's Model for Heat Capacity of Solid(1907)

Excitations $\to$ Solid property? Quantum?

N atoms, 等效于 $3N$ independent oscillators. Total energy: U, distributed to $3N$ oscillators. 等效为将 $\dfrac{U}{\hbar\omega_0}$ 个竖隔板插入由 $3N$ 个球间隔出的 $(3N-1)$ 的缝隙中.

微观态数 $W = \dfrac{\left[(3N-1)+\left(\dfrac{U}{\hbar\omega_0}\right)\right]!}{(3N-1)!\left(\dfrac{U}{\hbar\omega_0}\right)!}$, 则每 1 mol 原子的熵为 $s(u) = k_B \ln W \simeq 3R\left[\ln\left(1+\dfrac{u}{u_0}\right)+\dfrac{u}{u_0}\ln\left(1+\dfrac{u_0}{u}\right)\right]$,

其中 $s = \dfrac{S}{N/N_A}$, $\quad u = \dfrac{U}{N/N_A}$, $\quad u_0 = 3N_A\hbar\omega_0$. 压强是某量对体积的偏导数 $P = \dfrac{\partial \sharp}{\partial V}$, $\quad \sharp: U, S\cdots$, 热容则是 $c = T\dfrac{\partial S}{\partial T}$.

温度 $\dfrac{1}{T} = \left[\dfrac{\partial S(U)}{\partial U}\right] = \dfrac{k_B}{\hbar\omega_0}\ln\left(1+\dfrac{3}{u}\hbar\omega_0\right)$, 代入即有 $\dfrac{1}{3N_A}u(T) = \dfrac{\hbar\omega_0}{e^{\hbar\omega_0/k_BT}-1}$, 正是 Boson 行为.

热容为 $c = \dfrac{\partial u}{\partial T} = 3N_A k_B\left(\dfrac{\hbar\omega_0}{k_BT}\right)^2 e^{-\dfrac{\hbar\omega_0}{k_BT}}$.

0.1.4 Canonical Ensemble

Macrostate: (N, V, T). 能量允许涨落. 又名: Entropy representation.

Equilibrium density function? @Gibbs: $\dfrac{\partial\rho}{\partial t} = -\vec{v}\cdot\nabla\rho$. If equilibrium $\dfrac{\partial\rho}{\partial t} = 0$, then $\vec{v}\cdot\nabla\rho = 0$.

$\displaystyle\sum_i\left(\dot{q}_i\frac{\partial\rho}{\partial q_i}+\dot{p}_i\frac{\partial\rho}{\partial q_i}\right) = 0 \Rightarrow \sum_i\left(\frac{\partial H}{\partial p_i}\frac{\partial\rho}{\partial q_i}-\frac{\partial H}{\partial q_i}\frac{\partial\rho}{\partial q_i}\right) = 0$. 若 ρ 为 H 函数 $\rho(H)$, 则方程自动满足.

$\rho_{1+2} = \rho_1\times\rho_2, \quad H_{1+2} = H_1 + H_2 \Rightarrow \ln\rho \propto \alpha H \Rightarrow \rho \propto e^{\alpha H}$

0.1.4.1 Connection to Microcanonical Ensemble

0.1.4.1.1 Environment & System Perspective 设环境为 A', 处于态 $|r'\rangle$; 体系为 A, 处于态 $|r\rangle$, $A+A'$ 整体是孤立系统. 那么有 $E_r + E_{r'} = E^{(0)} = \text{const.}$; 设 Ω' 为环境微观态数, 则体系处于态 $|r\rangle$ 的概率 $P_r \propto \Omega'(E_{r'}) = \Omega'(E^{(0)}-E_r)$. 假定体系所占能量足够小, 即 $E_r \ll E^{(0)}$, 则可 Taylor 展开: $\ln\Omega'(E^{(0)}-E_r) = \ln\Omega'(E^{(0)}) + \left.\dfrac{\partial\ln\Omega'}{\partial E'}\right|_{E'=E^{(0)}}\overbrace{(E_{r'}-E^{(0)})}^{-E_r}+\cdots = \text{const.}-\beta E_r$

于是得到 Boltzmann factor/Canonical distribution $\quad P_r = \dfrac{e^{-\beta E_r}}{\displaystyle\sum_r e^{-\beta E_r}}$.

