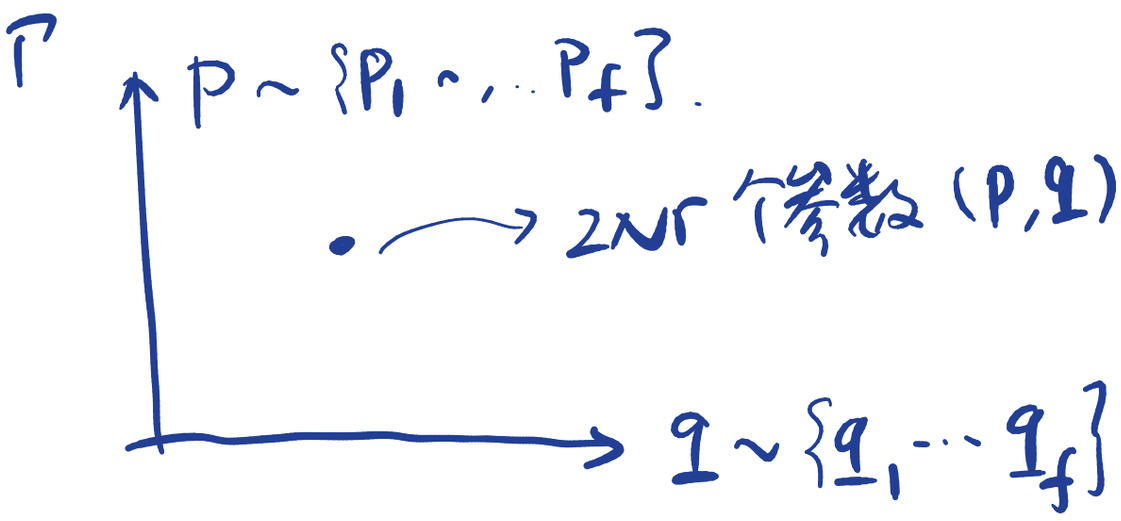
2017.11.29　　星期三.　　2次/13周.

系综理论的基本概念.

1. 系统的相空间

自由度 $f = Nr$.　r是单个粒子的自由度.



• $2Nr$个参数(p, q)对应系统的一个状态.

• 运动方程

$$\begin{cases} \dot{q}_i = \dfrac{\partial H}{\partial p_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{cases}$$

一条不自交的曲线.

• 能量曲面 $2Nr-1$维, $H(p, q) = E$.

没有绝对的孤立系 → 能层. 是$2Nr$维的.

• 代表点数密度.

$$d\Omega = dp\,dq \quad (2Nr\text{维})$$

状态密度: $\tilde{\rho}(p, q, t)\,d\Omega = dN$ 状态个数.

实际上取 $\dfrac{\tilde{\rho}}{N} \equiv \rho(p, q, t)$, $N \equiv \int dN = \int \tilde{\rho}\, d\Omega$

有 $\int \rho\, d\Omega = 1$　$\rho\, d\Omega$是在$d\Omega$内找到系统的概率.

$B(q, p)$ —— 是随时间变化的力学量, 要得到其对应的宏观量, 应对它进行长时间的平均 $\overline{B} = \int B(q, p) \dfrac{dt}{T}$

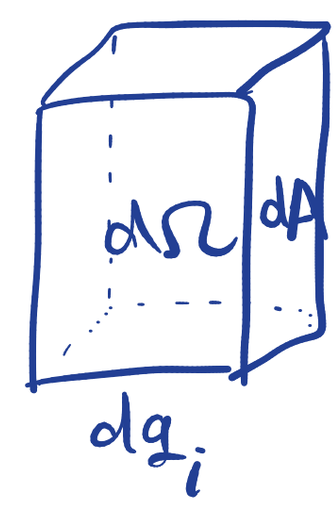
系综平均 $\overline{B} = \int B \rho \, d\Omega$

2、刘维定理

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i}\frac{dq_i}{dt} + \sum_i \frac{\partial \rho}{\partial p_i}\frac{dp_i}{dt}$$

$$= \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i}\frac{\partial H}{\partial p_i} - \sum_i \frac{\partial \rho}{\partial p_i}\frac{\partial H}{\partial q_i}$$

$$= \frac{\partial \rho}{\partial t} + \{\rho, H\}$$



$$dN = \frac{\partial \rho}{\partial t} dt\, d\Omega = \rho \dot{q}_i \, dt\, dA - \rho' \dot{q}_i' \, dt\, dA$$

$$\rho' = \rho(q_i + dq_i) = \rho(q_i) + \frac{\partial \rho}{\partial q_i} dq_i$$

