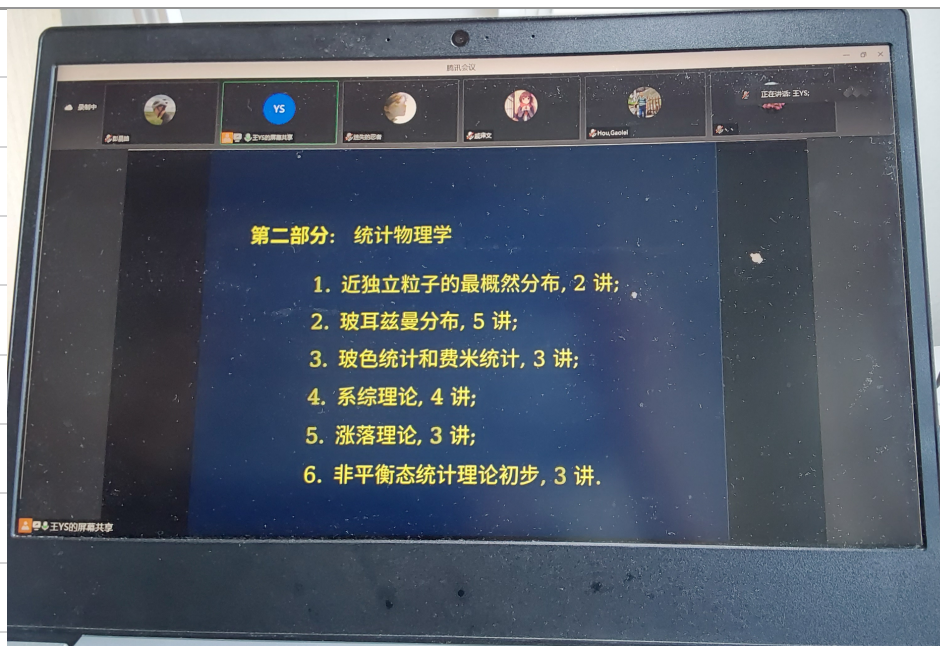


课程内容 忘记之前的热力学部分。



• 课程要求: 20% 作业 15% + 15% 两次阶段测试。

(Maxwell 关系式 (单元多项); 统计物理第一部分。(两次阶段测试)。

期末主要考统计物理部分。

第一讲。

• 第一章作业。(汪志诚) 思源学堂上有照片。

I 热力学简介。

• 理论架构: (从四大定律出发)

热力学宏观参量。

• 理论上的几个基本概念。

• 热力学 又指: 大量粒子组成的系统。其性质可唯一定义并完全被某宏观参量描述。

热力学极限 $N \rightarrow +\infty$, $V \rightarrow +\infty$, N/V 有限。

任务: 系统中热运动和其对宏观性质的影响。

组分 单元, 多元。

• 热力学系统 按能量交换 孤立系, 闭系, 开系。
分类 (无交换) (仅能量) (粒子与能量)

按性质分类。

均匀系统 任一各部分性质相同

不均匀系统 系统在一定界面上有突变

相: 不均匀系统的均匀部分

• 稳恒态: 稳恒指各个物理量不随时间改变。

• 平衡态性质: (也可用于判断) 1. 同相内各部分物性相同。(可以是无穷小呀)

2. 各部分物性不随时间变化。(稳恒态条件) (平衡态是特殊的稳恒态)

3. 系统内部无宏观流。(这一点重要)

• 弛豫时间: 从初态到平衡状态用的时间。

• 状态参量: 系统的其它宏观量可用状态函数表示出。
分为几何参量, 力学参量, 化学参量, 电磁参量。

热力学第一定律:

• $U_2 - U_1 - W = Q$

W : 外界对系统做的功: $\int -P dV = W$

Q : 系统从外界吸热。

热容和焓

• 定容比热: (V, T 是态参量)

$$C_V = \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$$

• 定压比热: (P, T 是态参量)

$$C_P = \frac{dQ}{dT} = \frac{dU + PdV}{dT} = \frac{\partial U}{\partial T} + P \frac{\partial V}{\partial T} \Big|_P$$

• 就此引入新的态函数 $H = U + PV$ $dQ = dH$ (定压时)

定压膨胀系数, 压强系数, 压缩系数。

• $\alpha = \frac{1}{V} \frac{\partial V}{\partial T} \Big|_P$ $\beta = \frac{1}{P} \frac{\partial P}{\partial T} \Big|_V$ $k_T = -\frac{1}{V} \frac{\partial V}{\partial P} \Big|_T$

• 考虑到有关系: $f(V, T, P) = 0$

$$\frac{\partial f}{\partial P} dP + \frac{\partial f}{\partial V} dV + \frac{\partial f}{\partial T} dT = 0$$

$$f_1 \quad f_2 \quad f_3$$

$$\alpha = \frac{1}{V} \left(-\frac{f_3}{f_2} \right) \quad \beta = \frac{1}{P} \left(-\frac{f_3}{f_1} \right) \quad k_T = -\frac{1}{V} \left(-\frac{f_1}{f_2} \right)$$

则:

$$\alpha = \beta \cdot k_T \cdot P$$

$$\left(\frac{\partial V}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P = -1$$

焦耳定律:

• $U = U(T, V)$ $dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial V} dV$ 则: $\frac{\partial U}{\partial T} \cdot \frac{\partial T}{\partial V} \cdot \frac{\partial V}{\partial U} = -1$ (代入算即可)

• 由上式, 可知 $\left(\frac{\partial U}{\partial V} \right)_T = - \left(\frac{\partial T}{\partial P} \right)_V \left(\frac{\partial P}{\partial U} \right)_T$

• $\left(\frac{\partial T}{\partial V} \right)_U$ 称为焦耳系数, 描述在内能不变的过程中温度随体积的变化率。

• 焦耳测得焦耳系数为 0。 $\left(\frac{\partial T}{\partial V} \right)_U = 0 \Rightarrow \left(\frac{\partial V}{\partial T} \right)_U = 0 \Rightarrow$ 焦耳定律: 气体内能只是温度的函数, 与体积无关。

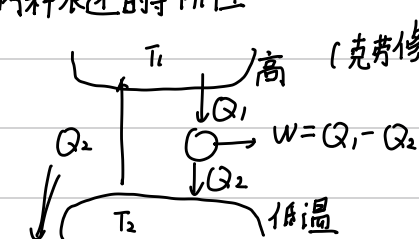
热力学第二定律

• 有两种不同的表述:

• 克劳修斯: 热量不可从低温源传向高温源而无其它变化。 — (1)

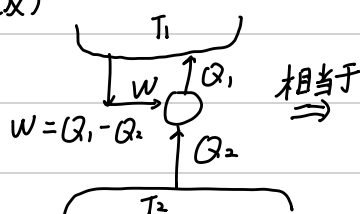
• 开尔文: 不可从单一热源吸热变有用功。 — (2)

• 两种表述的等价性:

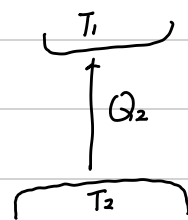


违反的循环

(克劳修斯表述被违反 $\rightarrow$ 开尔文也违反)



(开尔文被违反 $\rightarrow$ 克也被违反)



$\uparrow$ Q. 开尔文不被违反, 但克不一定违反!

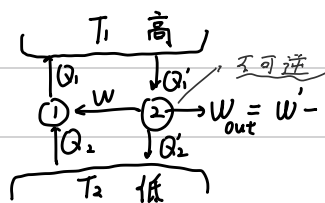
T_1 是低温, T_2 是高温. 时,

克并未被违反. 为何说他俩等价

卡诺定理

文字表述：工作于两个热源间的热机，可逆热机效率最高。
 推论：工作于两个确定温度之间的可逆热机，它们的效率相等。
 $\eta = 1 - \frac{T_2}{T_1}$

证明利用反证法：



①是可逆机

②是不可逆机 ($\eta_2 > \eta_1$)

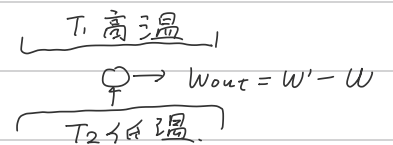
则可用②带动①逆运行。

$$\eta_1 = \frac{W}{Q_1}$$

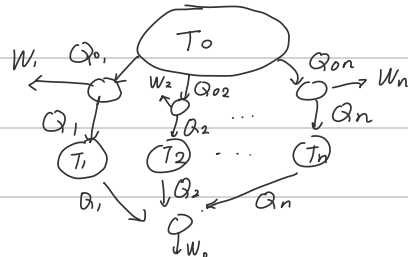
$$\eta_2 = \frac{W'}{Q_1'}$$

取 $Q_1 = Q_1'$; $\eta_2 > \eta_1 \Rightarrow W' > W$

相当于：



克劳修斯不等式



引入 n 个辅助热机。

$$Q_0 = \sum Q_{0i} = \sum Q_i \frac{T_0}{T_i} = T_0 \sum \frac{Q_i}{T_i}$$

$$W = W_0 + \dots + W_n$$

$$= (Q_1 + \dots + Q_n) + (Q_{01} - Q_1) + (Q_{02} - Q_2) + \dots$$

$$= \sum Q_{0i} = Q_0$$

$$\sum \frac{Q_i}{T_i} \leq 0$$

若一个热机在工作一个周期后回到初始状态，则 $\oint \frac{dQ}{T} \leq 0$ 。

可逆过程 $\oint \frac{dQ}{T} = 0$ 。

热力学第二定律的数学表示。

$$S_B - S_A = \int_A^B \frac{dQ}{T}$$

若 $A \rightarrow B$ 是不可逆过程， $B \rightarrow A$ 是可逆过程。

$$-(S_B - S_A) + \int_A^B \frac{dQ}{T} \leq 0$$

微分形式

$$dS \geq \frac{dQ}{T}$$

引入自由能，吉布斯函数。

由热力学第二定律的数学表示。

$$dQ \leq T dS$$

由热力学第一定律

$$dQ = dU - dW \Rightarrow -dW = dQ - dU$$

$$-dW \leq -dU + T dS$$

定义

$$F = U - TS$$

等温过程

$$F_B - F_A = dU - T dS \rightarrow -dF \geq -dW \quad dW \geq dF$$

等温过程 ($A \rightarrow B$) 自由能的减少量大于系统对外做功量
 等 T, 等 V 过程 ($A \rightarrow B$) 自由能永不增加!

$$G = U - TS + PV$$

等温，等压过程。

$$dG = dU - T dS + P dV$$

$$= dQ - T dS \leq 0$$

等温等压过程中 $dG \leq 0$ 。 (G 永不增加)

热力学基本方程 $dS = \frac{dU + P dV}{T}$

$A \rightarrow B$ 状态积分。

$$\int_A^B \frac{dQ}{T} = dS \rightarrow dS = \frac{dU + P dV}{T} \Rightarrow dU = T dS - P dV \quad dU = T dS + \sum_i Y_i dy_i \quad (1)$$

$dQ = dU - dW$ ，可逆过程中，只有体积变化功。

表示外界对系统做的功。

特性函数 (最重要的特性函数是 F, G)

特性函数是特殊的热力学函数。

$$F(T, V) = U - TS$$

$$dF = dU - T dS - S dT = dU - dQ - S dT$$

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_V$$

用它们的偏导可得其它的热力学函数。

$$G(T, P) = U - TS + PV$$

$$dG = V dP - S dT - (2)$$

Gibbs-Helmholtz equation

$$S = - \left(\frac{\partial F}{\partial T} \right)_V \quad P = - \left(\frac{\partial F}{\partial V} \right)_T$$

$$dG = V dP - S dT - (3)$$

$$S = - \left(\frac{\partial G}{\partial T} \right)_P \quad V = \left(\frac{\partial G}{\partial P} \right)_T$$

$$U = G - T\left(\frac{\partial G}{\partial T}\right)_P - P\left(\frac{\partial G}{\partial P}\right)_T$$

$\{T, V, P, U, S\}$

(1) (2) (3) 都是热力学基本方程。 $\begin{matrix} S & P & U \\ S & V & U \end{matrix}$ 是基本热力学函数, 可由 Gibbs-Helmholtz 方程求出。

□ Maxwell 关系. 他们源自热力学基本方程)

$$\begin{cases} dU = TdS - PdV \\ dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \end{cases} \Rightarrow \begin{cases} \left(\frac{\partial U}{\partial S}\right)_V = T & \left(\frac{\partial U}{\partial V}\right)_S = -P \\ \text{由于 } \frac{\partial^2 U}{\partial S \partial V} = \frac{\partial^2 U}{\partial V \partial S} \end{cases} \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\begin{cases} dF = d(U - TS) = -SdT - PdV \\ dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \end{cases} \Rightarrow \begin{cases} \left(\frac{\partial F}{\partial T}\right)_V = -S & \left(\frac{\partial F}{\partial V}\right)_T = -P \\ \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \end{cases}$$

$$\begin{cases} dG = d(U - TS + PV) = -SdT + VdP \\ dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \end{cases} \Rightarrow \begin{cases} \left(\frac{\partial G}{\partial T}\right)_P = -S & \left(\frac{\partial G}{\partial P}\right)_T = V \\ \Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \end{cases}$$

□ 例: T, V 做变量.

$$\begin{aligned} dU &= TdS - PdV \\ &= T\left(\frac{\partial S}{\partial T}\right)_V dT + (T\left(\frac{\partial S}{\partial V}\right)_T - P)dV \end{aligned}$$

$$\begin{aligned} C_V &= \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \\ \left(\frac{\partial U}{\partial V}\right)_T &= T\left(\frac{\partial S}{\partial V}\right)_T - P \\ &= T\left(\frac{\partial P}{\partial T}\right)_V - P \end{aligned}$$

黄色的是可测量的. 可用能观测到的 to derive variables unobservable!

□ 例 T, P 为自变量.

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \\ dH &= TdS + VdP \\ dH &= T\left(\frac{\partial S}{\partial T}\right)_P dT + (T\left(\frac{\partial S}{\partial P}\right)_T + V)dP \\ C_P &= \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \\ \left(\frac{\partial H}{\partial P}\right)_T &= T\left(\frac{\partial S}{\partial P}\right)_T + V \\ &= -T\left(\frac{\partial V}{\partial T}\right)_P + V \end{aligned}$$

□ 例. 物态方程与两种热容之间的关系.

$$\begin{cases} C_P - C_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V \\ S = S(T, V(T, P)) \end{cases}$$

$$C_P - C_V = T\left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P\right] - T\left(\frac{\partial S}{\partial T}\right)_V$$

$$= T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

↓ Maxwell Relation

$$= T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

← This relates to Equation Of State (EOS)

$$= TV\left(\frac{\partial P}{\partial T}\right)_V \alpha \quad \begin{matrix} \text{等压膨胀系数} & \text{等温压缩系数} & \text{等体压强系数} \\ \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P & k_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T & \beta \equiv \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \end{matrix}$$

$$= TVP \cdot \beta \cdot \alpha$$

$$= TVP \left(\frac{\alpha}{P k_T}\right) \alpha$$

$$= TV \frac{\alpha^2}{k_T}$$

$$f(T, V, P) = 0 \quad (\text{EOS}) \Rightarrow f_1 dT + f_2 dV + f_3 dP = 0$$

$$\alpha = \frac{1}{V} \left(-\frac{f_1}{f_2}\right) \quad k_T = -\frac{1}{V} \left(-\frac{f_2}{f_3}\right) \quad \beta = \frac{1}{P} \left(-\frac{f_1}{f_3}\right)$$

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_P = -1$$

$$\alpha = P k_T \beta \quad \text{or} \quad \beta = \frac{\alpha}{P k_T}$$

0 Jacobi determinant and it's some usage

1°

$$k_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_s$$

$$k_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$\frac{k_s}{k_T} = \frac{\left(\frac{\partial V}{\partial P} \right)_s}{\left(\frac{\partial V}{\partial P} \right)_T} = \frac{\frac{\partial(V, S)}{\partial(P, S)}}{\frac{\partial(V, T)}{\partial(P, T)}} = \frac{\frac{\partial(V, S)}{\partial(V, T)}}{\frac{\partial(P, S)}{\partial(P, T)}} = \frac{\left(\frac{\partial S}{\partial T} \right)_V}{\left(\frac{\partial S}{\partial T} \right)_P} = \frac{C_V}{C_P}$$

2°

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P = T \frac{\frac{\partial(S, P)}{\partial(T, P)}}{\frac{\partial(T, P)}{\partial(T, V)}} = T \frac{\frac{\partial(S, P)}{\partial(T, V)}}{\left(\frac{\partial P}{\partial V} \right)_T} = T \frac{\left(\frac{\partial S}{\partial T} \right)_V \left(\frac{\partial P}{\partial V} \right)_T - \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial P}{\partial T} \right)_V}{\left(\frac{\partial P}{\partial V} \right)_T}$$

$$= C_V - T \frac{\left(\frac{\partial P}{\partial T} \right)_V^2}{\left(\frac{\partial P}{\partial V} \right)_T}$$

(A.10) ↓

$$\frac{\partial(u, v)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} \quad \left(\frac{\partial u}{\partial x} \right)_y = \frac{\partial(u, y)}{\partial(x, y)} \quad (A.11)$$

$$\frac{\partial(u, v)}{\partial(x, y)} = -\frac{\partial(v, u)}{\partial(x, y)} \quad (A.12)$$

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(r, s)} \frac{\partial(r, s)}{\partial(x, y)} \quad (A.13)$$

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{1}{\frac{\partial(x, y)}{\partial(u, v)}} \quad (A.14)$$

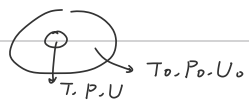
$$\left(\frac{\partial u}{\partial x} \right)_y = \frac{\partial(u, y)}{\partial(x, y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ 0 & 1 \end{vmatrix} = \left(\frac{\partial u}{\partial x} \right)_y$$

0 孤立系的热判据:

孤立系, 由热二: $dS \geq \frac{dQ}{T}$, 且 $dU=0$ $dV=0$

热判据: $\Delta S < 0$ Maximal

例:



$$dU = Tds - PdV$$

$$\Delta \tilde{S} = \Delta S + \Delta S_0 = dU(\frac{1}{T} - \frac{1}{T_0}) + dV(\frac{P}{T} - \frac{P_0}{T_0})$$

$$P = P_0 \quad T = T_0$$

S, U, V 是广延量, $(\frac{\partial S}{\partial U}, \frac{\partial S}{\partial V})$ 是强度量, $\frac{\partial^2 S}{\partial U^2}, \frac{\partial^2 S}{\partial V^2} \sim \frac{1}{N}$. $\delta^2 \tilde{S} = \delta^2 S + \delta^2 S_0 \approx \delta^2 S$

$$\delta^2 S = (\frac{\partial}{\partial U}(\frac{\partial S}{\partial U}))_V \delta U + \frac{\partial}{\partial V}(\frac{\partial S}{\partial U})_V \delta V + (\frac{\partial}{\partial U}(\frac{\partial S}{\partial V}))_V \delta U + \frac{\partial}{\partial V}(\frac{\partial S}{\partial V})_V \delta V$$

由于:

$$TdS = dU + PdV$$

$$(\frac{\partial S}{\partial U})_V = \frac{1}{T} \quad (\frac{\partial S}{\partial V})_U = \frac{P}{T}$$

$$\delta^2 S = (\frac{\partial}{\partial U}(\frac{1}{T}))_V \delta U + \frac{\partial}{\partial V}(\frac{1}{T})_V \delta V + (\frac{\partial}{\partial U}(\frac{P}{T}))_V \delta U + \frac{\partial}{\partial V}(\frac{P}{T})_V \delta V$$

$$= \delta(\frac{1}{T}) \cdot \delta U + \delta(\frac{P}{T}) \delta V$$

$$= -\frac{C_V}{T^2} (\delta T)^2 + \frac{1}{T} (\frac{\partial P}{\partial V})_T (\delta V)^2 < 0$$

$$\left\{ \begin{aligned} \delta U &= (\frac{\partial U}{\partial T})_V \delta T + (\frac{\partial U}{\partial V})_T \delta V \\ &= C_V \delta T + (T(\frac{\partial P}{\partial T})_V - P) \delta V \end{aligned} \right. \quad \begin{aligned} dU &= TdS - PdV \\ S &= S(T, V) \end{aligned} \quad \text{Maxwell Relation.}$$

Require: $C_V > 0$ $(\frac{\partial P}{\partial V})_T < 0$

0 等温等压系统热力学平衡判据.

$$F = U - TS \quad dF = dQ + dW - TdS - SdT = dQ - TdS \leq 0 \quad \text{where } dS \geq dQ/T$$

热力学平衡判据:

$$\Delta F \geq 0$$

✓ minimal

0 等温等压系统热力学平衡判据.

$$G = U - TS + PV \quad \delta G = dQ + dW - TdS + PdV = dQ - TdS \leq 0$$

$$\Delta G \geq 0$$

✓ minimal

单元系的相变理论.