[Discussion] Taylor 展开时, 为何不需要保留更高次? $\Rightarrow$ 为了保持 S 的广延性.

0.1.4.1.2 Multiple Systems Perspective 制备 N 个正则系综, 整体组成一个微正则系综. 设 n_r 个系统处于状态 $|r\rangle$, 能量为 E_r. 则存在约束条件 $\displaystyle\sum_r n_r = N, \quad \sum_r n_rE_r = NU = N\langle E_r\rangle$. 微观态数为 $W = \dfrac{N!}{\displaystyle\prod_r n_r!}$, 寻找 $\{n_r\}$ 使得 W 最大化.

$\Rightarrow \dfrac{n_r^*}{N} = \dfrac{e^{-\beta E_r}}{\displaystyle\sum_r e^{-\beta E_r}}$.

[Dsicussion] Why is $\ln\rho\propto\alpha E \Rightarrow \rho\propto e^{\alpha E}$ simple: 1. No dynamics information; 2. Time-reversal symmetry. Detailed-balance(细致平衡); 3. 具有可加性. 引申为 $\ln\rho = \alpha+\beta E$; 4. 设 $f(\epsilon)$ 为体系处于能量 ϵ 的概率, 则有 $\dfrac{f(\epsilon_1)}{f(\epsilon_2)} = \dfrac{f(\epsilon_1+\epsilon)}{f(\epsilon_2+\epsilon)}$. 定义

$f(\epsilon) = g(\epsilon-\epsilon_2) \Rightarrow g(\epsilon)g(\epsilon_1-\epsilon_2) = g(0)g(\epsilon_1-\epsilon_2-\epsilon) \Rightarrow g(\epsilon) = g(0)e^{-\beta\epsilon} \Rightarrow \dfrac{f(\epsilon_1)}{f(\epsilon_2)} = e^{-\beta(\epsilon_1-\epsilon_2)}$

0.1.4.2 Revisit Maxwell Distribution

0.1.4.2.1 Galton's Statistical Model

0.1.4.2.2 Based on Symmetry 各向同性: $f(\vec{v}) = f(v) = f_0(v_x)f_0(v_y)f_0(v_z)$

0.1.4.2.3 Boltzmann

能量离散化. $\exists\{n_r\}, \quad \text{s.t. } W = \dfrac{N!}{\prod\limits_{\alpha} n_\alpha!}$

0.1.4.2.4 Based on Ensemble Theory

能量中动量和位置分离: $E(q,p) = \overset{\text{kinetic}}{K(p)} + \overset{\text{potential}}{U(q)}$

因此统计独立: $\rho(q,p) \propto e^{-\beta E(q,p)} \Rightarrow \rho(q,p) = Ae^{-\beta[K(p)+U(q)]} = Ae^{-\beta K(p)} \cdot e^{-\beta U(q)}$.

其中动能部分: $e^{-\beta K(p)} = \exp\left[-\beta\left(\dfrac{p_1^2}{2m} + \dfrac{p_1^2}{2m} + \cdots + \dfrac{p_N^2}{2m}\right)\right] = \overbrace{e^{-\beta\frac{p_1^2}{2m}}}^{e^{-\beta\frac{p_{1x}^2}{2m}} e^{-\beta\frac{p_{1y}^2}{2m}} e^{-\beta\frac{p_{1z}^2}{2m}}} \cdot e^{-\beta\frac{p_2^2}{2m}} \cdot e^{-\beta\frac{p_3^2}{2m}} \cdots e^{-\beta\frac{p_N^2}{2m}}$.

New perspective on gas model: 将各粒子单独视为一个系统, 只有 E 交换而没有 N 交换: $\rho_1 = Ae^{-\beta\frac{p_1^2}{2m}}$

0.1.4.2.5 Geometric Viewpoint

在 $(p_{1x}, p_{1y}, p_{1z}, p_{2x}, p_{2y}, \cdots)$ $3N$-dim 空间中, 挑任意一轴(以 p_{1x} 为例), 系统处于该轴上的概率分布为? $\Rightarrow \rho(p_{1x}) \sim e^{-\beta p_{1x}^2}$ (Energy partition theorem).

