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大学物理笔记

多普勒效应

source: v_s , observer: v_o , distance L

issued at $t = 0, x = 0$, received at $t'_1, L + v_o t'_1$

issued at $t = T, x = v_s T$, received at $t'_2, L + v_o t'_2$

由运动学:

$$\begin{aligned} v_P t'_1 &= L + v_o t'_1 \\ v_P (t'_2 - T) &= L + v_o t'_2 - v_s T \end{aligned}$$

于是

$$\begin{aligned}
t'_1 &= \frac{L}{v_P - v_O} \\
t'_2 &= \frac{L}{v_P - v_O} + \frac{v_P - v_S}{v_P - v_O} T \\
T' &= t'_2 - t'_1 = \frac{v_P - v_S}{v_P - v_O} T \\
\nu' &= \frac{v_P - v_O}{v_P - v_S} \nu
\end{aligned}$$

Discussion:

$v_O > v_S$ (including $v_S \leq 0$): separating, $\nu' < \nu$, Doppler redshift

$v_S > v_O$ (including $v_O \leq 0$): approaching, $\nu' > \nu$, Doppler blueshift

靠近: 频率变高; 远离: 频率变低

考虑波源的运动与波振面的运动 (supersonic speed $v_S > v_P$)

马赫锥: $\sin\theta = \frac{v_P}{v_S}$

驻波(stationary wave)

- 推导

由 $kx - \omega t - \phi = \text{const}$, 求导得 $v = \frac{\omega}{k}$

$$u_1 = A \cos(kx - \omega t - \phi)$$

$$u_2 = A \cos(kx + \omega t)$$

$$= A \cos\left(k\left(x + \frac{\omega}{k}t\right)\right) \quad (1)$$

$$\text{从而 } u_1 + u_2 = 2A \cos\left(kx - \frac{\phi}{2}\right) \cos\left(\omega t + \frac{\phi}{2}\right)$$

令 $(u_1 + u_2)_{x=0} = 0$, 得 $\phi = \pi$; 令 $(u_1 + u_2)_{x=L} = 0$, 得 $L = \frac{n\pi}{k} = \frac{n\lambda}{2}$

注意 $\lambda = T \cdot v_P = \frac{2\pi}{\omega} \cdot \frac{\omega}{k} = \frac{2\pi}{k}$, $k = \frac{2\pi}{\lambda}$, $\omega = vk$, 有

$$\begin{aligned}
f &= \frac{\omega}{2\pi} = \frac{kv}{2\pi} = n \frac{v}{2L} \\
&= f_n \\
&= nf_1
\end{aligned}$$

波节(node), 波腹(antinode)的定义

- 半波损失

fixed hard boundary; from high speed to low speed

由(1)式, 令 $(u_1 + u_2)_{x=0} = 0$, 得 $\phi = \pi$, 即为在固定端的相差

第九章 Relativistic Mechanics 相对论力学

9.1 伽利略变换

- 观测者:一套矫正好的时钟,可记录 x, y, z, t
- 结果 $t'_A - t'_B = t_A - t_B, x'_A - x'_B = x_A - x_B - u(t_A - t_B)$

同时测量: $x'_A - x'_B = x_A - x_B$

速度直接叠加,加速度不变

- Galileo's relativity: 力学定律在不同惯性参考系中相同
- 电学:不满足麦克斯韦方程组

9.2 洛伦兹变换 Lorentz Transformation

- Two basic principles of Special Theory of Relativity
 - 所有惯性参考系中物理定律相同(力学,电学等)
 - 光速不变
- 推导

假定变换为线性变换(考虑匀速直线运动);

待定系数:

$$\begin{aligned}x' &= a_{11}x + a_{12}y + a_{13}z + a_{14}t \\y' &= y \\z' &= z\end{aligned}$$

For arbitrary y, z if $x' = 0, x = ut$; 则

$$x' = a_{11}(u)(x - ut), a_{11}(0) = 1 \quad (1.1)$$

By the principle of relativity, we have

$$\begin{aligned}x &= a_{11}(-u)(x' + ut'), \text{ 带入(1.1), 有} \\t' &= f(x, x'(u, t)) = a_{44}t + a_{41}x\end{aligned}$$

从而

$$\begin{aligned}x' &= a(x - ut) \\t' &= b(t - ex)\end{aligned} \quad (1.2)$$

解得 $x = \frac{1}{\Delta}(bx' + aut')$

与 $x = a_{11}(-u)(x' + ut')$ 比较, 得 $a = b$

考虑光速不变: 假设 $t = t' = 0$ 时在原点发出光信号, 有

$$\begin{aligned}x^2 + y^2 + z^2 &= c^2 t^2 \\x'^2 + y'^2 + z'^2 &= c^2 t'^2\end{aligned}$$