0 特性函数与热力学基本方程.

热力学基本方程

$$\begin{aligned} F &= U - TS \\ G &= nG_m(T, P) \quad G = U - TS + PV \\ dG &= -SdT + VdP + \mu dn \quad \rightarrow \quad \mu = \left(\frac{\partial G}{\partial n} \right)_{T, P} = G_m. \\ dF &= d(G - PV) = -SdT - PdV + \mu dn \\ dU &= d(G - PV + TS) = TdS - PdV + \mu dn \end{aligned}$$

▽ 定义新的热力学特性函数. 巨热力学势.

$$J = F - \mu n$$

$$dJ = -SdT - PdV - nd\mu$$

热力学量: $S = -\left(\frac{\partial J}{\partial T} \right)_{V, \mu} \quad P = -\left(\frac{\partial J}{\partial V} \right)_{T, \mu} \quad n = -\left(\frac{\partial J}{\partial \mu} \right)_{T, V}$

0 单元系复相平衡条件.

▽ 单元指一个化学组元. 复相指有多个均匀的部分.

$$U^\alpha + U^\beta = C \quad V^\alpha + V^\beta = C \quad n^\alpha + n^\beta = C$$

$$\delta U^\alpha + \delta U^\beta = 0$$

$$\delta V^\alpha + \delta V^\beta = 0$$

$$\delta n^\alpha + \delta n^\beta = 0$$

$$dU = TdS - PdV + \mu dn$$

$$\delta S = \delta S^\alpha + \delta S^\beta = \delta U^\alpha \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) + \delta V^\alpha \left(\frac{P^\alpha}{T^\alpha} - \frac{P^\beta}{T^\beta} \right) - \delta n^\alpha \left(\frac{\mu^\alpha}{T^\alpha} - \frac{\mu^\beta}{T^\beta} \right)$$

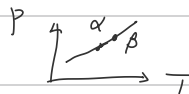
$$T^\alpha = T^\beta, \quad P^\alpha = P^\beta, \quad \mu^\alpha = \mu^\beta$$

▽ Clapeyron Equation

↓ 由于G是广延量.

$$\mu = \frac{G}{n} = G_m$$

$$d\mu = dG_m = -S_m dT + V_m dP$$



相变平衡条件: $\mu^\alpha = \mu^\beta$.

$$-S_m^\alpha dT + V_m^\alpha dP = -S_m^\beta dT + V_m^\beta dP$$

$$\frac{dP}{dT} = \frac{S_m^\alpha - S_m^\beta}{V_m^\alpha - V_m^\beta} \quad \text{定义: 相变潜热 } L = T(S_m^\alpha - S_m^\beta)$$

$$\frac{dP}{dT} = \frac{L}{T(V_m^\alpha - V_m^\beta)}$$

▽ 相变分类.

1类. 如上, $\mu^\alpha = \mu^\beta$. $S_m^\alpha \neq S_m^\beta$ $V_m^\alpha \neq V_m^\beta$

2类. $\mu^\alpha = \mu^\beta$. $S_m^\alpha = S_m^\beta$, $V_m^\alpha = V_m^\beta$ $\rightarrow \frac{dP}{dT} = \frac{\alpha^{(2)} - \alpha^{(1)}}{k_T^{(2)} - k_T^{(1)}}$ 埃伦菲斯特方程.

基本热力学函数的确定

◦ T, V 为变量

物态方程 $P = P(T, V)$

内能:

$$dU = TdS - PdV = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right)dV$$

$$= C_V dT + \left(T\left(\frac{\partial S}{\partial V}\right)_T - P\right)dV$$

$$= C_V dT + \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)dV \quad \text{Maxwell 关系}$$

$$U = \int C_V dT + \int \left(T\left(\frac{\partial P}{\partial T}\right)_V - P\right)dV + U_0$$

焓:

由物态方程决定

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \frac{1}{T} C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$S = \int \frac{1}{T} C_V dT + \int \left(\frac{\partial P}{\partial T}\right)_V dV + S_0$$

◦ T, P 为变量 (一般用这个, 因为液体、固体的 C_V 不好测量)

物态方程: $V = V(T, P)$

焓:

$$dH = TdS + VdP$$

$$= T\left(\frac{\partial S}{\partial T}\right)_P dT + \left(T\left(\frac{\partial S}{\partial P}\right)_T + V\right)dP \quad \text{Maxwell 关系}$$

$$= C_P dT + \left(-T\left(\frac{\partial V}{\partial T}\right)_P + V\right)dP$$

$$H = \int C_P dT + \int \left(-T\left(\frac{\partial V}{\partial T}\right)_P + V\right)dP + H_0$$

内能:

$$U = H - PV$$

焓:

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$

$$S = \int \frac{C_P}{T} dT - \int \left(\frac{\partial V}{\partial T}\right)_P dP + S_0$$

◦ 理想气体的基本热力学函数

$$PV_m = RT \quad V_m = \frac{RT}{P}$$

焓:

$$\rightarrow = -T \cdot \frac{R}{P} = -V_m$$

$$H_m = \int C_{P,m} dT + \int \left(-T\left(\frac{\partial V_m}{\partial T}\right)_P + V_m\right)dP + H_0$$

$$= \int C_{P,m} dT + H_{m,0}$$

内能:

$$U_m = H_m - PV_m = \int C_{P,m} dT - RT + H_{m,0}$$

焓:

$$S_m = \int \frac{C_{P,m}}{T} dT - \int \left(\frac{\partial V_m}{\partial T}\right)_P dP + S_{m,0}$$

$$= \int \frac{C_{P,m}}{T} dT - \int \frac{R}{P} dP + S_{m,0}$$

$$= \int \frac{C_{P,m}}{T} dT - R \ln(P) + S_{m,0}$$

Gibbs 自由能:

$$\begin{aligned} G_m &= U_m - TS_m + PV_m \\ &= \underbrace{\left(\int C_{p,m} dT - RT + H_{m,0} \right)}_{U_m} - \underbrace{T \int \frac{C_{p,m}}{T} dT + RT \ln(P) - TS_{m,0}}_{-TS_m} + RT \\ &= \int C_{p,m} dT - T \int \frac{C_{p,m}}{T} dT + RT \ln(P) - TS_{m,0} + H_{m,0} \\ &= RT \left(\underbrace{\frac{1}{RT} \int C_{p,m} dT - \frac{1}{R} \int \frac{C_{p,m}}{T} dT - \frac{1}{R} S_{m,0} + \frac{1}{RT} H_{m,0} + \ln(P)}_{\varphi(T,P)} \right) \\ &= RT(\varphi + \ln P) \end{aligned}$$

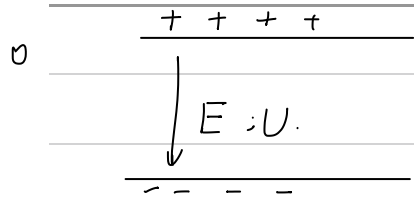
理想气体 $C_{p,m}$ 与 P 无关且为 const!

$$\begin{aligned} \varphi(T,P) = \varphi(T) &= \frac{1}{R} C_{p,m} - \frac{C_{p,m}}{R} \ln(T) - \frac{1}{R} S_{m,0} + \frac{H_{m,0}}{RT} \\ &= \frac{H_{m,0}}{RT} - \frac{C_{p,m}}{R} \ln(T) + \frac{C_{p,m} - S_{m,0}}{R} \end{aligned}$$

用 c 代表摩尔热容; s_0 代表 $\sim$; h_0 代表 $\sim$

$$\varphi(T,P) = \frac{h_0}{RT} - \frac{C_p}{R} \ln(T) + \frac{C_p - S_0}{R} = \varphi(T)$$

电介质的热力学 / 磁介质的热力学.



当将 dq 的电量加入到电容器中.

外界做功:

$$dW = U dq = E \cdot l \cdot dq = E \cdot l \cdot A \cdot d\epsilon.$$

Gauss 定理.

$$\epsilon = D$$

$$dW = l \cdot A \cdot E \cdot dD$$

$$= V \cdot E dD$$

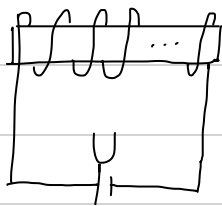
电介质学知识:

$$D = \epsilon_0 E + P$$

$$dW = V \cdot E (\epsilon_0 dE + dP) = V \cdot d(\frac{1}{2} \epsilon_0 E^2) + V E dP.$$

一般无此项

磁介质.



$$U = \frac{d\Phi}{dt} = N \frac{d}{dt} (A \cdot B)$$

磁感应强度矢量.

安培环路定理:

$$\mathcal{H}l = N \cdot I \quad I = \mathcal{H} \cdot \frac{l}{N}.$$

做功, 外界做功:

$$dW = U \cdot I dt = N \cdot d(A \cdot B) \cdot \mathcal{H} \cdot \frac{l}{N} = \mathcal{H} \cdot l \cdot A \cdot dB = V \cdot \mathcal{H} dB.$$

磁化强度矢量.

$$B = \mu_0 (\mathcal{H} + M)$$

$$dW = V \mu_0 (d\mathcal{H} + dM) \cdot \mathcal{H}$$

$$= V \cdot d(\frac{1}{2} \mu_0 \mathcal{H}^2) + V \cdot \mu_0 \mathcal{H} \cdot dM$$

一般无此项.

热力学基本方程:

$$dU = T dS + \mu_0 V \cdot \mathcal{H} \cdot dM.$$

取: $m = V \cdot M.$

$$dU = T dS + \mu_0 \mathcal{H} \cdot dm.$$

$$P \rightarrow -\mu_0 \mathcal{H} \quad V \rightarrow m.$$

Maxwell 关系改写: $PV = TS$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$\Downarrow$

$$-\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial m}{\partial T}\right)_H$$

$$\left(\frac{\partial S}{\partial H}\right)_T = \mu_0 \left(\frac{\partial m}{\partial T}\right)_H$$

定压热容改写:

$$dH = TdS + VdP$$

$$= T\left(\frac{\partial S}{\partial T}\right)_P dT + (T\left(\frac{\partial S}{\partial P}\right)_T + V)dP$$

$$C_H = C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$= T\left(\frac{\partial S}{\partial T}\right)_H$$

○ 石兹制冷效应: 指 (H, S) 为变量, S 不变, $H \downarrow$, $T \downarrow$.

求: $\left(\frac{\partial T}{\partial H}\right)_S$!

关系: $f(S, T, H) = 0 \Rightarrow f_1 dS + f_2 dT + f_3 dH = 0$.

$$\left(\frac{\partial T}{\partial H}\right)_S = -\frac{f_3}{f_2} = -\left(-\frac{f_3}{f_1}\right)\left(-\frac{f_1}{f_2}\right) = -\left(\frac{\partial S}{\partial H}\right)_T \cdot \frac{1}{\left(\frac{\partial S}{\partial T}\right)_H}$$

$$= -\left(\frac{\partial S}{\partial H}\right)_T \cdot \frac{T}{C_H}$$

$$= -\mu_0 \frac{T}{C_H} \cdot \left(\frac{\partial m}{\partial T}\right)_H$$

若石兹介质服从居里定律

$$m = \frac{C_V}{T} H$$

则: $\left(\frac{\partial m}{\partial T}\right)_H = -\frac{C_V}{T^2} H$

$$\left(\frac{\partial T}{\partial H}\right)_S = \mu_0 \frac{C_V}{C_H T} \cdot H > 0$$

$S = C$; $H \downarrow$; $T \downarrow$. 可得 1 K 以下的低温.

○ 石兹致伸缩效应 和 压石兹效应 间的关系

$$\left(\frac{\partial V}{\partial H}\right)_{T,P}$$

$$\left(\frac{\partial m}{\partial P}\right)_{T,H}$$

热力学基本方程

$$dU = TdS - PdV + \mu_0 H \cdot dm$$

$$dG = -SdT + VdP - \mu_0 m \cdot dH$$

Maxwell 关系:

$$\left(\frac{\partial V}{\partial H}\right)_{T,P} = -\mu_0 \left(\frac{\partial m}{\partial P}\right)_{T,H}$$

第四章 多元系的复相平衡和化学平衡, 热力学第三定理.

(实际上在研究单相多元系)

4.1 多元系的热力学函数和热力学方程。(本节用的变量为 $T, P, n_1, \dots, n_k$) ($n_1, \dots, n_k$ 表示不同化学组分的组元)

$$V = \sum_i n_i \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j} = \sum_i n_i v_i$$

$$U = \sum_i n_i \left(\frac{\partial U}{\partial n_i} \right)_{T, P, n_j} = \sum_i n_i u_i$$

$$S = \sum_i n_i \left(\frac{\partial S}{\partial n_i} \right)_{T, P, n_j} = \sum_i n_i s_i$$

$$G = \sum_i n_i \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} = \sum_i n_i \mu_i \quad \mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j} \text{ 称为 } i \text{ 组元的化学势.}$$

多元系的热力学基本方程和特性函数自变量的考察:

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \quad (G \text{ 是特性 Function, 它的自变量是 } T, P, n_i)$$

$$dU = dG + d(TS) - d(PV) = TdS - PdV + \sum_i \mu_i dn_i \quad (\text{热力学基本方程}) \quad (\text{自变量 of } U \text{ 为 } S, V, n)$$

$$dF = dG - d(PV) = -SdT - PdV + \sum_i \mu_i dn_i \quad (F \text{ 是特性 Function, 自变量是 } T, V, n)$$

均匀系的吉布斯关系:

均匀系是指单相的, or 多相中的一个相。(但是是多元的).

Gibbs关系是这样引入的.

对于单相多元系,

$$dG = d(n_i \mu_i) = \mu_i dn_i + n_i d\mu_i = -SdT + VdP + \mu_i dn_i$$

则

$$SdT - VdP + n_i d\mu_i = 0$$

这个微分关系就叫 Gibbs 关系! (实际上在说: $P, T, n_1, \dots, n_k$ 中只有 $k+1$ 个独立量).

对于多元复相系, $dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha$, $V = \sum V^\alpha$, $U = \sum U^\alpha$, $S = \sum S^\alpha$, $n_i = \sum n_i^\alpha$.

等压时 $H = \sum H^\alpha$, 等 T 时, $F = \sum F^\alpha$ 等 T, P 时, $G = \sum G^\alpha$

4.2 多元系的复相平衡。(研究的是多元两相系).

多元系相变平衡条件. 两相的系统 (相由 α 和 β 表示不同的相)! T, P 不变且已平衡!

$$\alpha \text{ 相的 } G \text{ 的变化: } dG^\alpha = -S^\alpha dT - V^\alpha dP + \sum_i \mu_i^\alpha dn_i^\alpha$$

$$dG^\alpha = \sum_i \mu_i^\alpha dn_i^\alpha$$

β 相:

$$dG^\beta = \sum_i \mu_i^\beta dn_i^\beta$$

分子总数的守恒条件:

$$dn_i^\alpha + dn_i^\beta = 0$$

总的 G 改变

$$dG = dG^\alpha + dG^\beta = \sum_i (\mu_i^\alpha - \mu_i^\beta) dn_i^\alpha \stackrel{\text{平衡态的 } G \text{ 最小 (定 } T, P)}{=} 0 \implies \mu_i^\alpha = \mu_i^\beta \quad (\text{多元系的相变平衡条件})$$

自然界存在半透膜. 若半透膜只让 i 组元通过, 则: 平衡时两相温度必相同. i 组元的化学势在两相中也必相同. 但两相压强虽可不同, 其它组元化学势可不同.

4.3 吉布斯相律.

k 元 φ 相系中 可以独立改变的强度量的数目.

各相热平衡条件:

$$T^1 = T^2 = \dots = T^\varphi$$

各相力学平衡条件:

$$p^1 \dots = p^q$$

相变平衡:

$$\mu_i^1 \dots = \mu_i^q \quad (i=1 \dots k)$$

上平3个条件相当于

$(q-1) \cdot (k+2)$ 个约束:

则自由强度量数目: (下面的 $k+1$ 相当于某一相中的变量 $T, p, \frac{n_1}{n}, \frac{n_2}{n}, \dots, \frac{n_k}{n}$ (共 $k+1$ 个))

$$f = (k+1) \cdot q - (k+2) \cdot (q-1)$$

—— 4.5 化学平衡条件: (研究多元系, 定义了反应度, 讨论反应平衡条件)

研究的是 多元系 (各组分可以发生化学反应).

• 首先表示化学反应:

$\sum \nu_i A_i = 0$ 表示化学反应 (A_i 是反应物 or 生成物). ($\nu < 0$ 表示反应物).

比如说: $2H_2O - 2H_2 - O_2 = 0$

• 接下来讨论反应平衡条件:

体系 Gibbs Function 的改变量: $dG = \sum \mu_i dn_i$.

$$dG = \sum \mu_i dn_i = \delta n \cdot \sum \nu_i \mu_i$$

要求: $dG = 0$

$$\sum \nu_i \mu_i = 0$$

• 反应度的定义:

按照上面写的化学反应方程式: ($\nu_i A_i = 0$)

则反应过后的物质的量写为:

$$n_i = n_i^0 + \nu_i \cdot \Delta n$$

要使: $n_i > 0$ ($i=1 \dots k$); 则: $\Delta n \in [n_b, n_a]$

反应度:

$$\varepsilon = \frac{\Delta n - n_b}{n_a - n_b}$$

—— 4.6 混合理想气体的性质.

研究对象: 混合气体, 共有 k 个组分. (各组分物质的量 $n_1 \dots n_k$).

研究对象: 混合气体, 共有 k 个组分, (各组分物质的量分别为 $n_1 \dots n_k$)

• Dalton 分压定理: 只适用于理想气体.