[Example] 受热浴谐振子: $H = \alpha p^2 + \beta q^2$; $\langle \alpha p^2 \rangle = \displaystyle\int \alpha p^2 A^{-\beta H} \mathrm{d}q\mathrm{d}p = \frac{1}{2}k_B T$.

[Example] 推广: $H = \displaystyle\sum_i \alpha p_i^n, \quad E_i = \alpha p_i^n, \quad \langle E_i \rangle = \int E_i e^{-\beta E_i} \mathrm{d}E_i \Big/ \int e^{-\beta E_i} \mathrm{d}E_i = -\frac{\partial}{\partial\beta} \ln\left(\int e^{-\beta E_i} \mathrm{d}p_i\right)$.

Let $y = \beta^{\frac{1}{n}} p_i \Rightarrow \displaystyle\int e^{-\beta E_i} \mathrm{d}p_i = \beta^{-\frac{1}{n}} \int e^{-\alpha y^n} \mathrm{d}y \Rightarrow \boxed{\langle E_i \rangle = \frac{1}{n} k_B T}$.

0.1.4.3 Thermodynamics

[Discussion] 已知 1st law: $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$, 如何将 $U(V,S)$ 转变为 V 和 T 的未知函数 $?(V,T)$.

定义 $F \equiv U - TS$, 全微分 $\mathrm{d}F = -p\mathrm{d}V - S\mathrm{d}T \Rightarrow F(V,T)$. 因此正则系综 (N,V,T) 也被称作 F-representation.

类似地, 定义 $G \equiv F + PV$ 从而得到 P 和 T 的函数 $G(P,T)$. $G = \mu N$.

平均能量 $\langle E_r \rangle = \dfrac{\sum\limits_r E_r e^{-\beta E_r}}{\sum\limits_r e^{-\beta E_r}} = -\dfrac{\partial}{\partial\beta} \ln\left(\sum\limits_r e^{-\beta E_r}\right)$

内能 $U = F + TS = F - T\left(\dfrac{\partial F}{\partial T}\right)_{N,V} = \dfrac{\partial}{\partial(1/T)}\left(\dfrac{F}{T}\right)_{N,V}$

记 $\beta = \dfrac{1}{k_B T}$, 则自由能 $F = -k_B T \ln Q_N(V,T)$, 其中正则配分函数对状态 $|r\rangle$ 求和形式为 $Q_N = \sum\limits_r e^{-\beta E_r}$.

求 $\langle \ln P_r \rangle = \left\langle \ln\left(\dfrac{e^{-\beta E_r}}{Q_N}\right)\right\rangle = -\ln Q_N - \beta\langle E_r \rangle = \beta(F - U) = -\dfrac{S}{k_B} \Rightarrow S = -k_B \sum\limits_r P_r \ln P_r$, 正是 Gibbs entropy 形式.

对能量 i 求和形式: $Q_N = \sum\limits_i g_i e^{-\beta E_i} = \displaystyle\int g(E) e^{-\beta E} \mathrm{d}E$, 其中 g_i 为 degeneracy of energy level E_i(能级的简并度).

微观态数/Γ-相空间体积的形式: $Q_N = \dfrac{1}{N! h^{3N}} \displaystyle\int e^{-\beta H(q,p)} \mathrm{d}^{3N}q \mathrm{d}^{3N}p$

[Discussion] $Q_N = \sum\limits_r e^{-\beta E_r}$, 根据 $e^{-\beta E_r}$ 能定论 $E_r = 0$ 是概率最高的能量吗? $(E_r)_{\text{most prob}} = U$. 因为还存在着 $g(E)$ 调控了概率, 使得 U 才是真正概率最高的能量. $e^{-\beta U} e^{S/k_B}$.