$$\dot{q}_i' = \dot{q}_i + d\dot{q}_i$$

$$\therefore dN = \rho \dot{q}_i \, dt\, dA - \left[\rho \dot{q}_i + \frac{\partial \rho}{\partial q_i} dq_i \dot{q}_i + \rho d\dot{q}_i\right] dt\, dA$$

$$= -\frac{\partial}{\partial q_i}(\rho \dot{q}_i)\, d\Omega\, dt \qquad (d\Omega = dq_i\, dA)$$

$$\cdots \quad \frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

$d\Omega$运动

$d\Omega$不变，内部密度的变化

平衡态 $\rho(q, p)$ 与时间无关 $\Rightarrow \{\rho, H\} = 0$

$\{\rho, H\}=0$ 表明 ρ 只是守恒量 $E, \vec{p}, \vec{M}$ 的函数.

$$\rho_{12} = \rho_1 \cdot \rho_2$$

$$\ln \rho_{12} = \ln \rho_1 + \ln \rho_2$$

$$\ln \rho = c_1 + c_2 E + \underbrace{\vec{c}_3 \cdot \vec{P} + \vec{c}_4 \cdot \vec{M}}_{\text{不考虑}}$$

3. 微正则系综 (E, N, V) 不变

经典 存在涨落 $E < H(p,q) < E+\Delta E$

量子 不确定原理 $\Delta E \Delta t > h$

相格 h^{Nr} 是 $2Nr$ 维的. 从数学上也要求能量曲面是有厚度的.

否则能量曲面是 $2Nr-1$ 维不可能有相格.

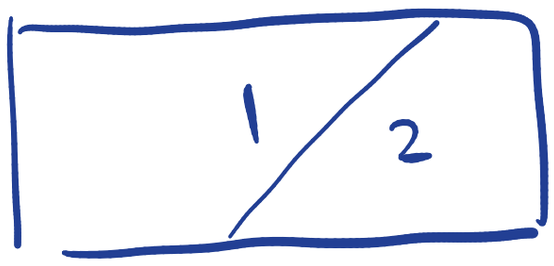
$$\rho = \begin{cases} \dfrac{1}{\Omega}, & E \le H \le E+\Delta E \\ 0, & H < E, \text{或 } H > E+\Delta E \end{cases}$$

Ω 是符合条件的代表点数.

经典: $$\Omega = \int_{E \le H \le E+\Delta E} \frac{dq\,dp}{h^{Nr}} = \int \delta(H-E) \frac{dq\,dp}{h^{Nr}}$$

量子: $$\frac{1}{N!\,h^{Nr}} \int \delta(H-E)\, d\Omega$$

下面求 U, S, P.



$$E = E_1 + E_2$$
$$N = N_1 + N_2$$
$$V = V_1 + V_2$$

先只考虑 N_i, V_i 不变 一情况.

$$\Omega(E) = \Omega_1(E_1)\Omega_2(E_2) = \Omega_1(E_1)\Omega_2(E-E_1)$$

$\frac{\partial \Omega}{\partial E_1} = 0$ 时达到平衡. $\Rightarrow \frac{\partial \Omega_1}{\partial E_1}\Omega_2 + \frac{\partial \Omega_2}{\partial E_2}(-1)\Omega_1 = 0$

$$\Rightarrow \frac{\partial \Omega_1}{\Omega_1 \partial E_1} = \frac{1}{\Omega_2}\frac{\partial \Omega_2}{\partial E_2} = \beta$$

又 $\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$ $\Rightarrow \boxed{S = k\ln\Omega}$

若 N, V 可变.

$$d\ln\Omega = \frac{\partial \ln\Omega}{\partial E}dE + \frac{\partial \ln\Omega}{\partial V}dV + \frac{\partial \ln\Omega}{\partial N}dN$$

$$\Leftrightarrow dS = \frac{\partial S}{\partial E}dE + \frac{\partial S}{\partial V}dV + \frac{\partial S}{\partial N}dN$$

又 $dS = \frac{1}{T}(dU + pdV - \mu dN)$

$$\Rightarrow -\mu = k\frac{\partial \ln\Omega}{\partial N}$$

$$p = k\frac{\partial \ln\Omega}{\partial V}$$

$$H \to \Omega \to \begin{cases} S \\ U \\ P \end{cases} \to \cdots$$

微正则系综的例子 —— 理想气体

$$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m}$$

$$\Omega = \frac{1}{h^{3N}} \int_{H \le E} dp\, dq$$

$$p_i = \sqrt{2mE}\; x_i$$

$$H =$$

N 维球体积的计算.