P_i 是 i 组分的分压, 是物质的量为 n_i 的 i 组分单独存在且与混合气体有相同体积和温度时的压强.

$$P = \sum P_i$$

↓ 推出 (混合理想气体的物态方程)

$$P = \sum_i \frac{n_i}{V} RT \Rightarrow PV = \sum_i (n_i) RT \Rightarrow P_i = P \cdot \frac{n_i}{\sum_i n_i}$$

• 纯 i 组元理想气体的化学势:

H 的全微分: 考虑到 $dH = dU + d(PV) = TdS + VdP$, 我们以 T, P 为变量.

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \\ &= T \left(\left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \right) + V dP \\ &= T \left(\frac{\partial S}{\partial T}\right)_P dT + \left(T \left(\frac{\partial S}{\partial P}\right)_T + V \right) dP \end{aligned}$$

如果定义定压热容 C_P 为 $C_P = (\partial H / \partial T)_P$; 则:

$$C_P = \frac{\partial H}{\partial T} = T \left(\frac{\partial S}{\partial T}\right)_P$$

则 S 的全微分可以写为:

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \\ &= \frac{C_P}{T} dT + \frac{\partial(V, P)}{\partial(P, T)} dP \\ &= \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP \end{aligned}$$

则在 (T, P) 状态下的 S 可以用积分表示为:

$$S = \int \frac{C_P}{T} dT - \int \left(\frac{\partial V}{\partial T}\right)_P dP + S_0 \quad - (1)$$

同样地, 在 (T, P) 状态下的 H 可以表示为:

$$\begin{aligned} H(T, P) &= \int \left(\frac{\partial H}{\partial T}\right)_P dT + \int \left(\frac{\partial H}{\partial P}\right)_T dP = \int C_P dT + \int \left(T \left(\frac{\partial S}{\partial P}\right)_T + V \right) dP \\ &= \int C_P dT + \left(V - \left(\frac{\partial V}{\partial T}\right)_P T \right) dP + H_m. \quad - (2) \end{aligned}$$

$\frac{\partial(S, T)}{\partial(P, T)} = -\frac{\partial(P, V)}{\partial(P, T)} = -\left(\frac{\partial V}{\partial T}\right)_P$

上面写的(1)与(2)都是有普适性的!!

对于理想气体: $PV = n \cdot R \cdot T$.

则: 1 mol 的物质对应的焓与 1 mol 物质对应的焓 S,

由于:

$$\left(\frac{\partial V_m}{\partial T}\right)_P = \left(\frac{\partial \left(\frac{RT}{P}\right)}{\partial T}\right)_P = \frac{R}{P} = \frac{V_m}{T}$$

则:

$$H_m(T, P) = \int C_P dT + H_{m0}$$

$$S_m(T, P) = \int \frac{C_P}{T} dT - R \ln P + S_{m0}$$

$$\begin{aligned} G_m(T, P) &= H_m(T, P) - TS_m = \int C_P dT - T \int \frac{C_P}{T} dT + RT \ln P + TS_{m0} + H_{m0} \\ &= RT(\varphi(T) + \ln P) \quad \leftarrow \text{通常将 } G \text{ 写为这个形式。} \end{aligned}$$

$$\varphi(T) = \frac{h_0}{RT} - \frac{C_P}{R} \ln(T) + \frac{C_P - S_0}{R} \quad \leftarrow (2.416 \text{ 田去 } m \neq 0)$$

$$\varphi(T) = \left(-\frac{S_{m0}}{R} + \frac{1}{RT} \int_0^T C_P dT - \frac{1}{R} \int_0^T \frac{C_P}{T} dT \right) - \text{简化版}$$

$$\varphi(T) = \left(-\frac{S_{m0}}{R} + \frac{1}{RT} \int C_P dT - \frac{1}{R} \int \frac{C_P}{T} dT + \frac{H_{m0}}{RT} \right)$$

积分常数指 T, P=0 时的热力学量.

• 混和理想气体的总焓, 总内能和总焓.

实验: 一个能通过半透膜的组元, 它在膜两边的分压在平衡时相等.

$$\mu_i = \mu'_i(T, P_i) \quad \leftarrow \text{外}$$

$$\mu_i = RT(\varphi_i + \ln P_i) = RT(\varphi_i + \ln(x_i P)) \quad \leftarrow \text{内}$$

$$\varphi_i(T) = \frac{h_{0i}}{RT} - \frac{C_{Pi}}{R} \ln T + \frac{C_{Pi} - S_{0i}}{R}$$

$$\text{总 } G: G = \sum_i n_i \mu_i = \sum_i n_i RT(\varphi_i(T) + \ln(x_i P))$$

$$\downarrow U = G + TS - PV = G - T \frac{\partial G}{\partial T} - P \frac{\partial G}{\partial P}$$

$$\downarrow H = G - T \frac{\partial G}{\partial T}$$

$$= G + TS$$

$$\downarrow dG = -SdT + VdP + \sum_i \mu_i dn_i$$

$$\leftarrow S = -\frac{\partial G}{\partial T}$$

$$U = \sum_i n_i \left(\int C_{Vi} dT + U_{i0} \right)$$

$$H = \sum_i n_i \left(\int C_{Pi} dT + H_{i0} \right)$$

$$S = \sum_i n_i \left(\int \frac{C_{Pi}}{T} dT - R \ln P + S_{i0} \right) - R \sum_i n_i \ln x_i$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = -\sum_i n_i R \left(\frac{h_{0i}}{RT} - \frac{C_{Pi}}{R} \ln T + \frac{C_{Pi} - S_{0i}}{R} + \ln(x_i P) \right)$$

$$- \sum_i n_i R T \left(- \frac{h_{0i}}{R T^2} - \frac{C_{pi}}{R} \frac{1}{T} \right)$$

$$= \sum_i n_i \left(- \frac{h_{0i}}{T} + C_{pi} \ln(T) - C_{pi} + S_{0i} - R \ln(x_i P) + \frac{h_{0i}}{T} + C_{pi} \right)$$

$$= \sum_i n_i \left(C_{pi} \ln(T) - R \ln(x_i P) + S_{0i} \right)$$

$$= \sum_i n_i \left(C_{pi} \ln(T) - R \ln(P) + S_{0i} \right) - \sum_i n_i R \ln(x_i)$$

$$= \sum_i n_i S_{i,m}(T, P) - \sum_i n_i R \ln(x_i)$$

○ Gibbs 定律:

在两种不同的气体相混合时, 总体系的焓不只是各个部分^{单独存在, 且具有混合理想气体的温度和压力时的}的相加, 还包括了^焓
 $-R \sum_i n_i \ln x_i$ 项!

但同种气体混合时没有这一项!

4.7 理想气体的化学平衡

由4.5中的化学平衡条件, 且由4.6 $\mu_i(T, P) = \mu(T, \chi_i P)$

$$\sum \nu_i \cdot R \cdot T \cdot (\ln(P_i) + \varphi_i(T)) = 0$$

$$T \cdot R \cdot (\ln(\prod_i P_i^{\nu_i}) + \sum \nu_i \varphi_i(T)) = 0$$

若: $\ln(K_P(T)) = -\sum \nu_i \varphi_i(T)$ ($K_P(T)$ 称为化学反应的定压平衡常量).

$$\prod_i P_i^{\nu_i} = K_P(T) \quad \leftarrow \text{质量作用定理; 化学反应的定压平衡常量 (平衡常量)}$$

若用 $P_i = \chi_i P$ 代入得:

$$\prod_i \chi_i^{\nu_i} = P^{-\sum \nu_i} K_P(T) = K(P, T)$$

• 定压平衡常量的一般表达式:

$$-\ln K_P(T) = \sum \nu_i \varphi_i(T) = \sum \nu_i \left(\frac{\Delta G_{f,i}^\circ}{R} + \frac{1}{R} \int_{T^\circ}^T C_{p,i} dT - \frac{1}{R} \int_{T^\circ}^T \frac{C_{p,i}}{T} dT + \frac{H_{f,i}^\circ}{RT} \right)$$

$$\ln K_P(T) = \sum \nu_i \left(-\frac{h_{f,i}^\circ}{R} \cdot \frac{1}{T} + \frac{S_{0,i}^\circ}{R} - \frac{C_{p,i}^\circ}{R} + \frac{1}{R} C_{p,i} \cdot \ln T \right) \quad (\text{认为 } C_{p,i} \text{ 为常数!})$$

$$= -A \cdot \frac{1}{T} + B + C \cdot \ln T$$

$$A = \sum \nu_i \frac{h_{f,i}^\circ}{R} \quad B = \sum \nu_i (S_{0,i}^\circ - C_{p,i}^\circ) \cdot \frac{1}{R} \quad C = \sum \nu_i C_{p,i}^\circ \cdot \frac{1}{R}$$

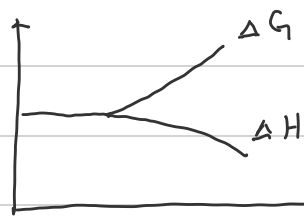
$$= \frac{\Delta H^\circ}{RT}$$

4.8 热力学第三定律:

$$\lim_{T \rightarrow 0} (\Delta S)_T = 0; \text{ This means: } \left(\frac{\partial S}{\partial P} \right)_T = 0 \quad \left(\frac{\partial S}{\partial V} \right)_T = 0!$$

• Nernst 的表述: 凝聚系的熵在等温过程中的改变随热力学温度趋于0.
不可能通过有限的步骤使一个物体冷却到热力学0度。

• Nernst定理的一个推论:



(等温过程中)

ΔG 和 ΔH 在 $T \rightarrow 0$ 时趋于同一固定的值且 ΔG 与 ΔH 与 T 轴的斜率都趋于0:

proof 由 ΔG 的定义:

$$\Delta G = \Delta H - T \Delta S \quad (G = H - TS)$$

$T \rightarrow 0$ 时有:

$$\Delta G = \Delta H - (1) \quad \frac{\Delta H - \Delta G}{T} = \Delta S \quad - (2)$$

由 (1): $\Delta G = \Delta H$ ($T \rightarrow 0$ 时)

由 (2):

$$\lim_{T \rightarrow 0} \frac{\partial(\Delta H)}{\partial T} = \frac{\partial(\Delta G)}{\partial T} \quad (\text{若 } \lim_{T \rightarrow 0} (\Delta S)_T = 0)$$

为什么?

而利用:

$$\frac{\partial G}{\partial T} = -S$$

$$\text{则: } \frac{\partial(\Delta G)}{\partial T} = -(\Delta S)_T = 0$$

得上: $(\Delta H)_T = (\Delta G)_T$

$$\lim_{T \rightarrow 0} \text{时: } \frac{\partial(\Delta H)}{\partial T} = \frac{\partial(\Delta G)}{\partial T} = 0$$

◦ Nernst 定理的另一个推论: $T \rightarrow 0$ 时, 物质系统的热容趋于 0:

proof:

$$C_y = T \left(\frac{\partial S}{\partial T} \right)_y \quad (\text{热容定义}):$$
$$= \left(\frac{\partial S}{\partial \ln T} \right)_y$$

考虑到: $T \rightarrow 0$ 时, $\ln T \rightarrow -\infty$, 而 S is limited. Thus: $C_y = 0$.

◦ Nernst $\rightarrow$ 体积膨胀, 压强系数 为 0 ($T \rightarrow 0$ 时)!

From Nernst Theory:

$$\partial(TS) = \partial(P, V)$$

$$\lim_{T \rightarrow 0} (\Delta S)_T = 0 \quad \begin{cases} \left(\frac{\partial S}{\partial P} \right)_T = 0 \rightarrow \frac{\partial(V, P)}{\partial(P, T)} = - \left(\frac{\partial V}{\partial T} \right)_P = 0 \Rightarrow \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = 0 \\ \left(\frac{\partial S}{\partial V} \right)_T = 0 \rightarrow \frac{\partial(V, P)}{\partial(V, T)} = \left(\frac{\partial P}{\partial T} \right)_V = 0 \Rightarrow \beta = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V = 0 \end{cases}$$

◦ Nernst $\rightarrow$ 相变: 如果: $\lim_{T \rightarrow 0} (\Delta S)_T = 0$ 中的 ΔS 表示的是相变时 S 的改变, 则:

由克拉伯龙方程:

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = 0 \quad \text{表示相变曲线在 } T \rightarrow 0 \text{ 时趋于平滑!}$$

◦ 热力学第三定律的又一种形式:

$$\lim_{T \rightarrow 0} S_0 = 0 \quad (S_0 \text{ 表示系统在不同状态下的熵}).$$

下面的笔记都是有关统计物理的:

• 粒子的分类: (可分辨与不可分辨)

定域子系: 粒子与粒子的波 Function 之间没有重叠, 粒子是可分辨的. (是否可分辨, 实际上这也是对系统的分类).
非定域子系: 粒子之间不可分辨。

Fermi 子: $\psi(r_1, r_2) = A(\psi_a(r_1)\psi_b(r_2) - \psi_a(r_2)\psi_b(r_1)) \Rightarrow$ 不可以 1, 2 粒子同时位于态 a 上!!! (Pauli 不相容原理)
Bose 子: $\psi(r_1, r_2) = A(\psi_a(r_1)\psi_b(r_2) + \psi_a(r_2)\psi_b(r_1))$ (量子力学 5 章, 全同粒子 (Griffiths 中))

• 三种统计分布的导出 (定域子系的 Maxwell 分布与非定域子系的 Bose-Einstein 分布与 Fermi-Dirac 分布)

• Maxwell-Boltzmann 分布: (用到了两个 Math knowledge: 1° $n! \ln n! \approx \ln n!$ (stirling 近似) 2° $f(x_1, x_2, \dots)$ 极值:

认为量子态 i 上有 a_i 个粒子, (即有分布 $\{a_i\}$, 在 i 量子态上有能量 ϵ_i).

$\Omega f - \alpha \Omega g - \beta \Omega h = 0$
(g, h 为约束).

总粒子数守恒:

$$\sum_i a_i = N$$

总能量守恒:

$$\sum_i a_i \epsilon_i = E$$

当 i 态的简并度为 w_i 时, $\{a_i\}$ 分布的微观状态数:

$$\Omega = \frac{N!}{\prod_i a_i!} \cdot \prod_i w_i^{a_i}$$

代表 a_i 个粒子占 w_i 个位置时共有的可能情况数量!

代表粒子在所有的能级上可能的分布数量!

则:

$$\ln \Omega = N \ln N + \sum_i a_i \ln w_i - \sum_i a_i (\ln a_i - 1)$$

$$d \ln \Omega = \sum_i \ln w_i \cdot da_i - \sum_i \ln a_i \cdot da_i + \sum_i da_i - \sum_i da_i$$

$$= \sum_i \ln \left(\frac{w_i}{a_i} \right) \cdot da_i$$

由于存在约束: $\sum_i a_i = N$ $\sum_i \epsilon_i a_i = E$

Lagrange 乘子法: Ω 取极大值时有条件:

$$d \ln \Omega - \alpha dN - \beta dE = 0$$

$$\sum_i \left(\ln \left(\frac{w_i}{a_i} \right) - \alpha - \beta \epsilon_i \right) da_i = 0$$

得到 Maxwell-Boltzmann 分布:

$$a_i = w_i \exp(-\alpha - \beta \epsilon_i) = w_i e^{-\alpha - \beta \epsilon_i}$$

• Fermi-Dirac 分布: (全同粒子的统计分布)(全同粒子就相当于非定域系统). 服从 Pauli 不相容原理.

当有分布为 $\{a_i\}$ 时, 系统的微观状态数:

$$\Omega = \prod_i \frac{w_i!}{a_i! (w_i - a_i)!} \quad \text{相当于: } \prod_i C_{w_i}^{a_i}$$

则:

$$\ln \Omega = \sum_i w_i \ln w_i - \sum_i a_i \ln a_i + \sum_i a_i - \sum_i (w_i - a_i) (\ln (w_i - a_i) + 1)$$

$$= \sum_i \ln w_i$$

$$\delta \ln \Omega = - \sum_i \ln a_i \cdot da_i + \sum_i \ln (w_i - a_i) da_i$$

则考虑约束:

$$\delta \ln \Omega - \alpha \delta N - \beta \delta E = 0$$

$$\sum_i \left(\ln \left(\frac{w_i - a_i}{a_i} \right) - \alpha - \beta \epsilon_i \right) da_i = 0$$

$$\frac{w_i - a_i}{a_i} = 1 + e^{\alpha + \beta \epsilon_i}$$

$$a_i = w_i \cdot \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$$

- Bose-Einstein 分布: (不服从 Pauli 不相容原理, 且各个粒子间不可分辨.)

$$\Omega = \prod_i \frac{(w_i + a_i - 1)!}{a_i! (w_i - 1)!}$$

$\overbrace{\quad \quad \quad}^{\text{共 } a_i \text{ 个球}}$
 $\square \circ \circ \circ \circ \square \circ \circ \circ \square \dots$
 $\uparrow \quad \quad \quad \uparrow$

不同方块代表不同量子态, 方块后的圆圈指这个量子态上的粒子数量.

$$\Omega = \prod_i \frac{(w_i + a_i - 1)!}{a_i! (w_i - 1)!}$$

$$\ln \Omega = \sum_i (w_i + a_i - 1) (\ln(w_i + a_i - 1) - 1) - \sum_i a_i (\ln a_i - 1) - \sum_i (w_i - 1) (\ln(w_i - 1) - 1)$$

$$\delta \ln \Omega = \sum_i \ln(w_i + a_i - 1) da_i - \sum_i \ln a_i da_i$$

Lagrange 乘子法: ($\delta \ln \Omega - \alpha \delta N - \beta \delta E = 0$).

$$\ln(w_i + a_i - 1) - \ln a_i - \alpha - \beta \epsilon_i = 0$$

$$\frac{w_i + a_i - 1}{a_i} = e^{\alpha + \beta \epsilon_i}$$

$$\frac{w_i}{a_i} = e^{\alpha + \beta \epsilon_i} - 1$$

$$a_i = \frac{w_i}{e^{\alpha + \beta \epsilon_i} - 1}$$

西己分 Function 和巨西己分 Function. 表示热力学函数.

• Maxwell-Boltzmann 分布的西己分 Function; Fermi-Dirac 分布与 Bose-Einstein 分布的巨西己分 Function.

• Maxwell-Boltzmann 分布的西己分 Function:

$$Z = \sum_i w_i e^{-\beta \epsilon_i}$$

Total number of atoms:

$$N = Z e^{-\alpha}$$

The Total Energy can then be written as:

$$E = \sum_i \epsilon_i w_i e^{-\beta \epsilon_i} e^{-\alpha} = - \sum_i w_i \frac{\partial}{\partial \beta} (e^{-\beta \epsilon_i}) e^{-\alpha} = - \frac{\partial}{\partial \beta} (Z) \frac{N}{Z} = - N \frac{\partial}{\partial \beta} (\ln Z)$$

Force can be derivate from this:

$$\begin{aligned} Y_i &= \sum_j \frac{\partial}{\partial y_i} (\epsilon_j) \cdot a_j = \sum_j \frac{\partial}{\partial y_i} (\epsilon_j) w_j e^{-\alpha} e^{-\beta \epsilon_j} = e^{-\alpha} \sum_j w_j \frac{\partial}{\partial y_i} (e^{-\beta \epsilon_j}) \cdot \frac{1}{-\beta} \\ &= - \frac{e^{-\alpha}}{\beta} \frac{\partial}{\partial y_i} (Z) \end{aligned}$$

$$= - \frac{N}{Z} \cdot \frac{1}{\beta} \frac{\partial}{\partial y_i} (Z)$$

$$= - \frac{N}{\beta} \frac{\partial}{\partial y_i} (\ln Z)$$

焓: (证明了 β 是 dQ 的积分因子) (由热二, 知 $\frac{1}{T}$ 是 dQ 的积分因子).

$$\begin{aligned} \frac{1}{k} dS &= \beta (dQ) = \beta (dE - \sum_i Y_i dy_i) = \beta (d(-N \frac{\partial}{\partial \beta} \ln Z) + \sum_i \frac{N}{\beta} \frac{\partial}{\partial y_i} (\ln Z) dy_i) \\ &= N (\sum_i \frac{\partial}{\partial y_i} (\ln Z) dy_i - \beta d(\frac{\partial}{\partial \beta} \ln Z)) = N (\sum_i \frac{\partial}{\partial y_i} (\ln Z) dy_i + \frac{\partial}{\partial \beta} (\ln Z) \cdot d\beta - d(\beta \frac{\partial}{\partial \beta} \ln Z)) \\ &= N d(\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z) \end{aligned}$$

不妨令: $S = kN (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z)$. 且由此, 可知: $\beta = \frac{1}{kT}$.