0.1.4.4 Fluctuations

已知内能 U 可通过对正则配分函数求 β 偏导得到: $U = -\dfrac{\partial}{\partial\beta}\left(\ln \sum\limits_r e^{-\beta E_r}\right)$. 若再对 U 求一次 β 偏导, 则有

$$\frac{\partial U}{\partial\beta} = -\frac{\sum\limits_r E_r^2 e^{-\beta E_r}}{\sum\limits_r e^{-\beta E_r}} + \left(\frac{\sum\limits_r E_r e^{-\beta E_r}}{\sum\limits_r e^{-\beta E_r}}\right)^2 = -\langle E^2 \rangle + \langle E \rangle^2 \equiv \langle (\Delta E)^2 \rangle = k_B T^2 C_v$$

定义相对变化量/涨落为 $\dfrac{\sqrt{\langle(\Delta E)^2\rangle}}{\langle E \rangle} = \dfrac{\sqrt{k_B T^2 C_v}}{U} \sim N^{-\frac{1}{2}}$

[Example] Classical harmonic oscillator ($\varepsilon_n = nh\nu$). Single oscillator:

$$\langle E_1\rangle = \frac{\sum_n \varepsilon_n e^{-\beta\varepsilon_n}}{\sum_n e^{-\beta\varepsilon_n}} = \frac{h\nu}{e^{\beta h\nu}-1}.\quad \langle E_1^2\rangle = (h\nu)^2\frac{1+e^{\beta h\nu}}{(e^{\beta h\nu}-1)^2},\ \langle(\Delta E_1)^2\rangle = (h\nu)^2\frac{e^{\beta h\nu}}{(e^{\beta h\nu}-1)^2},\ \frac{\sqrt{\langle(\Delta E_1)^2\rangle}}{\langle E_1\rangle} = e^{\frac{1}{2}\beta h\nu}.\ T\to 0,$$

涨落趋于发散.

N oscillators: $\langle(\Delta E)^2\rangle = N\langle(\Delta E_1)^2\rangle,\quad \dfrac{\sqrt{\langle(\Delta E)^2\rangle}}{\langle E\rangle} = N^{-\frac{1}{2}}\dfrac{\sqrt{\langle(\Delta E_1)^2\rangle}}{\langle E_1\rangle}$.

[Example] Reletive fluctuation of speed in Maxwell distribution. $f(v) = A\exp\left\{-\dfrac{mv^2}{2k_BT}\right\} v^2\mathrm{d}v$, where v^2 for 3D gas.

$$\langle g(v)\rangle = \frac{\int g(v)f(v)\mathrm{d}v}{\int f(v)\mathrm{d}v},\quad \frac{\sqrt{\langle v^2\rangle}}{\langle v\rangle} = \sqrt{\frac{3\pi}{8}-1}$$

[Example] Ideal gas. $H = \sum_{i=1}^{N}\dfrac{\vec{p}_i^2}{2m}$.

1. **使用正则系综方法**. 配分函数为

$$Q_N(V,T) = \sum_r e^{-\beta E_r} = \frac{1}{N!h^{3N}}\int e^{-\beta\sum_{i=1}^{N}\frac{\vec{p}_i^2}{2m}}\mathrm{d}^{3N}q\,\mathrm{d}^{3N}p = \frac{1}{N!}\left(\frac{1}{h^3}\int_{-\infty}^{+\infty}e^{-\beta\frac{p_1^2}{2m}}4\pi p_1^2\mathrm{d}p_1\underbrace{\int\mathrm{d}^3\vec{q}_1}_{V}\right)^N = \frac{Q_1(T,V)^N}{N!},$$

即各粒子统计独立. 单粒子配分函数 $Q_1 = \dfrac{V}{h^3}(2\pi mk_BT)^{\frac{3}{2}} = \dfrac{V}{\lambda_T^3}$, 其中 $\lambda_T = \dfrac{h}{\sqrt{2\pi mk_BT}}$ 为热波长. 粒子间平均间距可估算为 $a\sim\left(\dfrac{V}{N}\right)^{\frac{1}{3}}$. 若 $\lambda_T \ll a$, 即可认为 $h\to 0$, 无量子效应. 更一般性地, 若 Hamiltonian 仅为动量 p 的函数 $H = H(p)$, 则单粒子配分函数形为 $Q_1 = Vf(T)$. 当 $H = \sum_i\dfrac{p_i^2}{2m}$ 特殊情形时, 有 $f(T) = \lambda_T^{-3}$. 继续一般性的讨论:

$$\ln Q_N = \ln\left[\frac{(Vf(T))^N}{N!}\right] = N\ln f(T) + \ln\frac{V^N}{N!} = N\ln f(T) + \ln\left(\frac{e^N}{N^N}V^N\right) = N\ln f(T) + N\ln\left(\frac{eV}{N}\right)$$