• Fermi-Dirac 分布和 Bose-Einstein 分布的巨西己分函数.

— B-E 分布的巨西己分 Function: (下面的 g_i 和 w_i 意义是一样的).

$$\Xi = \prod_i (1 - e^{-\alpha - \beta \epsilon_i})^{-g_i}$$

$$\ln \Xi = \sum_i -g_i \ln (1 - e^{-\alpha - \beta \epsilon_i})$$

$$N = - \frac{\partial}{\partial \alpha} \ln \Xi = \sum_i g_i \cdot \frac{1}{1 - e^{-\alpha - \beta \epsilon_i} \cdot (-1) \cdot (-1) e^{-\alpha - \beta \epsilon_i}} = \sum_i g_i \cdot \frac{1}{e^{\alpha + \beta \epsilon_i} - 1}$$

$$E = - \frac{\partial}{\partial \beta} \ln \Xi = \sum_i g_i \cdot \frac{\epsilon_i}{1 - e^{-\alpha - \beta \epsilon_i}} e^{-\alpha - \beta \epsilon_i} = \sum_i \epsilon_i \cdot g_i \frac{1}{e^{\alpha + \beta \epsilon_i} - 1}$$

$$Y_i = - \frac{1}{\beta} \frac{\partial}{\partial y_i} (\ln \Xi) = \sum_j \frac{1}{\beta} g_j \cdot \frac{1}{1 - e^{-\alpha - \beta \epsilon_j}} e^{-\alpha - \beta \epsilon_j} (\beta) \frac{\partial \epsilon_j}{\partial y_i} = \sum_j \frac{\partial \epsilon_j}{\partial y_i} g_j \frac{1}{e^{\alpha + \beta \epsilon_j} - 1}$$

$$\begin{aligned} \frac{1}{k} dS &= \beta (dE - \sum_i Y_i dy_i) = \beta (d(- \frac{\partial}{\partial \beta} \ln \Xi) + \sum_i \frac{1}{\beta} \frac{\partial}{\partial y_i} (\ln \Xi) dy_i) = - \beta d(\frac{\partial}{\partial \beta} \ln \Xi) + \sum_i \frac{\partial}{\partial y_i} (\ln \Xi) dy_i \\ &= d(\ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi) - \frac{\partial}{\partial \alpha} \ln \Xi d\alpha = d(\ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi - \alpha \frac{\partial}{\partial \alpha} \ln \Xi) + \alpha d(\frac{\partial}{\partial \alpha} \ln \Xi) \end{aligned}$$

$$S = k(\ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi - \alpha \frac{\partial}{\partial \alpha} \ln \Xi) = k(\ln \Xi + \beta E + \alpha N)$$

— F-D 分布的巨西己分 Function:

$$\Xi = \prod_i (1 + e^{-\alpha - \beta \epsilon_i})^{w_i}$$

$$\ln \Xi = \sum_i w_i \ln (1 + e^{-\alpha - \beta \epsilon_i})$$

$$N = - \frac{\partial}{\partial \alpha} \ln \Xi = - \sum_i w_i \frac{1}{1 + e^{-\alpha - \beta \epsilon_i} \cdot (-1) \cdot (-1) e^{-\alpha - \beta \epsilon_i}} = \sum_i w_i \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$$

$$E = - \frac{\partial}{\partial \beta} (\ln \Xi) = - \sum_i w_i \frac{1}{1 + e^{-\alpha - \beta \epsilon_i} \cdot (-\epsilon_i) \cdot (-1) e^{-\alpha - \beta \epsilon_i}} = \sum_i \epsilon_i w_i \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$$

$$Y_i = - \frac{1}{\beta} \frac{\partial}{\partial y_i} (\ln \Xi) = - \sum_j \frac{w_j}{\beta} \frac{1}{1 + e^{-\alpha - \beta \epsilon_j} \cdot (-\beta) \cdot (-1) e^{-\alpha - \beta \epsilon_j}} \frac{\partial \epsilon_j}{\partial y_i} = \sum_j \frac{\partial \epsilon_j}{\partial y_i} w_j \frac{1}{e^{\alpha + \beta \epsilon_j} + 1} = \sum_j \frac{\partial \epsilon_j}{\partial y_i} n_j$$

$$dS = k\beta (dE - \sum_i Y_i dy_i) = k[\beta d(\frac{\partial}{\partial \beta} \ln \Xi) + \sum_i \frac{\partial}{\partial y_i} (\ln \Xi) dy_i] = k d(\ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi - \alpha \frac{\partial}{\partial \alpha} \ln \Xi) + k\alpha d(\frac{\partial}{\partial \alpha} \ln \Xi)$$

最后一步为 0!
-k\alpha d(N)

——又对于化学势 μ 和 α 的联系: (在 F-D 分布 和 B-E 分布中):

单看前面 F-D 分布和 B-E 分布最后的一项 (S 的表达式中):

在考虑粒子数改变的情况下:

$$E = G + TS - PV$$

$$dE = \mu \cdot dN + TdS - PdV$$

$$(dE + PdV) = \mu dN + TdS$$

$$\beta(dE + PdV) = \frac{\mu}{kT} dN + \frac{1}{k} dS$$

$$dS = k\beta(dE + PdV) - \frac{\mu}{T} dN$$

则:

$$\alpha = -\frac{\mu}{kT}$$

基本热力学函数(比如火商)的理角平:

• 什么是基本热力学函数: E 的表达式, S 的表达式, 物态方程(外力 Y_i 的表达式):
(内能)

• 考虑到了巨配分 Function 后对 S 的理角平: (Boltzmann 关系).

• Maxwell - Boltzmann 分布:

$$S = N (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z) \cdot k$$

$$Z = \sum_i W_i \cdot e^{-\beta E_i} = N \cdot e^{\alpha}$$

$$S = kN (\ln(N) + \alpha - \beta \frac{\partial}{\partial \beta} \ln(Z))$$

$$= (N \ln N + N \cdot \alpha - \beta N \frac{1}{Z} \cdot \frac{\partial}{\partial \beta} Z) k$$

$$= (N \ln N + N \cdot \alpha - \beta \frac{N}{Z} \cdot (-1) \cdot \sum_i W_i \cdot e^{-\beta E_i} \cdot E_i) k$$

$$= (N \ln N + N \cdot \alpha + \sum_i \beta E_i W_i \cdot e^{-\alpha - \beta E_i}) k$$

$$= (N \ln N - \sum_i (-\alpha - E_i \cdot \beta) \cdot a_i) k$$

$$= (N \ln N - \sum_i a_i \ln e^{-\alpha - \beta E_i}) k$$

$$= (N \ln N - \sum_i a_i \ln (\frac{a_i}{W_i})) \cdot k$$

$$= k \ln (\frac{N!}{\prod_i a_i!} \cdot \prod_i W_i^{a_i})$$

$$= k \ln (\Omega_{\max})$$

$$S = k \ln (\Omega_{\max}) \quad \text{不被称为 Boltzmann 关系!}$$

• Fermi - Dirac 分布: $\left[\frac{a_i}{W_i} \right] \quad a_i = \frac{W_i}{e^{\alpha + \beta E_i} + 1} \quad \hat{v} = \prod_i (1 + e^{-\alpha - \beta E_i})^{W_i}$

$$\ln W_{\max} = \ln (\prod_i \frac{W_i!}{a_i! (W_i - a_i)!}) = \sum_i (W_i \ln W_i - a_i \ln a_i - (W_i - a_i) \ln (W_i - a_i))$$

$$= \sum_i \cdot (W_i \ln \frac{W_i}{W_i - a_i} + a_i \ln (\frac{W_i - a_i}{a_i}))$$

$$= \sum_i \cdot (W_i \ln (1 + e^{\alpha + \beta E_i}) + a_i \ln (e^{\alpha + \beta E_i}))$$

$$= \sum_i (\ln \varepsilon + \alpha N + \beta E)$$

$$S = k \cdot \ln W_{\max} \quad (\text{结合巨配分 Function 的知识})$$

• Bose - Einstein 分布:

$$\ln W_{\max} = \ln (\prod_i \frac{(W_i + a_i - 1)!}{(W_i - 1)! \cdot a_i!}) = \sum_i ((W_i + a_i) \ln (W_i + a_i) - W_i \ln W_i - a_i \ln a_i)$$

$$= \sum_i \cdot (W_i \ln \frac{W_i + a_i}{W_i} + a_i \ln \frac{W_i + a_i}{a_i})$$

$$= \sum_i (-W_i \ln (1 - e^{-\alpha - \beta E_i}) + a_i \cdot \ln (e^{\alpha + \beta E_i})) = \ln \varepsilon + \alpha N + \beta E$$

$$S = k \ln W_{\max} \quad \text{依然成立 (用了巨配分 Function 的知识).}$$

• 重新认识外力与绝热过程: 与热量的统计表达!

外力在统计理论中的定义: (a_i 是分布).

$$Y_i = \sum_j \frac{\partial y_j}{\partial y_i} (E_i) a_i$$

热量的统计表达:

$$dQ = dE - Y_i dy_i = \sum_i d(E_i a_i) - \sum_i d(E_i) a_i = \sum_i E_i \cdot da_i$$

就此, 我们对绝热过程可以理角平为: 分布不发生改变的过程。

二能级系统与 schottky 热容.

- Consider A system with two energy: $(-\epsilon \text{ and } \epsilon)$ ($w_1 = w_2 = 1$)

Thus:

$$Z = \sum_i w_i \cdot e^{-\beta \epsilon_i} = 1 \cdot e^{-\frac{\epsilon}{kT}} + 1 \cdot e^{\frac{\epsilon}{kT}}$$

$$N = e^{-\alpha} Z$$

$$e^{\alpha} = \frac{Z}{N} = \frac{1}{N} (e^{\frac{\epsilon}{kT}} + e^{-\frac{\epsilon}{kT}})$$

$$E = -N \frac{\partial}{\partial \beta} (\ln Z) = -N \frac{\partial}{\partial \beta} (\ln(e^{-\beta \epsilon} + e^{\beta \epsilon})) = \epsilon N \cdot \frac{1}{e^{-\beta \epsilon} + e^{\beta \epsilon}} \cdot (e^{-\beta \epsilon} - e^{\beta \epsilon}) \quad (e^{\epsilon/kT} + e^{-\epsilon/kT})$$

Which we should consider is: E can be less than 0!

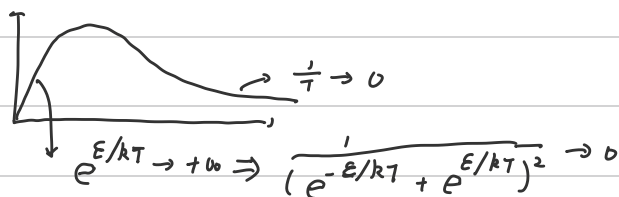
$$C = \frac{\partial E}{\partial T} = \epsilon N \frac{\partial}{\partial T} \left(\frac{e^{-\frac{\epsilon}{kT}} - e^{\frac{\epsilon}{kT}}}{e^{\epsilon/kT} + e^{-\epsilon/kT}} \right) = \epsilon N \cdot \left(\frac{-(e^{-\beta \epsilon} - e^{\beta \epsilon})(e^{-\beta \epsilon} + e^{\beta \epsilon}) + (-e^{-\beta \epsilon} - e^{\beta \epsilon})}{(e^{-\beta \epsilon} + e^{\beta \epsilon})^2} \right) \cdot \left(-\frac{\epsilon}{kT^2} \right)$$

$$= \epsilon N \cdot \left(-\frac{\epsilon}{kT^2} \right) \cdot \frac{e^{-2\beta \epsilon} + e^{2\beta \epsilon} - 2 - e^{2\beta \epsilon} - e^{-2\beta \epsilon}}{(e^{-\beta \epsilon} + e^{\beta \epsilon})^2}$$

$$= \epsilon N \cdot \frac{\epsilon}{kT^2} \cdot \frac{4}{(e^{-\beta \epsilon} + e^{\beta \epsilon})^2}$$

$$= 4N \cdot \frac{\epsilon^2}{kT^2} \cdot \frac{1}{(e^{-\epsilon/kT} + e^{\epsilon/kT})^2}$$

C Has a distribution Which is called schottky 热容:



(光子气体)

热辐射场的统计解释(包含 plunk 的统计理论. 瑞利-金斯理论):

按照波动的观点: 得到 Density of states:

对于长, 宽, 高均为 L 的正方形容器中. 波动在 x, y, z 三方向上分别有: $k_x = \frac{2\pi}{L} n_x, k_y = \frac{2\pi}{L} n_y, k_z = \frac{2\pi}{L} n_z$

则: 总的 frequency: ($\nu = \frac{1}{\lambda} c = k \cdot \frac{c}{2\pi}$).

$$\nu^2 = (k_x^2 + k_y^2 + k_z^2) \cdot \frac{c^2}{(2\pi)^2} = \left(\frac{1}{L} \cdot c\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

相当于:

$$n_x^2 + n_y^2 + n_z^2 = \left(\frac{L}{c}\right)^2 \nu^2$$

对于固定的 ν , 可以有的总量子态:

$$G(\nu) = \frac{4}{3}\pi \left(\frac{L}{c}\nu\right)^3 = \frac{4\pi}{3} \frac{V}{c^3} \cdot \nu^3$$

若认为波动有横纵波之分, 则: ($G(\nu)$ 应该再乘以 2).

$$\begin{cases} G(\nu) = \frac{8\pi}{3} \cdot \frac{V}{c^3} \cdot \nu^3 \\ g(\nu) = \frac{dG(\nu)}{d\nu} = 8\pi \cdot \frac{V}{c^3} \cdot \nu^2 \end{cases}$$

瑞利, 金斯的理论: (经典理论)

对于振动 frequency 是 ν 的电磁波, 由能均分定理:

$$\epsilon = kT$$

则, 总能量 (单位体积):

$$U = \int_0^{\infty} kT \cdot g(\nu) \cdot \frac{1}{\nu} \cdot d\nu = +\infty$$

瑞利-金斯公式这样写:

$$U(\nu, T) = 8\pi kT \frac{1}{c^3} \cdot \nu^2$$

普朗克的理论:

认为振动 frequency 是 ν 的电磁波, 有能级: $n h \nu$. 服从 M-B 分布:

频率为 ν 的光子能量并不是 $h\nu$, 而是 $\frac{h\nu}{e^{\beta h\nu} - 1}$ (原因是有能级 $n h \nu$)

$$\begin{aligned} Z &= \sum e^{-n h \nu \cdot \beta} = \frac{1}{1 - e^{-\beta h \nu}} \\ \epsilon &= -\frac{\partial}{\partial \beta} \ln Z = (1 - e^{-\beta h \nu}) \cdot \frac{e^{-\beta h \nu} \cdot h \nu}{(1 - e^{-\beta h \nu})^2} \\ &= \frac{h \nu}{e^{\beta h \nu} - 1} \end{aligned}$$

$$\begin{cases} U(\nu, T) = \frac{8\pi}{c^3} \cdot h \nu^3 \cdot \frac{1}{e^{h\nu/kT} - 1} \\ U = \int_0^{\infty} U(\nu, T) d\nu = \frac{8\pi}{c^3} \cdot \frac{(kT)^4}{h^3} \cdot \int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{8\pi}{c^3} \cdot \frac{(kT)^4}{h^3} \cdot \frac{\pi^4}{15} \\ = \frac{8\pi^5}{15 c^3} \cdot \frac{(kT)^4}{h^3} \end{cases}$$

这是正则系综的算法.

$Z = \sum e^{-\beta E_s}$ 加代表光子的能级.

$$= \sum_{\{n_\nu\}} e^{-\beta \sum n_\nu h \nu} g(\nu) d\nu$$

$$\ln Z = \int_0^{\infty} d\nu g(\nu) \ln \left(\sum_{n_\nu} e^{-\beta n_\nu h \nu} \right)$$

$$U = -\frac{\partial}{\partial \beta} \ln Z$$

另一种方式, 用 Bose-Einstein 分布.

$$\alpha_i = \frac{W_i}{e^{\alpha + \beta E_i} - 1}$$

特殊之处在于由于 N 不守恒, 只有 E 守恒, 只引入一个 Lagrange 乘子 ($\alpha = 0$)

$$\alpha_i = \frac{W_i}{e^{\beta E_i} - 1}$$

总光子数:

$$N = \int D(\nu) \cdot \frac{1}{e^{\beta h \nu} - 1} d\nu = \int \frac{8\pi V}{c^3} h \nu^3 \frac{1}{e^{h\nu/kT} - 1} d\nu = \frac{V}{\pi^2 c^3} \int_0^{\infty} \frac{w^2}{e^{hw/kT} - 1} dw$$

$$U = \int D(\nu) \cdot \frac{h \nu}{e^{\beta h \nu} - 1} d\nu = \int \frac{8\pi V}{c^3} h^2 \nu^4 \frac{1}{e^{h\nu/kT} - 1} d\nu = \frac{V}{\pi^2 c^3} \int_0^{\infty} \frac{hw^3}{e^{hw/kT} - 1} dw = \frac{\pi^2 k^4}{15 c^3 h^3} VT^4$$

巨配分 Function 的对数.

$$\ln \Xi = - \sum_{\mathbf{k}} \ln(1 - e^{-\alpha - \beta \epsilon_{\mathbf{k}}})^{-w_{\mathbf{k}}} = - \frac{V}{\pi c^3} \int_0^{+\infty} w^2 dw \ln(1 - e^{-\beta \hbar w})$$

$$= - \frac{V}{\pi^2 c^3} \frac{1}{(\beta \hbar)^3} \int_0^{+\infty} \frac{x^2 dx}{e^x - 1} \quad \chi = \frac{\hbar w}{k T}$$

$$\int_0^{+\infty} x^2 \ln(1 - e^{-x}) dx = \left(\frac{x^2}{3} \ln(1 - e^{-x}) \right) \Big|_0^{+\infty} - \frac{1}{3} \int_0^{+\infty} \frac{x^3 dx}{e^x - 1}$$

$$\ln \Xi = \frac{V}{3 \pi^2 c^3} \cdot \frac{1}{(\beta \hbar)^3} \cdot \int_0^{+\infty} \frac{x^3 dx}{e^x - 1}$$

$$= \frac{\pi^2 V}{45 c^3} \frac{1}{(\beta \hbar)^3}$$

$$\begin{aligned} \downarrow \\ \left| \begin{aligned} U &= - \frac{\partial}{\partial \beta} \ln \Xi = \frac{\pi^2 k^4 V}{15 c^3 \hbar^3} T^4 \\ P &= \frac{1}{\beta} \frac{\partial}{\partial V} \ln \Xi = \frac{\pi^2 k^4}{45 c^3 \hbar^3} T^4 \end{aligned} \right. \longrightarrow P = \frac{1}{3} \frac{U}{V} \end{aligned}$$

$$S = k \left(\ln \Xi - \beta \frac{\partial}{\partial \beta} \ln \Xi \right) = \frac{4}{45} \frac{\pi^2 k^4}{c^3 \hbar^3} T^3 V$$

固体热容的有关理论

• 固体热容的经典理论:

一个固体内共有 N 个原子, 则按照能均分定理:

$$E = 3N \cdot kT$$

$$\text{则 } C = \frac{\partial E}{\partial T} = 3Nk$$

• 固体热容的 Einstein 理论:

对于每一个原子, 它具有特征 frequency ν $\nu = \omega \cdot \frac{1}{2\pi}$: 由势能和质量决定.