记 $n = \dfrac{N}{V}$, 则 $\dfrac{F}{V} = nk_BT\left[\ln\left(\dfrac{n}{f}\right)-1\right] \Rightarrow P = \left(\dfrac{\partial F}{\partial V}\right)_{N,T} = \dfrac{Nk_BT}{V}$, 和理想气体相同. 这说明满足该形式的状态方程, 真正重要的是各粒子统计独立.

$S = -\left(\dfrac{\partial F}{\partial T}\right)_{N,V} = k_BV\left[-n\ln\left(\dfrac{n}{f}\right)+\dfrac{5}{2}n\right]$, extensive by adding $N!$.

2. **通过态密度分析配分函数**. $Q_N = \int g(E)e^{-\beta E}\mathrm{d}E,\quad g(E)\sim E^{\frac{3N}{2}-1}$. 那么概率则是 $P(E)\mathrm{d}E = g(E)e^{-\beta E}\mathrm{d}E$

概率 $P(E)$ 对能量 E 导数为 0 以寻找极值点 E_0:

$$\begin{aligned}\frac{\partial}{\partial E}\left[g(E)e^{-\beta E}\right] &= g'(E)e^{-\beta E} + g(E)(-\beta)e^{-\beta E} = \left(\frac{3N}{2}-1\right)E^{\frac{3N}{2}-2}e^{-\beta E} + E^{\frac{3N}{2}-1}(-\beta)e^{-\beta E}\\ &= \left[\left(\frac{3N}{2}-1\right)E^{-1}-\beta\right]\times\sharp = 0 \Rightarrow E_0 = \left(\frac{3N}{2}-1\right)\frac{1}{\beta} \Rightarrow \lim_{N\to\infty}E_0 = \frac{3N}{2}k_BT\end{aligned}$$

[Example] Colored Ideal Gas. N red atoms, N blue atoms, N green atoms. Statistically independent. microstate: (q,p,color)

1. **存在三种颜色时的熵** S_{3c}: 单种颜色的配分函数 $Q_N(T,V) = \dfrac{1}{N!}\left(\dfrac{V}{\lambda_T}\right)^N$, 则三种颜色总共的配分函数为 $Q = Q_N^3$. 那么自由能为 $F = -k_BT\ln Q = -3k_BT\ln\left(\dfrac{V}{N\lambda_T}\right)$. 熵为 $S_{3c} = -\left(\dfrac{\partial F}{\partial T}\right)_{N,V} = 3Nk_B\ln\left(\dfrac{eV}{N}\right) - 3Nf'(T)$

2. **只存在一种颜色时的熵** S_{1c}: $S_{1c} = 3Nk_B\ln\left(\dfrac{eV}{3N}\right) - 3Nf'$

比较以上两个结果, 就会发现由于多出颜色自由度产生的混合熵 $\Delta S = S_{3c} - S_{1c} = k_B\ln 3^{3N}$.

[Discussion] 1. How to understand $\ln 3^{3N}$? statistically independent $\to$ analyze a single particle. 底数 3: 3 种颜色/状态. 2.

$S_{\text{tot}} = S_{\{q,p\}} + S_{\text{color}}$. 新的自由度独立于 (q,p), 则熵直接相加.

[Example] 2-state. $|1\rangle : P_1 = r; |2\rangle : P_2 = 1-r$. For a single particle,

$\widetilde{S}_{\text{mix}} = -k_B \sum_{r=1}^{2} P_r \ln P_r == -k_B[r\ln r + (1-r)\ln(1-r)]$. 取极值: $r = \frac{1}{2} \Rightarrow \widetilde{S}_{\text{mix}} = k_B \ln 2$

0.1.5 Grand Canonical Ensemble

exchange energy, matter. (T,V,μ). $|rs\rangle$: 粒子数为 N_r, 能量为 E_r. 令该系统 A 与环境 A' 整体组成一个孤立系统.

$P_{rs} = \dfrac{e^{-\alpha N_r - \beta E_s}}{\sum_{r,s} e^{-\alpha N_r - \beta E_s}}$

系综中能量的延拓: $U(S,V,N) \overset{F=U-TS}{\longrightarrow} F(T,V,N) \overset{\Phi=F-\mu N}{\longrightarrow} \Phi(T,V,\mu)$, 即 Grand potential.

$\langle N\rangle = \sum_{r,s} NP_{rs} = \dfrac{\sum_{r,s} N_r e^{-\alpha N_r-\beta E_s}}{\sum_{r,s} e^{-\alpha N_r-\beta E_s}} = -\dfrac{\partial q}{\partial\alpha}, q = \ln\left(\sum_{r,s} e^{-\alpha N_r - \beta E_s}\right)$. 可类比于 $\langle E\rangle = -\dfrac{\partial q}{\partial \beta} \Rightarrow$ q-potential

$Q(Z,V,T) = \sum_{N_r=0}^{\infty} Z^{N_r} Q_{N_r}(V,T), \quad Z \equiv e^{-\alpha}$, fugacity(逸度)

导出 Gibbs entropy(for open system): $\langle \ln P_{rs}\rangle = \sum_{r,s} P_{rs}(\ln P_{rs}) \Rightarrow S = -k_B \sum_{r,s} P_{rs}\ln P_{rs}$.

粒子数涨落: $\langle(\Delta N)^2\rangle = \dfrac{\langle N\rangle^2 k_B T\kappa_T}{V} \Rightarrow \dfrac{\langle(\Delta n)^2\rangle}{\langle n^2\rangle} = \dfrac{k_B T}{V}\kappa_T, \quad \kappa_T = -\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)$.

[Example] **Ideal gas**. $Q_N(V,T) = \dfrac{Q_1^N}{N!}, Q_1(V,T) = \dfrac{1}{h^3}\int e^{-\beta\frac{p^2}{2m}} \mathrm{d}^3\vec{q}\mathrm{d}^3\vec{p} = \dfrac{V}{\lambda_T^3}$. 若 $H = H(p)$, 则形式为 $Q_1(V,T) = Vf(T)$.

从巨正则系综角度出发, 配分函数为 $Q(Z,V,T) = \sum_{N_r=0}^{\infty} Z^{N_r}\dfrac{[Vf(T)]^{N_r}}{N_r!} = e^{ZVf(T)}$, 其中 $Z = e^{-\alpha}$.

那么 q-potential 为 $q(Z,V,T) = \ln Q = ZVf(T)$. 各热力学量根据与 q 的关系分别导出: 压强 $P = \dfrac{k_B T}{V} q = Zk_B T f(T)$;

粒子数 $N = -\dfrac{\partial q}{\partial \alpha} = ZVf(T)$; 内能 $U = -\dfrac{\partial q}{\partial\beta} = ZVk_BT^2 f'(T)$; 状态方程 $PV = Nk_BT$.

[Example] Fluctuation of number of particles. 考虑体系 (V,N) 中的小区域 Ω, 体积为 v, 粒子数为 n. 则 Ω 中有 n 个粒子的概率 $P_n = \dfrac{\sum_s e^{-\alpha n - \beta E_n^{(s)}}}{Q}$. 猜测平均粒子数为 $\langle n\rangle = \dfrac{N}{V}v$. 独立同分布. 单个粒子在/不在 Ω 中的概率: $P_1 = \dfrac{v}{V}, \quad P_0 = 1 - \dfrac{v}{V}$. 则 Ω 中有 n 个粒子的概率为 $P(n) = \dfrac{N!}{(N-n)!n!}P_1^n P_0^{N-n}$, $\lim_{N\to\infty} P(n)$ 将化为 Poisson 分布: $P(n) = \dfrac{\langle n\rangle^n}{n!}e^{-\langle n\rangle}$, 其中 $\langle n\rangle = \dfrac{N}{V}v$.