对于每一个原子的每一个振动自由度:

Einstein 认为有能级:

$$(n + \frac{1}{2}) h\nu$$

服从 M-B 分布:

$$Z = \sum_n e^{-\beta(n+\frac{1}{2})h\nu} = \frac{e^{-\frac{1}{2}\beta h\nu}}{1 - e^{-\beta h\nu}}$$

则此振动自由度的平均能量:

$$\bar{E} = -\frac{\partial}{\partial \beta} (\ln Z) = -\frac{(1 - e^{-\beta h\nu})}{e^{-\frac{1}{2}\beta h\nu}} \cdot \frac{-e^{-\frac{1}{2}\beta h\nu} \cdot (-1) \cdot (-h\nu) \cdot e^{-\beta h\nu} - \frac{1}{2}h\nu e^{-\frac{1}{2}\beta h\nu} \cdot (1 - e^{-\beta h\nu})}{(1 - e^{-\beta h\nu})^2}$$

$$= \frac{h\nu}{2} \frac{1 + e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

则: 共有 $3N$ 个自由度, 内能:

$$E = \bar{E} \cdot 3N = \frac{3}{2} N h\nu \cdot \frac{1 + e^{-h\nu/kT}}{1 - e^{-h\nu/kT}} = \frac{3}{2} N h\nu (1 + \frac{2e^{-h\nu/kT}}{1 - e^{-h\nu/kT}})$$

则: 热容:

$$C = \frac{\partial E}{\partial T} = 3N h\nu \frac{(-1) \cdot (-\frac{h\nu}{kT^2})}{(e^{h\nu/kT} - 1)^2} = 3N (h\nu)^2 \cdot \frac{1}{kT^2} \frac{1}{(e^{h\nu/kT} - 1)^2}$$

按照统计物理中的粒子的概念, (其实相当于是有 $3N$ 个粒子)

• 固体热容的德拜理论:

他认为固体中有 $3N$ 个振动模式!

按照空间中的波的 Density of state: (t 代表横波, l 代表纵波).

$$g(\nu) d\nu = 4\pi V \cdot (\frac{2}{c_t^3} + \frac{1}{c_l^3}) \cdot \nu^2 \cdot d\nu$$

对于以 ν 振动的波, 认为它具有能级: $(n + \frac{1}{2}) h\nu$

则同 Einstein 的固体热容理论: 这样平均每个振动模式的能量为:

$$\frac{h\nu}{2} \frac{1 + e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} = \frac{h\nu}{2} (1 + \frac{2}{e^{\beta h\nu} - 1})$$

(总的振动模式数)

考虑到总的自由度数目是存在限制的! (可以认为存在一个截止 frequency).

$$3N = \int_0^{\nu_D} 4\pi V \cdot (\frac{2}{c_t^3} + \frac{1}{c_l^3}) \cdot \nu^2 \cdot d\nu$$

$$3N = \frac{4\pi}{3} V \cdot (\frac{2}{c_t^3} + \frac{1}{c_l^3}) \cdot \nu_D^3$$

$$\nu_D = \left(\frac{9N}{4\pi V (\frac{2}{c_t^3} + \frac{1}{c_l^3})} \right)^{\frac{1}{3}}$$

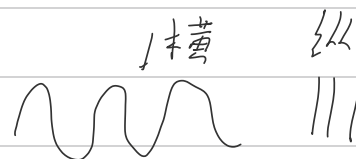
则, 系统的总的能量可以写为:

这不是 M-B 分布而是正则系综

$$U = -\frac{\partial}{\partial \beta} (\ln Z)$$

$$Z = \sum_s e^{-\beta E_s} = \sum_{\{n_i\}} e^{-\beta \left(\int_0^{\nu_D} (n_i + \frac{1}{2}) h\nu \cdot g(\nu) d\nu \right)}$$

$$\ln Z = \int_0^{\nu_D} \ln \left(\sum_{n_i} e^{-\beta(n_i + \frac{1}{2}) h\nu} \right) g(\nu) d\nu$$



$$\begin{aligned}
 E &= \int_0^{\nu_0} g(\nu) \cdot \bar{E}(\nu) \cdot d\nu = \int_0^{\nu_0} 4\pi V \cdot \left(\frac{2}{c^3} + \frac{1}{c^2} \right) \nu^2 \cdot \frac{h\nu}{2} \cdot \left(1 + \frac{2}{e^{\beta h\nu} - 1} \right) \cdot d\nu \\
 &= 3N \cdot \frac{3}{8} h \nu_0 + \int_0^{\nu_0} 4\pi V \cdot \left(\frac{2}{c^3} + \frac{1}{c^2} \right) \cdot h \nu^3 \cdot \frac{1}{e^{\beta h\nu} - 1} d\nu \\
 &= \frac{9}{8} N h \nu_0 + \int_0^{\nu_0} 4\pi V \cdot \left(\frac{2}{c^3} + \frac{1}{c^2} \right) \cdot \frac{1}{\beta^4 h^3} \cdot \frac{(\beta h\nu)^3}{e^{\beta h\nu} - 1} d(\beta h\nu)
 \end{aligned}$$

令 $x = \beta h\nu$, 可令 $D(x) = \left(\int_0^x \frac{y^3 dy}{e^y - 1} \right) \cdot \frac{3}{x^3}$

E 可以写为简单的开/式: ($x = \beta h\nu$)

$$E = E_0(\nu) + 3NkT \cdot D(x)$$

热容: ($\frac{dx}{dT} = -\frac{x}{T}$)

$$\begin{aligned}
 C_V = \left(\frac{\partial E}{\partial T} \right)_V &= 3Nk \cdot D(x) + 3NkT \cdot \left(-\frac{9}{x^4} \cdot \int_0^x \frac{y^3 dy}{e^y - 1} + \frac{3}{x^3} \cdot \frac{x^3}{e^x - 1} \right) \cdot \left(-\frac{x}{T} \right) \\
 &= 3Nk D(x) + 3Nk \cdot 3 D(x) - 9Nk \frac{3^x}{e^x - 1} \\
 &= 3Nk \left(4D(x) - \frac{3^x}{e^x - 1} \right)
 \end{aligned}$$

MB分布的经典极限条件 这个似乎不叫经典极限条件
就叫箱归一化吧...

• MB分布中的配分 Function 在正常情况下写为: (也叫量子态和子相体积间的关系)

$$Z = \sum W_i e^{-\beta \epsilon_i}$$

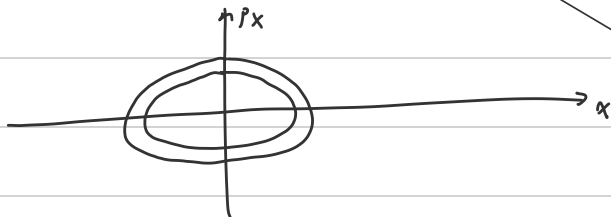
在经典极限条件下 ($\Delta \epsilon_n / kT \ll 1$)

$$Z = \int \dots \int W \frac{dq_1 ds_1 dp_1 \dots dp_r}{h^r} e^{-\beta \epsilon(q, p)}$$

(W 代表积分能量上的简并度)

(比如 $g_s = 2s+1$ 表示因为自旋而产生的简并)

• 如何理解又归一化谐振子:



在相空间上, 允许的运动可以画为一个圈, 则, 这个定理说: 可以认为简并度在能级间距离小时写为 $W_i = \frac{dx dp_x}{h}$

• 实际上, 经典极限条件不一定是 M-B 分布. 在 BEC 和电子气部分都用到了!

• 箱归一化的 DOS 问题:



$L, k = \frac{2\pi}{L} (n_x, n_y, n_z)$

$$\left(\frac{L}{2\pi}\right)^2 k^2 = n_x^2 + n_y^2 + n_z^2$$

$$\frac{L}{2\pi} |k| = r$$

$$dn = 4\pi r^2 dr$$

$$= 4\pi \left(\frac{L}{2\pi}\right)^2 k^2 \left(\frac{L}{2\pi}\right) dk$$

$$= \frac{4\pi}{8\pi^3} V \cdot k^2 dk$$

$$= \frac{1}{2\pi^2} V k^2 dk$$

$$\frac{dx dy dz dp_x dp_y dp_z}{h^3}$$

电子气体

$$\epsilon = \frac{\hbar^2}{2m} k^2 \quad |k| = \sqrt{2m\epsilon} \frac{1}{\hbar}$$

$$\begin{aligned} \hookrightarrow \quad dk &= \frac{1}{2} \frac{\sqrt{2m}}{\hbar} \frac{1}{\sqrt{\epsilon}} d\epsilon \\ k^2 &= 2m\epsilon \frac{1}{\hbar^2} \end{aligned}$$

$$dn = \frac{1}{2\pi^2} V \cdot \frac{2m\epsilon}{\hbar^2} \cdot \frac{1}{2} \frac{\sqrt{2m}}{\hbar} \frac{1}{\sqrt{\epsilon}} d\epsilon$$

$$= \frac{1}{4\pi^2} \frac{1}{\hbar^3} (2m)^{3/2} V \cdot \epsilon^{1/2} d\epsilon$$

$$= \frac{2\pi}{h^3} (2m)^{3/2} V \cdot \epsilon^{1/2} d\epsilon$$

$$D(\epsilon) = 2 \frac{dn}{d\epsilon} = \frac{4\pi V}{h^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon$$

光子气体

$$E = \hbar \omega = PC = \hbar k C \quad \omega = k C$$

$$dn = \frac{1}{2\pi^2} V \frac{1}{C^3} \omega^2 d\omega$$

$$= \frac{1}{2} \frac{1}{\pi^2} V \frac{1}{C^3} \omega^2 d\omega$$

$$D(\omega) = 2 \frac{dn}{d\omega} \quad (\text{由于光子自旋有两个投影})$$

有个更简单的方法

$$2 \frac{dx dy dz dp_x dp_y dp_z}{h^3}$$

$$\begin{aligned} \downarrow p = \frac{\hbar \omega}{C} \\ 2 \frac{V}{C^3} 4\pi v^2 dv \quad \uparrow \frac{V}{\pi^2} \frac{1}{C^3} \omega^2 d\omega \\ v = \frac{1}{\hbar} = \frac{1}{2\pi} \frac{2\pi}{\hbar} = \frac{1}{2\pi} \omega \end{aligned}$$

有个更简单的方法

$$2 \frac{dx dy dz dp_x dp_y dp_z}{h^3} \rightarrow \frac{2V dp^3}{h^3} \quad p = \sqrt{2m\epsilon}$$

$$2 \frac{V \cdot 4\pi p^2 dp}{h^3} \rightarrow \frac{2V \cdot 4\pi \cdot 2m\epsilon \cdot \frac{\sqrt{2m}}{\hbar} \frac{1}{2} d\epsilon}{h^3}$$

非定域子系的经典极限条件 / 理想气体

经典极限 = 非定域条件 = $e^\alpha \gg 1$

• 什么是非简并条件: 与满足非简并条件时, 热力学量和一些其他量的性质.

• 当: $e^\alpha \rightarrow +\infty$ 时:

$$\left. \begin{array}{l} \text{F-D 分布: } a_i = \frac{W_i}{e^{\alpha + \beta \epsilon_i} + 1} \\ \text{B-E 分布: } a_i = \frac{W_i}{e^{\alpha + \beta \epsilon_i} - 1} \end{array} \right\} = W_i e^{-\alpha - \beta \epsilon_i} \ll W_i \quad (\text{正是因为 } a_i \ll W_i, \text{ 则 Pauli 不相容原理显得不重要了})$$

此时, 这个叫做非简并条件

• 非简并条件成立时, 微观状态数的关系:

$$W_{\text{F-D}} = \prod_i \frac{W_i!}{a_i! (W_i - a_i)!} = \prod_i \frac{W_i (W_i - 1) \dots (W_i - a_i + 1)}{a_i!} = \prod_i \frac{W_i^{a_i}}{a_i!} \underbrace{\left(1 - \frac{1}{W_i}\right) \dots \left(1 - \frac{a_i - 1}{W_i}\right)}_{\approx 1} \approx \prod_i \frac{W_i^{a_i}}{a_i!} = \frac{1}{N!} \cdot W_{\text{M-B}}$$

$$W_{\text{B-E}} = \prod_i \frac{(W_i + a_i - 1)!}{(W_i - 1)! \cdot a_i!} = \prod_i \frac{(W_i + a_i - 1) (W_i + a_i - 2) \dots (W_i)}{a_i!} = \prod_i \frac{W_i^{a_i}}{a_i!} \underbrace{\left(1 + \frac{a_i - 1}{W_i}\right) \dots}_{\approx 1} \approx \frac{1}{N!} \cdot W_{\text{M-B}}$$

• 非简并条件成立时子系的热力学量的表达.

此处从配分 Function 开始:

$$\xi = \prod_i (1 \pm e^{-\alpha - \beta \epsilon_i})^{g_i} \quad (+: \text{F-D 分布}; -: \text{B-E 分布}):$$

$$\ln \xi = \pm \sum_i g_i \ln(1 \pm e^{-\alpha - \beta \epsilon_i}) = \pm \sum_i g_i (\pm e^{-\alpha - \beta \epsilon_i}) = \sum_i g_i e^{-\alpha - \beta \epsilon_i} \cdot e^{-\alpha} = e^{-\alpha} \cdot Z$$

则: 定义非定域子系的热力学量:

$$E = - \frac{\partial}{\partial \beta} \ln \xi = - e^{-\alpha} \frac{\partial}{\partial \beta} Z = - N \frac{\partial}{\partial \beta} \ln Z$$

$$N = - \frac{\partial}{\partial \alpha} \ln \xi = Z \cdot e^{-\alpha}$$

$$Y_i = - \frac{1}{\beta} \frac{\partial}{\partial y_i} \ln \xi = - \frac{N}{\beta} \frac{\partial}{\partial y_i} \ln Z \quad (\text{外力}).$$

$$S = k (\ln \xi + \alpha N + \beta E) = k (N + (\ln Z - \ln N) \cdot N + \beta E) = k (N - N \ln N + N \ln Z + \beta E) = k N (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z) - k \ln N!$$

$$d = k \ln \left(\frac{Z}{N} \right) = \frac{\mu}{kT} \Rightarrow \mu = kT \ln \left(\frac{Z}{N} \right)$$

• 以自由气体为例, 讨论非简并条件 ($e^\alpha \gg 1$) 的要求.

理想气体处于体积为 L^3 的容器中.

有波矢:

$$\vec{k} = \frac{2\pi}{L} (n_x, n_y, n_z)$$

动能:

$$\vec{p} = \hbar \cdot \vec{k} = \frac{2\pi \hbar}{L} \cdot (n_x, n_y, n_z)$$

$$E_k = \frac{p^2}{2m} = \frac{1}{2m} \cdot \left(\frac{2\pi \hbar}{L} \right)^2 \cdot (n_x^2 + n_y^2 + n_z^2)$$

$$\text{则: } \delta \epsilon \approx \frac{\hbar^2}{2m L^2} \ll kT$$

则, 是始终满足: $\delta \epsilon / kT \ll 1$ 的.

此时: (考虑自旋): (自旋的简并度 $g_s = 2S + 1$)

$$Z_1 = \int g_s \frac{dx dy dz dx' dy' dz'}{h^3} e^{-\beta \left(\frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \right)}$$

$$= g_s V \cdot \frac{1}{h^3} \left(\int_0^{\infty} e^{-\beta \frac{1}{2m} p_x^2} dp_x \right)^3$$

$$= g_s \frac{V}{h^3} \cdot \left(\frac{2m\pi}{\beta} \right)^{3/2} = g_s V \cdot \left(\frac{1}{h} \sqrt{\frac{2\pi m}{\beta}} \right)^3$$

$$e^\alpha = \frac{Z}{N} = g_s \cdot \frac{1}{n} \cdot \left(\frac{\sqrt{2\pi m kT}}{h} \right)^3 \quad (n \text{ 为粒子数密度}) \quad \epsilon_r = \frac{1}{n^{1/3}}$$

$$\text{定义: } \lambda_T = \frac{h}{\sqrt{2\pi m kT}} \quad \text{则: 当 } \frac{1}{n \lambda_T^3} \gg 1 \text{ 时, 非简并成立 } (\lambda_T \ll \epsilon_r)$$

理想气体:

$$p = N \frac{1}{\beta} \frac{\partial}{\partial V} (\ln Z)$$

$$= N \frac{1}{\beta} \frac{\partial}{\partial V} (\ln V) = \frac{N kT}{V}$$

$$\downarrow$$

$$PV = N kT$$

$$U = -N \frac{\partial}{\partial \beta} (\ln Z) = -N \frac{\partial}{\partial \beta} \left(-\frac{3}{2} \ln \beta \right)$$

$$= \frac{3}{2} N kT$$

$$S = N k (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z) \quad g_s = 1$$

$$= N k \left\{ \ln \left[V \left(\frac{\sqrt{2\pi m kT}}{h} \right)^3 \right] + \frac{1}{kT} \frac{3}{2} kT \right\}$$

$$= \frac{3}{2} N k + N k \ln \left[V \cdot \left(\frac{\sqrt{2\pi m kT}}{h} \right)^3 \right]$$

• 非定域子系的经典极限条件: $\delta \epsilon / kT \ll 1$ 且: $e^\alpha \gg 1$!!! (相当于经典极限条件 + 非定域极限条件 = 非定域子系的经典极限条件)

MB - Maxwell 速度分布. 与能均分定理.

0 Maxwell 速度分布.

$$\epsilon = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

$$W_1 = \frac{V}{h^3} dp_x dp_y dp_z = \frac{m^3 V}{h^3} dV_x dV_y dV_z$$

$$dN = \frac{N}{Z} \left(\frac{m^3 V}{h^3} \right) e^{-\frac{1}{2m}(V_x^2 + V_y^2 + V_z^2)} dV_x dV_y dV_z$$

$$= N \cdot \left(\frac{1}{2\pi m kT} \right)^{3/2} e^{-\frac{1}{2mkT}(p_x^2 + p_y^2 + p_z^2)} dp_x dp_y dp_z$$

单位时间, 单位面积, 单位速度数.

$$P = n \left(\frac{m}{2\pi kT} \right)^{1/2} \int_0^{+\infty} V_x e^{-\frac{m}{2kT} V_x^2} dV_x = n \sqrt{\frac{kT}{2\pi m}} = \frac{1}{4} n \bar{v}$$

↓ $f(V_x)$ that satisfies $f(V_x) f(V_y) f(V_z) = f(V_x, V_y, V_z)$

0 能量均分定理.

对于处在温度为 T 的平衡状态的经典系统. 粒子能量中每一个独立的平方项的平均值 = $\frac{1}{2} kT$.

证明:

假如有一项能量: $\epsilon = \frac{1}{2} a_i p_i^2$ a_i 不是 p_i 的 Function

$$\bar{\epsilon} = \int \frac{1}{2} a_i p_i^2 \frac{1}{Z} e^{-\frac{1}{2} a_i p_i^2} e^{-\beta \epsilon_{\text{其他}}} dq_1 \dots d\vec{r} dp_1 \dots dp_r$$

$$Z = \int e^{-\frac{1}{2} a_i p_i^2} e^{-\beta \epsilon_{\text{其他}}} dq_1 \dots d\vec{r} dp_1 \dots dp_r$$

$$\bar{\epsilon} = \frac{\int_0^{+\infty} \frac{1}{2} a_i p_i^2 e^{-\beta \frac{1}{2} a_i p_i^2} dp_i}{\int_0^{+\infty} e^{-\beta \frac{1}{2} a_i p_i^2} dp_i}$$

由分部积分:

$$\int_0^{+\infty} \frac{1}{2} a_i p_i^2 e^{-\beta \frac{1}{2} a_i p_i^2} dp_i = \int_0^{+\infty} p_i e^{-\beta \frac{1}{2} a_i p_i^2} \left(\frac{1}{2\beta} \right) \cdot \frac{1}{2} \beta p_i dp_i$$

$$= \int_0^{+\infty} -p_i \frac{1}{2\beta} d(e^{-\frac{\beta}{2} a_i p_i^2})$$

$$= - \left(\frac{1}{2\beta} p_i e^{-\frac{\beta}{2} a_i p_i^2} \right) \Big|_0^{+\infty} + \frac{1}{2\beta} \int_0^{+\infty} e^{-\frac{\beta}{2} a_i p_i^2} dp_i$$

$$\bar{\epsilon} = \frac{1}{2} kT$$

对于 $\epsilon = \frac{1}{2} b_i q_i^2$ (b_i 不是 q_i 的 func), 同理!

理想气体的 Bose-Einstein-Condensation

- Bose-Einstein 分布: (全同近独立玻色子): ($\alpha = \mu/kT$) (这里似乎是不用考虑简并什么的了...)

$$Q_i = \frac{W_i}{e^{\alpha + \beta \epsilon_i} - 1}$$

组成的系统

- 由于: $\Delta \epsilon/kT \ll 1$: 可以认为: $W_i = \frac{dx \cdot dy \cdot dz \cdot dp_x \cdot dp_y \cdot dp_z}{h^3} = V \cdot \frac{1}{h^3} \cdot dp_x \cdot dp_y \cdot dp_z$

则可以认为:

$$N = \sum Q_i = \int \frac{V}{h^3} \cdot m^3 \cdot \frac{1}{e^{\frac{m}{2kT} (V_x^2 + V_y^2 + V_z^2)} - 1} dV_x \cdot dV_y \cdot dV_z$$

发现当: N, T, V 固定时, μ 也是固定的。相当于有 (N, T, V, μ) 的联合关系。

由于: $Q_i > 0$ $Q_i = \frac{W_i}{e^{\alpha + \beta \epsilon_i} - 1}$

则: $\epsilon_0 - \mu > 0$ $\alpha = \mu/kT = -\mu/\beta$

$$\mu < \epsilon_0$$

$$Q_i = \frac{W_i}{e^{\alpha + \beta \epsilon_i} - 1} \text{ 有意义的条件}$$

当: $\epsilon_0 = 0$ 时 (三维自由粒子的量子化):

$$\mu < 0$$

但由 N 的表达式, T 很小时, μ 会不得不得大于 0! $\longrightarrow$ 由 N 的积分表达式, $N(T, V, \mu)$ ($\mu < 0$ 时)
随着 μ 的增大而增大
随着 T 的减小而减小

我们考虑 $\mu = 0$ 时:

$$N = \int \frac{V}{h^3} \cdot m^3 \cdot \frac{1}{e^{\frac{m}{2kT} (V_x^2 + V_y^2 + V_z^2)} - 1} dV_x \cdot dV_y \cdot dV_z \quad | \quad T = T_c$$

$$= \int_0^{+\infty} 2\pi \cdot \frac{V}{h^3} \cdot m^3 \cdot \left(\frac{2kT}{m} \right)^{3/2} \frac{1}{e^x - 1} \sqrt{x} \cdot dx \quad | \quad T = T_c$$

$$= V \cdot 2\pi \cdot \left(\frac{2mkT}{h^2} \right)^{3/2} \int_0^{+\infty} \frac{\sqrt{x} \cdot dx}{e^x - 1} \quad | \quad T = T_c$$

$$1 = \left(\frac{T}{T_c} \right)^{3/2} \quad | \quad T = T_c$$

$$T_c = \left(\frac{N}{V \cdot 2\pi \cdot \int_0^{+\infty} \frac{\sqrt{x} \cdot dx}{e^x - 1}} \right)^{2/3} \cdot \frac{h^2}{2mk}$$

由积分学:

$$\int_0^{+\infty} \frac{\sqrt{x} \cdot dx}{e^x - 1} = \frac{\sqrt{\pi}}{2} \cdot 2.612$$

$$T_c = \left(\frac{N}{V \cdot \frac{\sqrt{\pi}}{2} \cdot 2.612} \right)^{2/3} \cdot \frac{h^2}{2\pi mk}$$

$$= \left(\frac{N}{V} \right)^{2/3} \cdot \frac{h^2}{2\pi mk} \cdot \frac{1}{(2.612)^{2/3}}$$

$$= n^{2/3} \cdot \frac{2\pi \hbar^2}{mk} \cdot \frac{1}{(2.612)^{2/3}}$$

则: 当: 温度低于此温度时: 认为处在基态的原子有 $N_0(T)$ 个, 则由原子总数守恒: (认为基态的不参与 B-E

$$N_0(T) + N \cdot \left(\frac{T}{T_c} \right)^{3/2} = N$$

分布, $N = N(T, V, 0) + N_0$)

$$N_0(T) = N \cdot (1 - (T/T_c)^{3/2})$$

- 考虑 $T < T_c$ 时, 气体的热容与内能: $\longrightarrow$ ($T < T_c$ 时, $\mu = 0$)

内能:

$$E = \int \frac{V}{h^3} \cdot m^3 \cdot \frac{1}{e^{\frac{m}{2kT} (V_x^2 + V_y^2 + V_z^2)} - 1} \cdot \frac{1}{2} m (V_x^2 + V_y^2 + V_z^2) dV_x \cdot dV_y \cdot dV_z$$

$$= 2\pi \cdot \frac{V}{h^3} \cdot m^3 \cdot \left(\frac{2kT}{m} \right)^{3/2} kT \int_0^{+\infty} \frac{x^{3/2}}{e^x - 1} \cdot dx$$

$$= 0.770 N kT \cdot \left(\frac{T}{T_c} \right)^{3/2}$$

则, 热容:

$$C_V = \frac{\partial E}{\partial T} = 1.925 \cdot Nk \cdot \left(\frac{T}{T_c}\right)^{3/2}$$

• BEC 发生的另一种表示

原子热波长的引入: (λ_c):

$$\begin{aligned} N &= \int_0^{+\infty} e^{-\alpha} \cdot e^{-\beta \cdot \frac{1}{2} m V^2} \cdot \frac{dx dy dz}{h^3} \cdot m^3 dV_x dV_y dV_z \\ &= e^{-\alpha} \iiint \frac{V}{h^3} e^{-\frac{1}{2} \beta \frac{1}{m} p^2} dp_x dp_y dp_z \\ &= e^{-\alpha} \cdot \frac{V}{h^3} \cdot (2\pi k T m)^{3/2} \cdot \pi^{3/2} \\ e^{\alpha} &= \left(\frac{V}{N}\right) \cdot \left(\frac{2\pi k T m}{h^2}\right)^{3/2} \\ &= \left(\frac{V}{N}\right) \cdot \frac{1}{\left(\frac{h}{\sqrt{2\pi k T m}}\right)^3} \end{aligned}$$

(经典极限条件的 M-B 分布)

则: $\lambda_c = \frac{h}{\sqrt{2\pi k T m}}$

发生 Bose - Einstein condensation 条件:

$$T < T_c = n^{2/3} \cdot \frac{2\pi \hbar^2}{m k} \cdot \frac{1}{(12.612)^{2/3}}$$

即:

$$(12.612) < n \cdot \left(\frac{h}{\sqrt{2\pi m k T}}\right)^3 = n \cdot \underline{\underline{\lambda_c^3}}$$

λ_c 表示量子效应的特征波长! $\lambda_c = \boxed{\lambda_c(T)}$ 只和温度与粒子的种类有关.

金属中的自由电子气

金属中的自由电子气的相关理论

Fermi-Dirac 分布

$$\left\{ \begin{array}{l} a_i = w_i \frac{1}{e^{\alpha + \beta \epsilon_i} + 1} \\ w_i = D(\epsilon_i) d\epsilon \end{array} \right. \quad (\text{经典极限条件})$$

$$N = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^{+\infty} \frac{\epsilon^{1/2} d\epsilon}{e^{\frac{\epsilon - \mu}{kT} + 1}}$$

↓ 实际上是 N, T, μ 的关系!

▽ $T=0$ 时得到电子气的简并压 (想知 $\mu(0)$)

$$T=0: f = \frac{1}{e^{(\epsilon - \mu)/kT} + 1} = \begin{cases} 0 & \epsilon > \mu(0) \\ 1 & \epsilon < \mu(0) \end{cases}$$

$$N = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^{\mu(0)} \epsilon^{1/2} d\epsilon$$

$$= \frac{8}{3} \frac{\pi V}{h^3} (2m)^{3/2} [\mu(0)]^{3/2}$$

$$\mu(0) = \left(\frac{3N}{8\pi V} \frac{h^3}{(2m)^{3/2}} \right)^{2/3} \frac{1}{2m}$$

$$= \left(\frac{3N}{8\pi V} \frac{h^3}{(2m)^{3/2}} \right)^{2/3} \frac{1}{2m}$$

$$= \left(\frac{3N\pi^2}{V} \right)^{2/3} \frac{\hbar^2}{2m}$$

内能, (不想算 Q&Q)

$$U(0) = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^{\mu(0)} \epsilon^{3/2} d\epsilon$$

$$= \frac{2}{5} \frac{3}{2} \cdot \frac{2}{3} \cdot \mu(0) \cdot \frac{4\pi V}{h^3} (2m)^{3/2} \mu(0)^{3/2} \quad (\text{蓝色部分组成 } N)$$

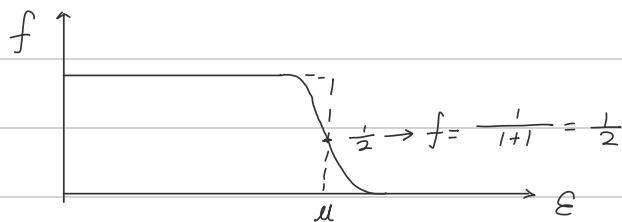
$$= \frac{3}{5} N \mu(0)$$

压强:

$$\text{由于 } \frac{\partial \epsilon}{\partial V} = \frac{\partial}{\partial V} \left(\frac{\hbar^2}{2m} \left(\frac{2\pi}{L} \right)^2 (n_x^2 + n_y^2 + n_z^2) \right) = \left(\frac{\partial}{\partial V} V^{-2/3} \right) = -\frac{2}{3} \frac{\epsilon}{V} \quad P = \sum_i e^{-\frac{\partial \epsilon_i}{\partial V}} a_i \quad P = \frac{2}{3} \frac{U}{V}$$

$$P(0) = \frac{2}{3} \frac{U(0)}{V} = \frac{2}{5} \mu(0) \frac{N}{V}$$

▽ $T \neq 0 \quad T \approx 0$



积分:

$$\epsilon - \mu = kT \chi$$

$$I = \int_{-\mu/kT}^{+\infty} \frac{h(\mu + kT\chi)}{e^{\chi} + 1} kT d\chi = kT \int_0^{\mu/kT} \frac{h(\mu - kT\chi)}{e^{-\chi} + 1} d\chi + kT \int_0^{+\infty} \frac{h(\mu + kT\chi)}{e^{\chi} + 1} d\chi$$

令:

$$\frac{1}{e^{-\chi} + 1} = 1 - \frac{1}{e^{\chi} + 1}$$

$$I = \int_0^{\mu} h(\epsilon) d\epsilon + kT \int_0^{+\infty} \frac{h(\mu + kT\chi) - h(\mu - kT\chi)}{e^{\chi} + 1} d\chi$$

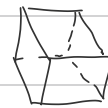
$$= \int_0^{\mu} h(\epsilon) d\epsilon + 2(kT)^2 h'(\mu) \int_0^{+\infty} \frac{\chi}{e^{\chi} + 1} d\chi$$

$$= \int_0^{\mu} h(\epsilon) d\epsilon + \frac{\pi^2}{6} (kT)^2 h'(\mu)$$

$$N = \frac{2}{3} C \mu^{3/2} \left(1 + \frac{\pi^2}{8} \left(\frac{kT}{\mu} \right)^2 \right) \quad \mu = \left(\frac{3N}{2C} \right)^{2/3} \left(1 + \frac{\pi^2}{8} \left(\frac{kT}{\mu} \right)^2 \right)^{-2/3}$$

$$U = \frac{2}{5} C \mu^{5/2} \left(1 + \frac{5\pi^2}{8} \left(\frac{kT}{\mu} \right)^2 \right)$$

$$C = \frac{4\pi V}{h^3} (2m)^{3/2}$$



$$L, \quad k = \frac{2\pi}{L} (n_x, n_y, n_z)$$

$$\left(\frac{L}{2\pi} \right)^2 k^2 = n_x^2 + n_y^2 + n_z^2$$

$$\frac{L}{2\pi} |k| = r$$

$$d n = 4\pi r^2 dr$$

$$= 4\pi \left(\frac{L}{2\pi} \right)^2 k^2 \cdot \left(\frac{L}{2\pi} \right) d|k|$$

$$= \frac{4\pi}{8\pi^3} V \cdot k^2 \cdot d|k|$$

$$= \frac{1}{2\pi^2} V k^2 d|k|$$

$$\epsilon = \frac{\hbar^2}{2m} k^2 \quad |k| = \sqrt{2m\epsilon} \frac{1}{\hbar}$$

$$\hookrightarrow \left\{ \begin{array}{l} d|k| = \frac{1}{2} \frac{\sqrt{2m}}{\hbar} \frac{1}{\sqrt{\epsilon}} d\epsilon \\ k^2 = 2m\epsilon \frac{1}{\hbar^2} \end{array} \right.$$

$$d n = \frac{1}{2\pi^2} V \cdot \frac{2m\epsilon}{\hbar^2} \cdot \frac{1}{2} \frac{\sqrt{2m}}{\hbar} \frac{1}{\sqrt{\epsilon}} d\epsilon$$

$$= \frac{1}{4\pi^2} \frac{1}{\hbar^3} (2m)^{3/2} V \cdot \epsilon^{1/2} d\epsilon$$

$$= \frac{2\pi}{h^3} (2m)^{3/2} V \cdot \epsilon^{1/2} d\epsilon$$

$$D(\epsilon) = 2 \frac{2\pi}{h^3} (2m)^{3/2} V \cdot \epsilon^{1/2}$$

本来积分上限是 μ/kT , 但 $\frac{\mu}{kT} \gg 1$, 且 e^x 会让其收敛.

年十又不同统计理论的总结

这玩意是真的学不来者都是什么玩意吧阿...

分布 $Q_i = W_i e^{-\alpha - \beta \epsilon_i}$ $Q_i = W_i \frac{1}{e^{\alpha + \beta \epsilon_i} + 1}$ $Q_i = W_i \frac{1}{e^{\alpha + \beta \epsilon_i} - 1}$

配分 Func $Z = \sum_i W_i e^{-\beta \epsilon_i}$ $\Omega = \prod_i (1 + e^{-\alpha - \beta \epsilon_i})^{W_i}$ $\Omega = \prod_i (1 - e^{-\alpha - \beta \epsilon_i})^{-W_i}$

热力学 Func $N = \sum_i e^{-\alpha} W_i e^{-\beta \epsilon_i} = e^{-\alpha} Z$ $N = -\frac{\partial}{\partial \alpha} (\ln \Omega)$ $N = -\frac{\partial}{\partial \alpha} (\ln \Omega)$

$U = \sum_i \epsilon_i W_i e^{-\alpha - \beta \epsilon_i} = -e^{-\alpha} \frac{\partial}{\partial \beta} (Z)$ $U = \sum_i W_i \frac{e^{-\alpha - \beta \epsilon_i}}{1 + e^{-\alpha - \beta \epsilon_i}}$ $U = -\frac{\partial}{\partial \beta} (\ln \Omega)$

$Y_i = \sum_i \frac{\partial \epsilon_i}{\partial y_i} W_i e^{-\alpha - \beta \epsilon_i} = -e^{-\alpha} \frac{1}{\beta} \frac{\partial}{\partial y_i} (Z)$ $Y_i = -\frac{1}{\beta} \frac{\partial}{\partial y_i} (\ln \Omega)$ $Y_i = -\frac{1}{\beta} \frac{\partial}{\partial y_i} (\ln \Omega)$

$dS = k\beta (dU - Y_i dy_i)$ $dS = k\beta (-N d(\frac{\partial}{\partial \beta} \ln Z) + N \frac{1}{\beta} \frac{\partial}{\partial y_i} (\ln Z) dy_i)$ $dS = k\beta (-N d(\frac{\partial}{\partial \beta} \ln \Omega) + N \frac{1}{\beta} \frac{\partial}{\partial y_i} (\ln \Omega) dy_i)$

$S = kN (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z)$ $S = kN (\ln \Omega - \beta \frac{\partial}{\partial \beta} \ln \Omega - \frac{\partial}{\partial \alpha} (\ln \Omega) \alpha)$ $S = kN (\ln \Omega - \beta \frac{\partial}{\partial \beta} \ln \Omega - \frac{\partial}{\partial \alpha} (\ln \Omega) \alpha)$

$S = kN (\ln Z + \beta U)$ $S = kN (\ln \Omega + \beta U + \alpha N)$ $S = kN (\ln \Omega + \beta U + \alpha N)$

箱归一化:



$L, k = \frac{2\pi}{L} (n_x, n_y, n_z)$

$(\frac{L}{2\pi})^2 k^2 = n_x^2 + n_y^2 + n_z^2$
 $\frac{L}{2\pi} |k| = r$

$d n = 4\pi r^2 dr$
 $= 4\pi (\frac{L}{2\pi})^2 k^2 (\frac{L}{2\pi}) dk$
 $= \frac{4\pi}{8\pi^3} V \cdot k^2 dk$
 $= \frac{1}{2\pi^2} V k^2 dk$

例子: Schottky = 能级系统

- 2° 固体热容 (德拜理论) 有截断 ν_D 使得粒子数为 $3N$; 单粒子配分 Func. 能级为 $(n+\frac{1}{2})h\nu$ 的平均能量 $\bar{\epsilon}$ (他俩的算法很怪! 应为它是量子理论...)
- 3° 光子气体 (version 1) / 单粒子配分 Func. 能级为 $nh\nu$, 平均能量 $\bar{\epsilon}$ / 有 2 种模式 (横纵, 类似于自旋 $\pm$ 分量)

4° 单原子理想气体 → 可得物态方程.

1° 电子气体. 自旋 $S = \frac{1}{2}$, $M(T=0)$ 是简并能

- 1° BEC. (无自旋). $\rightarrow$ 在 $T=T_c$ 时, $\mu(T_c)=0$. $T < T_c$ 时 $\mu=0$. $N_0 = N(1 - (T/T_c)^{3/2})$
- 2° 光子气体. (version 2) / 无 $dN=0$ 约束 ($\alpha=0$) / 有 2 个振动模式

Liouville Theorem.

相空间的分布.

大量结构完全相同的系统, 各自从其初态出发, 独立沿着正则运动方程运动, 在相空间

中形成分布. $\rho d\Omega = dq_1 \dots dq_r dp_1 \dots dp_r$ ρ 代表相空间元中系统数目.

系统运动描述

$q_1 \dots q_f, p_1 \dots p_f$. f 为系统的总自由度.

运动方程

$$-\frac{\partial H}{\partial q_i} = \dot{p}_i \quad \frac{\partial H}{\partial p_i} = \dot{q}_i$$

Liouville Theorem, 若有很多系统, 他们在相空间的分布用 ρ 描述.

$$\begin{aligned} \frac{d\rho}{dt} &= \frac{d}{dt} [\rho(q_1 \dots q_f, p_1 \dots p_f)] = \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} \right) \\ &= \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right) \end{aligned}$$

$\frac{\partial \rho}{\partial t} dt d\Omega$ 代表 $d\Omega$ 体内流入的态数目

$$\dot{q}_i \left| \dots \right|_{q_i} \rightarrow q_i \rightarrow \rho \dot{q}_i (dq_1 \dots dq_{i-1} dq_{i+1} \dots dp_1 \dots dp_r) dt = \frac{1}{dq_i} (\rho \dot{q}_i) d\Omega \cdot dt$$

$$\frac{\partial \rho}{\partial t} dt d\Omega = - \sum_i \left(\frac{\partial (\rho \dot{q}_i)}{\partial q_i} + \frac{\partial (\rho \dot{p}_i)}{\partial p_i} \right) dt d\Omega$$

$$\frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial (\rho \dot{q}_i)}{\partial q_i} + \frac{\partial (\rho \dot{p}_i)}{\partial p_i} \right) = 0$$

$$\Downarrow \text{由于 } \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} = 0$$

$$\frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = 0 \longrightarrow \frac{d\rho}{dt} = 0!$$

为什么要系综.

1° 一个系统中有 r 个自由度, 则其微观状态可用 $(q_1, \dots, q_r, p_1, \dots, p_r)$, 简记为 (q, p) .

一个可观测量观測值是一 $\overline{B(t)}$ (时间平均值).

$$\int B(q, p) \rho(q, p, t) d\Omega \quad (\text{也可理解为分布平均值})$$

$\rho(q, p) d\Omega$ 可理解为有很多宏观相同的系统, (q, p) 出现的几率.

这定义为系综.

2° 量子理论中, 固定宏观态, 系统可能有量子态 S . t 时刻态 S 存在的几率为 $P_S(t)$. 归一化:

$$\sum_S P_S(t) = 1$$

$$\overline{B(t)} = \sum_S P_S(t) B_S$$

微正则系综 (固定 N, V, E) 特性函数是 $E(S, V)$

微正则分布, 平衡状态的系综分布具有形式:

$$\left\{ \begin{array}{ll} P(q, p) = \text{常量} & E \leq H(q, p) \leq E + \Delta E \\ P(q, p) = 0 & \text{others} \end{array} \right. \rightarrow \text{称为等概率原理/微正则分布}$$

微正则系综理论下的热力学公式.

微正则系综的微观状态数和热力学量的关系.

孤立系有两个子系 A_1, A_2 , 可交换能量.

$$E_1 + E_2 = E''$$

$$\Omega''(E_1, E'' - E_1) = \Omega_1(E_1) \Omega_2(E'' - E_1)$$

From My perspective

$$\Omega(E'') = \sum_{\text{Different Combination of } (E_1, E_2)} \Omega_1(E_1) \Omega_2(E'' - E_1)$$

由等概率原理, 平衡时 Ω'' 极大!

$$\frac{\partial \Omega''}{\partial E_1} = 0$$

$$\frac{\partial \Omega_1(E_1)}{\partial E_1} \Omega_2(E_2) + \Omega_1(E_1) \frac{\partial \Omega_2(E_2)}{\partial E_2} \frac{\partial E_2}{\partial E_1} = 0$$

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} = \frac{\partial \ln \Omega_2(E_2)}{\partial E_2}$$

$$\text{令: } \beta = \left(\frac{\partial \ln \Omega(N, E, V)}{\partial E} \right)_{N, V}, \quad \beta_1 = \beta_2 \quad (\text{也称为热平衡条件})$$

$$\text{又: } \left(\frac{\partial S_1}{\partial U_1} \right)_{N_1, V_1} = \left(\frac{\partial S_2}{\partial U_2} \right)_{N_2, V_2} = \frac{1}{T}$$

$$S = k \ln \Omega$$

若 A_1, A_2 之间不仅可以交换能量, 也可改变体积与交换粒子, 可得平衡条件.

$$\left(\frac{\partial \ln \Omega_1}{\partial E_1} \right)_{N_1, V_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2} \right)_{N_2, V_2} \equiv \beta_1 = \beta_2$$

$$\left(\frac{\partial \ln \Omega_1}{\partial V_1} \right)_{N_1, E_1} = \left(\frac{\partial \ln \Omega_2}{\partial V_2} \right)_{N_2, E_2} \equiv \gamma_1 = \gamma_2$$

$$\left(\frac{\partial \ln \Omega_1}{\partial N_1} \right)_{V_1, E_1} = \left(\frac{\partial \ln \Omega_2}{\partial N_2} \right)_{V_2, E_2} \equiv \alpha_1 = \alpha_2$$

$$\text{由 } d \ln \Omega = \beta dE + \gamma dV + \alpha dN$$

$$dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN \quad (\text{热力学基本方程}) \quad dU = d(G - PV + TS) = TdS - PdV + \mu dN$$

$$\gamma = \frac{P}{kT}, \quad \alpha = -\frac{\mu}{kT}$$

用微正则系综求热力学函数的程序.

先求 $\Omega(N, E, V)$

由 $S(N, E, V) = k \ln \Omega(N, E, V)$, 原则上可得 $E = E(S, V, N)$

$$dE = dU = TdS - PdV \quad (\text{内能作为 } S, V \text{ 的 Function 时是特性函数})$$

$$T = \left(\frac{\partial E}{\partial S} \right)_{V, N}, \quad P = - \left(\frac{\partial E}{\partial V} \right)_{S, N}$$

$$S = S(T, V, N), \quad P = P(T, V, N)$$

$$E = E(T, V, N)$$

例: 用微正则系综求单原子理想气体的热力学函数.

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

$$\Omega(E) = \frac{1}{N! h^{3N}} \int_{E \leq H(q, p) \leq E + \Delta E} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N}$$

$$\Sigma(E) = \frac{1}{N! h^{3N}} \int_{H \leq E} dq_1 \dots dq_{3N} dp_1 \dots dp_{3N} = \frac{V^N}{N! h^{3N}} \int_{H \leq E} dp_1 \dots dp_{3N}$$

$$\text{取 } p_i = \sqrt{2mE} \chi_i$$

$$\Sigma(E) = \frac{V^N (2mE)^{3N/2}}{N! h^{3N}} \cdot \int \dots \int_{\sum \chi_i^2 \leq 1} d\chi_1 \dots d\chi_{3N} = \left(\frac{V}{h^3} \right)^N \frac{(2\pi mE)^{3N/2}}{N! (3N/2)!}$$

$$K = \frac{\pi^{3N/2}}{(3N/2)!}$$

$$\Omega(E) = \frac{\partial \Sigma}{\partial E} \Delta E = \frac{3N}{2} \frac{\Delta E}{E} \Sigma(E) \quad \left(\begin{array}{l} \ln(N) = N \ln(N) - N \\ \ln\left(\frac{3N!}{2}\right) = \frac{3N}{2} \ln\left(\frac{3N}{2}\right) - \frac{3N}{2} \end{array} \right)$$

$$S = k \ln[\Omega(E)] = Nk \cdot \ln\left(\frac{V}{h^{3N}} \left(\frac{4\pi m E}{3N}\right)^{3/2}\right) + \frac{5}{2} Nk + k \left(\ln\left(\frac{3N}{2}\right) + \ln\left(\frac{\Delta E}{E}\right)\right)$$

热力学极限, 忽略最后一项.

$$S = Nk \ln\left(\frac{V}{h^{3N}} \left(\frac{4\pi m E}{3N}\right)^{3/2}\right) + \frac{5}{2} Nk$$

$$E(N, S, V) = \frac{3h^2 N^{5/3}}{4\pi m V^{2/3}} e^{\frac{2S}{3Nk} - \frac{5}{3}}$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N, V} = \frac{2}{3} \frac{E}{Nk}$$

$$E = \frac{3}{2} NkT$$

$$P = -\left(\frac{\partial E}{\partial V}\right)_{N, S} = \frac{2}{3} \frac{E}{V} \rightarrow PV = NkT$$

(P215)

证明归一化积分 K:

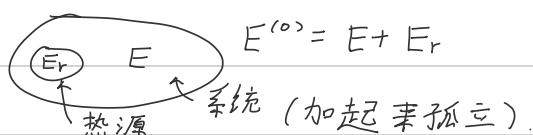
$$\begin{aligned} \text{计算积分} \int e^{-\beta E} \frac{dq_1 \cdots dq_{3N} dp_1 \cdots dp_{3N}}{h^{3N} N!} &= \frac{V^N}{N! h^{3N}} \prod_{i=1}^{3N} \int_{-\infty}^{\infty} e^{-\frac{p_i^2}{2m}} dp_i = \frac{V^N}{N! h^{3N}} \left(\frac{2\pi m}{\beta}\right)^{3N/2} \\ &\downarrow \\ &= \int_0^{\infty} e^{-\beta E} \frac{d\Sigma}{dE} dE = \int e^{-\beta E} \frac{dq_1 \cdots dq_{3N} dp_1 \cdots dp_{3N}}{N! h^{3N}} = K \frac{V^N}{N! h^{3N}} (2m)^{\frac{3N}{2}} \frac{3N}{2} \int_0^{\infty} e^{-\beta E} E^{\frac{3N}{2}-1} dE \\ &= K \frac{V^N}{N! h^{3N}} \left(\frac{2m}{\beta}\right)^{\frac{3N}{2}} \left(\frac{3N}{2}\right)! \end{aligned}$$

对比得 K.

正则系综: (N, V, T) , $F(N, V, T)$ 是特性 Function

正则分布在相空间的分布.

实际系统非孤立系固定 (N, V, T)



$$P_s \propto \Omega_r(E^{(0)} - E_s)$$

$$\ln \Omega_r(E^{(0)} - E_s) = \ln \Omega_r(E^{(0)}) + \left(\frac{\partial \ln \Omega_r}{\partial E_r} \right)_{E_r = E^{(0)}} (-E_s) \\ = \ln \Omega_r(E^{(0)}) - \beta E_s$$

归一化: $P_s = \frac{1}{Z} e^{-\beta E_s}$ $Z = \sum_s e^{-\beta E_s}$

正则分布的经典表达式

$$\rho(q, p) d\Omega = \frac{1}{N! h^{Nr}} \cdot \frac{e^{-\beta E(q, p)}}{Z} d\Omega \\ Z = \frac{1}{N! h^{Nr}} \int e^{-\beta E(q, p)} d\Omega$$

正则系综的热力学量表达式.

内能:

$$U = \overline{E} = \frac{1}{Z} \sum_s E_s e^{-\beta E_s} = \frac{1}{Z} \left(-\frac{\partial}{\partial \beta} \right) Z = -\frac{\partial}{\partial \beta} \ln Z$$

$$Y = \frac{1}{Z} \sum_s \frac{\partial E}{\partial y} e^{-\beta E_s} = -\frac{1}{\beta} \frac{\partial}{\partial y} \ln Z$$

$$\downarrow \\ P = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z$$

$$S = k (\ln Z - \beta \frac{\partial}{\partial \beta} \ln Z)$$

$$F = U - TS = -kT \ln Z \quad (\text{特性 Func!})$$

▽ 能量涨落:

$$\overline{(E - \overline{E})^2} = \sum_s P_s (E_s - \overline{E})^2 = \sum_s P_s (E_s^2 - 2\overline{E}E_s + \overline{E}^2) = \overline{E^2} - (\overline{E})^2$$

$$\text{由于: } \frac{\partial \overline{E}}{\partial \beta} = \frac{\partial}{\partial \beta} \left(\frac{\sum_s E_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} \right) = - \frac{\sum_s E_s^2 e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} + \frac{(\sum_s E_s e^{-\beta E_s})^2}{(\sum_s e^{-\beta E_s})^2} = - [\overline{E^2} - (\overline{E})^2]$$

So:

$$\overline{(E^2 - \overline{E})^2} = - \frac{\partial \overline{E}}{\partial \beta} = kT^2 \frac{\partial}{\partial T} (\overline{E})_V = kT^2 C_V \sim N$$

能量相对涨落:

$$\frac{\overline{(E - \overline{E})^2}}{(\overline{E})^2} = \frac{kT^2 C_V}{(\overline{E})^2} \sim \frac{1}{N}$$

实际气体的物态方程.

$$E = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i < j} \phi(r_{ij})$$

$$Z = \frac{1}{N! h^{3N}} \int \dots \int e^{-\beta E} dq_1 \dots dp_{3N}$$

$$\prod_{i=1}^{3N} \int_{-\infty}^{+\infty} e^{-\beta p_i^2/2m} dp_i = \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}}$$

$$Z = \frac{1}{N!} \cdot \left(\frac{2\pi m}{\beta h^2} \right)^{3N/2} Q$$

$$Q = \int \dots \int e^{-\beta \sum_{i < j} \phi(r_{ij})} d\tau_1 \dots d\tau_N$$

$d\tau_i$ 是 i 分子体积元积分.

Q 称为位形积分.

$$f_{ij} = e^{-\beta \phi(r_{ij})} - 1 \quad (\text{定义 Function})$$

位形积分表示为

$$Q = \int \cdots \int_{\Omega} (1 + f_{ij}) d\tau_1 \cdots d\tau_N$$

$$= \int \cdots \int (1 + \sum_{i < j} f_{ij} + \sum_{i < j} \sum_{i' < j'} f_{ij} f_{i'j'} + \cdots) d\tau_1 \cdots d\tau_N$$

$$Q = \int \cdots \int (1 + \sum_{i < j} f_{ij}) d\tau_1 \cdots d\tau_N \quad (\text{仅计算二阶位力系数})$$

$$\int \cdots \int f_{12} d\tau_1 \cdots d\tau_N = V^{N-2} \iint f_{12}(r_{12}) d\tau_1 d\tau_2$$

$$= V^{N-1} \int f_{12}(r) dr \quad \leftarrow \text{相对距离}$$

$$Q = V^N + \frac{N^2}{2} V^{N-1} \int f_{12}(r) dr = V^N \left(1 + \frac{N^2}{2V} \int f_{12} dr \right)$$

$$(N-1)!(N-2)! \cdots 1! = \frac{(N-1)! N}{2} \sim \frac{N^2}{2} \quad \downarrow$$

$$\ln Q = N \ln V + \ln \left(1 + \frac{N^2}{2V} \int f_{12} dr \right)$$

$$\approx N \ln V + \frac{N^2}{2V} \int f_{12} dr$$

$$p = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Z = \frac{1}{\beta} \frac{\partial}{\partial V} \ln Q = \frac{1}{\beta} \frac{N}{V} \left(1 - \frac{N}{2V} \int f_{12} dr \right)$$

$$pV = NkT \left(1 + \frac{n\beta}{V} B \right) \quad B = -\frac{N\lambda}{2} \int f_{12} dr$$

例:

$$\left(\begin{array}{l} \phi(r) = +\infty \quad r < r_0 \\ \phi(r) = -\phi_0 \left(\frac{r_0}{r} \right)^6 \quad r > r_0 \end{array} \right) \rightarrow B = -2\pi N_A \int_0^{+\infty} (e^{-\phi(r)/kT} - 1) r^2 dr \quad \nearrow \sim -\frac{\phi(r)}{kT}$$

$$= 2\pi N_A \left\{ \int_0^{r_0} r^2 dr - \int_{r_0}^{+\infty} (e^{-\frac{\phi_0}{kT} \left(\frac{r_0}{r} \right)^6} - 1) r^2 dr \right\}$$

$$= 2\pi N_A \left(\frac{r_0^3}{3} - \frac{\phi_0 r_0^3}{3kT} \right) = b - \frac{a}{N_A kT}$$

$$pV = NkT \left(1 + \frac{n}{V} \left(b - \frac{a}{N_A kT} \right) \right) = NkT \left(1 + \frac{nb}{V} \right) - \frac{n^2 a}{V}$$

$$(pV + \frac{n^2 a}{V^2})(V - nb) = NkT \quad \left| \begin{array}{l} b = \frac{2\pi}{3} N_A r_0^3 \\ a = \frac{2\pi}{3} N_A^2 \phi_0 r_0^3 \end{array} \right.$$

巨正则系综微观态分布.

$$\left(\begin{array}{c} E_r \\ E \end{array} \right) \left| \begin{array}{l} E_r + E = E^{(0)} \\ N + N_r = N^{(0)} \end{array} \right.$$

$$P_{N,S} \propto \Omega_r(N^{(0)} - N, E^{(0)} - E_s)$$

$$\ln \Omega_r(N^{(0)} - N, E^{(0)} - E_s) = \ln \Omega_r(N^{(0)}, E^{(0)}) + \left(\frac{\partial \ln \Omega_r}{\partial N_r} \right)_{N_r=N^{(0)}} (-N) + \left(\frac{\partial \ln \Omega_r}{\partial E_r} \right)_{E_r=E^{(0)}} (-E_s)$$

$$= \ln \Omega_r(N^{(0)}, E^{(0)}) - \alpha N - \beta E$$

$$\alpha = \left(\frac{\partial \ln \Omega_r}{\partial N_r} \right)_{N_r=N^{(0)}} = - \frac{\mu}{kT} \quad (\text{巨正则系综的结论})$$

$$\beta = \left(\frac{\partial \ln \Omega_r}{\partial E_r} \right) = \frac{1}{kT}$$

$$\Xi = \sum_{N=0}^{+\infty} \sum_s e^{-\alpha N - \beta E_s} \quad \rho = \frac{1}{\Xi} e^{-\alpha N - \beta E_s}$$

巨正则分布的经典表达式:

$$P_N d\mathcal{Q} dP = \frac{1}{N! h^{Nr}} \frac{e^{-\alpha N - \beta E(\mathcal{Q}, P)}}{\Xi} d\mathcal{Q}$$

$$\Xi = \sum_N \frac{e^{-\alpha N}}{N! h^{Nr}} \int e^{-\beta E(\mathcal{Q}, P)} d\mathcal{Q}$$

巨正则系综理论的热力学公式. $(\mu, T, V \sim \alpha, \beta, \gamma)$

$$\bar{N} = \frac{1}{\Xi} \sum_N \sum_s N e^{-\alpha N - \beta E_s} = \frac{1}{\Xi} \left(-\frac{\partial}{\partial \alpha} \right) \sum_N \sum_s e^{-\alpha N - \beta E_s} = -\frac{\partial}{\partial \alpha} \ln \Xi$$

$$U = \bar{E} = \frac{1}{\Xi} \sum_N \sum_s E_s e^{-\alpha N - \beta E_s} = -\frac{\partial}{\partial \beta} \ln \Xi$$

$$\gamma = \frac{1}{\Xi} \sum_N \sum_s \frac{\partial E_s}{\partial \gamma} e^{-\alpha N - \beta E_s} = -\frac{1}{\beta} \frac{\partial}{\partial \gamma} \ln \Xi$$

$$S = k \left(\ln \Xi - \alpha \frac{\partial \ln \Xi}{\partial \alpha} - \beta \frac{\partial \ln \Xi}{\partial \beta} \right)$$

涨落:

$$\overline{(N - \bar{N})^2} = - \left(\frac{\partial \bar{N}}{\partial \alpha} \right)_{\beta, \gamma} = kT \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V} \sim N$$

$$\frac{\overline{(N - \bar{N})^2}}{(\bar{N})^2} = \frac{kT}{(\bar{N})^2} \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V} \sim \frac{1}{N}$$

由于:

$$dG = -S dT + V dP + \mu dN$$

$$d(\bar{N}\mu) = -(\bar{N}s) dT + (\bar{N}v) dP + \mu d\bar{N} \quad \mu, v, s \text{ 分别为单个粒子的化学势 ...}$$

$$d\mu = v dP - s dT$$

$$\leftarrow \quad v = \frac{V}{N} \quad s = \frac{S}{N}$$

$$\left(\frac{\partial \mu}{\partial v} \right)_T = v \left(\frac{\partial P}{\partial v} \right)_T$$

$$- \frac{(\bar{N})^2}{V} \left(\frac{\partial \mu}{\partial \bar{N}} \right)_{T, V} = v \left(\frac{\partial P}{\partial v} \right)_T$$

代入 $(\gamma, 11, 0)$

$$\frac{\overline{(N - \bar{N})^2}}{(\bar{N})^2} = - \frac{kT}{V} \frac{1}{\bar{N}} \left(\frac{\partial v}{\partial P} \right)_T = \frac{kT}{V} kT$$

非平衡统计物理

Boltzmann 方程的弛豫时间近似.

o 单位体积元, 单位速度空间体积元内分子数 $f(x, y, z, v_x, v_y, v_z, t)$

$$d\eta = f(r, v, t) d\tau dW \quad d\tau = dx dy dz \quad dW = dv_x dv_y dv_z$$

After time evolution

$$d\eta' = f(r, v, t+dt) d\tau dW$$

$$d\eta' - d\eta = \frac{\partial f(r, v, t)}{\partial t} d\tau dW$$

Consider reasons for $\frac{\partial f(r, v, t)}{\partial t}$

$$\frac{\partial f(r, v, t)}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_1 + \dots$$

$\left(\frac{\partial f}{\partial t} \right)_1$ means for area $dx dy dz dv_x dv_y dv_z$; atoms getting in and out!

$$\begin{aligned} \left(\frac{\partial f}{\partial t} \right)_1 dt &= \left[(f \cdot v_x)_x \cdot dt - (f \cdot v_x)_x \cdot dt \right] dy dz dv_x dv_y dv_z + \dots \\ &= - \left(\frac{\partial f \cdot v_x}{\partial x} + \frac{\partial (f v_y)}{\partial y} + \frac{\partial (f v_z)}{\partial z} + \frac{\partial (f \cdot v_x)}{\partial v_x} + \frac{\partial (f v_y)}{\partial v_y} + \frac{\partial (f v_z)}{\partial v_z} \right) dt dx dy dz dv_x dv_y dv_z \end{aligned}$$

Suppose :

$$m(\dot{v}_x, \dot{v}_y, \dot{v}_z) = (F_x, F_y, F_z), \quad \frac{\partial F_x}{\partial v_x} = 0, \frac{\partial F_y}{\partial v_y} = 0, \frac{\partial F_z}{\partial v_z} = 0. \quad \left. \begin{array}{l} 1^\circ \text{ For } F = -\nabla V(r), \text{ true} \\ 2^\circ \text{ For } F = q\vec{v} \times \vec{B}, \text{ true} \end{array} \right\}$$

$$= (mX, mY, mZ)$$

$$\left(\frac{\partial f}{\partial t} \right)_1 = - \left(v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \right) d\tau dW$$

o 局域平衡假定(怪!)(平衡状态下分子服从 Maxwell-Boltzmann 分布)

$$f^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} (v - v_0)^2}$$

认为: 任何偏离终将被绳之以法!

$$\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t} \right)_1 - \frac{f - f^{(0)}}{\tau}$$

则: Boltzmann 方程的弛豫时间近似式!

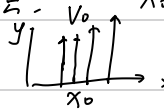
$$\frac{\partial f}{\partial t} + \left(v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \right) = - \frac{f - f^{(0)}}{\tau}$$

$$\Downarrow \frac{\partial f}{\partial t} = 0$$

$$\left(v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} \right) = - \frac{f - f^{(0)}}{\tau}$$

气体的粘性现象

- 牛顿粘性定理, P_{xy} 表示单位面积, x_0+ 气体作用于 x_0- 气体的力.

$$P_{xy} = \eta \frac{dV_y}{dx}$$


η 为粘度, 单位为 $\text{Pa} \cdot \text{s}$.

- 微观角度推导 η :

$$\nabla f = f(V_x, V_y, V_z, x_0) ; f^{(0)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} [V_x^2 + (V_y - V_0)^2 + V_z^2]}$$

$$\left(V_x \frac{\partial f}{\partial x} + V_y \frac{\partial f}{\partial y} + V_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial x} + Y \frac{\partial f}{\partial y} + Z \frac{\partial f}{\partial z} \right) = - \frac{f - f^{(0)}}{\tau_0} \leftarrow \text{Boltzmann Func, 弛豫象时附近似.}$$

$(x, y, z) = 0$
没有外力; $f = f(x, V_x, V_y, V_z)$

$$V_x \frac{\partial f}{\partial x} = - \frac{f - f^{(0)}}{\tau_0}$$

取:

$$f = f^{(0)} + f^{(1)}$$

$$V_x \frac{\partial f^{(0)}}{\partial x} = - \frac{f^{(1)}}{\tau_0}$$

则:

$$f^{(1)} = - \tau_0 V_x \frac{\partial f^{(0)}}{\partial x}$$

$$= \tau_0 V_x \frac{\partial f^{(0)}}{\partial (V_y - V_0)} \frac{\partial V_0}{\partial x}$$

$$= \tau_0 V_x \frac{\partial f^{(0)}}{\partial V_y} \frac{\partial V_0}{\partial x}$$

$$f = f^{(0)} + f^{(1)} = f^{(0)} + \tau_0 V_x \frac{\partial f^{(0)}}{\partial V_y} \frac{dV_0}{dx}$$

— (1)

Relation between f & P_{xy}

单位时间, 单位面积, 通过 x_0- 到 x_0+ 的粒子数

$$dP = V_x f dV_x dV_y dV_z$$

从右方进入正方的动量 (unit area, unit time)

$$\int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} m V_x V_y f dV_x dV_y dV_z$$

$\rightarrow$ momentum flow
 x_0

(unit area, unit time), $x_0+ \rightarrow x_0-$; momentum translation; = force per area.

$$- \int_{-\infty}^0 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} m V_x V_y f dV_x dV_y dV_z$$

$\leftarrow$ P flow

$$P_{xy} = - \int_{-\infty}^{+\infty} m V_x V_y f dV_x dV_y dV_z$$

— (2)

Combine (1) (2)

$$P_{xy} = - \iiint_{-\infty}^{+\infty} m V_x V_y \left(f^{(0)} + \tau_0 V_x \frac{\partial f^{(0)}}{\partial V_y} \frac{dV_0}{dx} \right) dV_x dV_y dV_z$$

$$= - \iiint_{-\infty}^{+\infty} m \tau_0 V_x^2 V_y \frac{dV_0}{dx} \frac{\partial f^{(0)}}{\partial V_y} dV_x dV_y dV_z$$

粘度

$$\eta = - m \iiint V_x^2 V_y \tau_0 \frac{\partial f^{(0)}}{\partial V_y} dV_x dV_y dV_z$$

Integral by parts

$$\int_{-\infty}^{+\infty} V_y \frac{\partial f^{(0)}}{\partial V_y} dV_y = \left[f^{(0)} V_y \right]_{-\infty}^{+\infty} - \int_{-\infty}^{+\infty} f^{(0)} dV_y = - \int_{-\infty}^{+\infty} f^{(0)} dV_y$$

$$\eta = m \tau_0 \iiint V_x^2 f^{(0)} dV_x dV_y dV_z = n m \tau_0 \overline{V_x^2}$$

$$\text{能均分 Theory } \frac{1}{2} m \overline{V_x^2} = \frac{1}{2} kT \Rightarrow \eta = \frac{1}{2} n kT \tau_0$$

金属的电导率

▽ Boltzmann Func 弛豫时间近似: (仅有 E_z)

$$-\frac{eE_z}{m} \frac{\partial f}{\partial v_z} = -\frac{f-f^{(0)}}{\tau_0}$$

suppose $f = f^{(0)} + f^{(1)}$

$$\frac{eE_z}{m} \frac{\partial f^{(0)}}{\partial v_z} = \frac{f^{(1)}}{\tau_0}$$

Then

$$f = f^{(0)} + f^{(1)} = f^{(0)} + \frac{eE_z}{m} \tau_0 \frac{\partial f^{(0)}}{\partial v_z}$$

▽ 用 $f \rightarrow$ derive $J = eE$ 中的 e .

Fermi-Dirac 分布:

$$f' = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}$$

处于 unit space 中, $dv_x dv_y dv_z$ 中的电子数量 (对体积数密度的贡献)

$$f' \cdot \frac{2}{h^3} d(mv_x) d(mv_y) d(mv_z) \rightarrow f^{(0)} = f' \cdot \frac{2m^3}{h^3}; \quad 2 \text{ 是自旋引起的简并}$$

电流密度

$$J_z = (-e) \int f \cdot v_z \frac{2m^3}{h^3} dv$$

Insert: $f = f^{(0)} + \frac{eE_z}{m} \tau_0 \frac{\partial f^{(0)}}{\partial v_z}$ $f^{(0)}$ leads to 0

$$J_z = -\frac{e^2 E_z}{m} \int \tau_0 v_z \frac{\partial f^{(0)}}{\partial v_z} \cdot \frac{2m^3}{h^3} dv \quad dv_x dv_y dv_z$$

Integral by parts $\int v_z \frac{df^{(0)}}{dv_z} dv_z = (f^{(0)} v_z) \Big|_{-}^{+} - \int f^{(0)} dv_z$

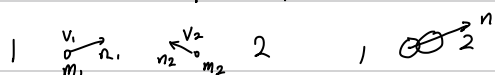
$$J_z = \frac{e^2 E_z}{m} \tau_F \int f^{(0)} \cdot \frac{2m^3}{h^3} dv_x dv_y dv_z$$

$$\underbrace{\frac{2 \cdot dP_x dP_y dP_z}{h^3}}$$

$$= n \frac{e \tau_F}{m} E_z$$

Boltzmann 积分微分方程.

经典力学的二体碰撞.



$$v_1' = v_1 + \frac{2m_2}{m_1+m_2} [(v_2-v_1) \cdot n] n$$

$$v_2' = v_2 - \frac{2m_1}{m_1+m_2} [(v_2-v_1) \cdot n] n$$

相对速度在碰撞前后改变符号

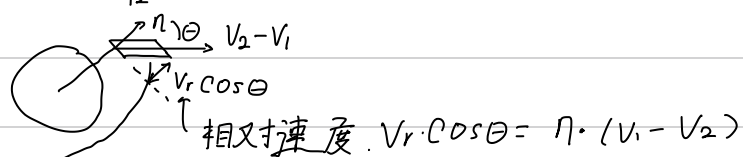
$$(v_2' - v_1') \cdot n = -(v_2 - v_1) \cdot n$$

反碰撞: 碰撞前速度为 v_1, v_2 , 碰撞方向 $n' = -n$

$$v_1 = v_1' + \frac{2m_2}{m_1+m_2} [(v_2' - v_1') \cdot (-n)] (-n)$$

$$v_2 = v_2' - \frac{2m_1}{m_1+m_2} [(v_2' - v_1') \cdot (-n)] (-n)$$

分子碰撞数 $d_{12} = \frac{1}{2}(d_1 + d_2)$



体积:

$$d_{12}^2 \cdot dV \cdot v_r \cdot \cos \theta \cdot dt$$

t 时刻, 体积元 $d\tau$ 内, 速度空间 dW 内 分子数 $f(r, v, t) \cdot d\tau \cdot dW$.

单位时间, 立体角在速度间隔 dW_2 内与分子 2 碰撞次数

$$f_2 \cdot dW_2 \cdot d_{12}^2 v_r \cdot \cos \theta \cdot dV \cdot dt$$

耳又:

$$\Lambda \cdot dV = d_{12}^2 \cdot (\vec{v}_1 - \vec{v}_2) \cdot \vec{n} \cdot dV = d_{12}^2 \cdot v_r \cdot \cos \theta \cdot dV \cdot dt$$

$$f_2 \cdot \Lambda \cdot dW_2 \cdot dV \cdot dt$$

总碰撞:

$$f_1 f_2 dW_1 dW_2 \Lambda dV dt d\tau$$

反元碰撞

$$f_1' f_2' dW_1' dW_2' \Lambda' dV dt d\tau \quad n' = -n$$

$$\Lambda' = d_{12}^2 (v_1' - v_2') \cdot n'$$

由于:

$$v_1 = v_1' + \frac{2m_2}{m_1+m_2} [(v_2' - v_1') \cdot n] n$$

$$v_2 = v_2' - \frac{2m_1}{m_1+m_2} [(v_2' - v_1') \cdot n] n$$

$$dW_1 dW_2 = |J| dW_1 dW_2 \quad |J| = \frac{\partial (V_1^x V_1^y V_1^z, \dots)}{\partial (V_1^x V_1^y V_1^z, \dots)} = 1$$

$$\Lambda' = d_{12}^2 (v_1' - v_2') \cdot n' = d_{12}^2 (v_1 - v_2) \cdot n = \Lambda$$

反元碰撞

$$f_1' f_2' dW_1 dW_2 \Lambda dV dt$$

由碰撞增加分子数

$$\left(\frac{\partial f}{\partial t}\right)_c dt d\tau \cdot dW_1 = dt d\tau dW_1 \iint (f'_1 f'_2 - f_1 f_2) dW_2 \wedge d\Omega$$

$\Downarrow$

$$\left(\frac{\partial f}{\partial t}\right)_c = \iint (f'_1 f'_2 - f_1 f_2) dW_2 \wedge d\Omega$$

确定分布 Func $\left(\frac{\partial f}{\partial t} = \left(\frac{\partial f}{\partial t}\right)_c + \left(\frac{\partial f}{\partial t}\right)_1\right) \Downarrow$ Boltzmann 方程微分 Func.

$$\frac{\partial f}{\partial t} + V_x \frac{\partial f}{\partial x} + V_y \frac{\partial f}{\partial y} + V_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial V_x} + Y \frac{\partial f}{\partial V_y} + Z \frac{\partial f}{\partial V_z} = \iint (f'_1 f'_2 - f_1 f_2) dW_2 \wedge d\Omega$$

$\int dW_1$ 为全空间.

$$\int d\Omega = \int_0^{2\pi} d\varphi \int_0^{\pi/2} \sin\theta d\theta.$$

H 定理

◦ H - Functional

$$H = \iint f(r, v, t) \ln f(r, v, t) \cdot d\tau dW = \iint f \ln f d\tau dW$$

$$\begin{aligned} \frac{dH}{dt} &= \frac{d}{dt} \left(\iint f \ln f d\tau dW \right) \\ &= \iint (1 + \ln f) \cdot \frac{\partial f}{\partial t} \cdot d\tau dW \end{aligned}$$

Boltzmann Eq.:

$$\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} + X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z} = \iint (f'f'_1 - ff_1) dW_1 \Lambda d\Omega$$

$$\begin{aligned} \frac{dH}{dt} &= - \iint (1 + \ln f) (v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z}) d\tau dW && - 1^\circ \\ &\quad - \iint (1 + \ln f) (X \frac{\partial f}{\partial v_x} + Y \frac{\partial f}{\partial v_y} + Z \frac{\partial f}{\partial v_z}) d\tau dW && - 2^\circ \\ &\quad - \iiint (1 + \ln f) (ff_1 - f'f'_1) d\tau dW_1 \Lambda d\Omega dW && - 3^\circ \end{aligned}$$

$$1^\circ \quad - \int (1 + \ln f) (v \cdot \nabla f) d\tau = - \int \nabla \cdot (v f \ln f) d\tau = - \oint dS \cdot v f \ln f = 0.$$

$$\leftarrow \frac{\partial X}{\partial v_x} = \frac{\partial Y}{\partial v_y} = \frac{\partial Z}{\partial v_z} = 0$$

$$\begin{aligned} 2^\circ \quad & - \int (1 + \ln f) \cdot \left(\frac{\partial}{\partial v_x} (Xf) + \frac{\partial}{\partial v_y} (Yf) + \frac{\partial}{\partial v_z} (Zf) \right) dW \\ &= - \int \left[\frac{\partial}{\partial v_x} (Xf \ln f) + \frac{\partial}{\partial v_y} (Yf \ln f) + \frac{\partial}{\partial v_z} (Zf \ln f) \right] dW \end{aligned}$$

$$\text{每一項都是 } 0 \quad \int d(Xf \ln f) dv_y dv_z = 0.$$

$$3^\circ \quad \frac{dH}{dt} = - \frac{1}{2} \cdot \iiint (1 + \ln f) (ff_1 - f'f'_1) dW dW_1 \Lambda d\Omega d\tau$$

$$= - \iiint (1 + \ln f_1) (ff_1 - f'f'_1) dW dW_1 \Lambda d\Omega d\tau$$

$$= - \frac{1}{2} \iiint (2 + \ln(f f_1)) \cdot (ff_1 - f'f'_1) dW dW_1 \Lambda d\Omega d\tau$$

$$= - \frac{1}{2} \iiint (2 + \ln(f f_1)) \cdot (f'f'_1 - ff_1) \cdot dW dW_1 \Lambda d\Omega d\tau$$

$$= - \frac{1}{4} \iiint \underbrace{(\ln(ff_1) - \ln(f'f'_1))}_{\geq 0} (ff_1 - f'f'_1) \cdot dW dW_1 \Lambda d\Omega d\tau$$

$$\leq 0. \quad ff_1 = f'f'_1 \text{ 时成立.}$$