代入 (1.2) 式, 有

$$e = \frac{u}{c^2}$$

$$a = \frac{1}{\sqrt{1 - \beta^2}} = \gamma = \sqrt{1 - \frac{v^2}{c^2}}$$

其中 $\beta = \frac{u}{c}$

完整的变换关系为

$$\begin{aligned}x' &= \gamma(x - ut) \\y' &= y \\z' &= z \\t' &= \gamma(t - \frac{u}{c^2}x)\end{aligned}$$

考虑事件对 $(x'_1, t'_1), (x'_2, t'_2)$, 洛伦兹变换是

$$\begin{aligned}\Delta x' &= \gamma(\Delta x - u\Delta t) \\ \Delta y' &= \Delta y \\ \Delta z' &= \Delta z \\ \Delta t' &= \gamma(\Delta t - \frac{u}{c^2}\Delta x)\end{aligned} \tag{1.3}$$

- 讨论

- 逆变换: $u \rightarrow -u$ 直接根据相对性原理
- Invariance of spacetime interval 时空间隔不变: $(\Delta s)^2 = (c\Delta t)^2 - (\Delta x)^2 - (\Delta y)^2 - (\Delta z)^2 = (\Delta s')^2$
- 伽利略变换: 时间归时间 空间归空间 时间空间分别不变

- 事件对

- 光信号联系: $(c\Delta t)^2 = (\Delta x)^2, \Delta s = 0$
- 固有时间间隔与固有空间间隔

- Simultaneous measurement $\Delta x' = \ell_0$ in $S' (\Delta t' = 0)$ 形成一个事件

the same pair of events in S:

$$\begin{aligned}\Delta x &= \gamma(\Delta x' + u\Delta t') = \gamma\Delta x' = \gamma\ell_0 \\ \Delta t &= \gamma(\Delta t + \frac{u}{c^2}\Delta x') = 0\end{aligned} \quad \text{同时的相对性}$$

也即 $\ell = \ell_0 \sqrt{1 - \frac{v^2}{c^2}} = \frac{\ell_0}{\gamma}$

- 用光速不变推出钟慢:

$$\Delta t' = \frac{2L_0}{c}$$

$$\left(\frac{u\Delta t}{2}\right)^2 + L_0^2 = \left(\frac{c\Delta t}{2}\right)^2 \text{ (用到光速不变)}$$

$$\Delta t = \frac{2L_0}{\sqrt{c^2 - u^2}} = \frac{2L_0/c}{\sqrt{1 - \beta^2}} = \gamma \Delta t'$$

- 用光速不变推出尺缩:

$$c\Delta t_1 = L + u\Delta t_1, c\Delta t_2 = L - u\Delta t_2$$

$$\Delta t = \Delta t_1 + \Delta t_2 = \frac{L}{c+u} + \frac{L}{c-u} = \frac{2L}{c} \frac{1}{1-\beta^2}$$

$$\Delta t' = \frac{2L_0}{c} = \gamma \Delta t$$

$$\frac{2L_0}{c\gamma} = \frac{2L}{c} \frac{1}{1-\beta^2}$$

$$\text{于是 } L = \frac{L_0}{\gamma}$$

- 因果律及信号传播(Causality and signal speed)
 - An event $P(x_P, t_P)$ causes an event $Q(x_Q, t_Q)$. 信号传输速度

$$v_S = \frac{x_Q - x_P}{t_Q - t_P} = \frac{\Delta x}{\Delta t}$$

在 $S'(u)$ 系中时间间隔为

$$\Delta t' = \gamma \Delta t \left(1 - \frac{uv_S}{c^2}\right)$$

为保证先后次序,必须有

$$1 - \frac{uv_S}{c^2} < 0$$

则 $v_S < c$

- 光多普勒效应

- 由(1.3), $\Delta t = \sqrt{\frac{1+\beta}{1-\beta}} \Delta t'$
- redshift: $\nu_0 = \sqrt{\frac{1-\beta}{1+\beta}} \nu_e$

- 波动方程: 用洛伦兹变换恰好符合(洛伦兹不变)

9.3 时空图和孪生paradox

- Minkowski Space
 - 洛伦兹变换在时空图中的体现
- Twin paradox: 在宇宙飞船加速,减速的过程中经历了非惯性系
- Pole-barn Paradox: 火车进隧道;火车系:隧道收缩;地面系:火车收缩
 - 涉及同时的相对性:看能否在地面系同时关上前门和后门(火车系觉得没有同时)
 - 地面系的观测者觉得能关进去,在火车系的观测者看来后门早就关起来了
- Visual Apperance

- 球不变 立方体转过一个角度

9.4 相对论运动学

- 速度变换公式(求导可得)

$$\begin{aligned}v'_x &= \frac{v_x - u}{1 - v_x \frac{u}{c^2}} \\v'_y &= \frac{v_y}{\gamma(1 - v_x \frac{u}{c^2})} \\v'_z &= \frac{v_z}{\gamma(1 - v_x \frac{u}{c^2})}\end{aligned}$$

9.5 相对论动力学(Relativistic Dynamics)

- 广义相对论: 引力场, 非惯性系
- 讨论 m, p, F, E_k, a
- Discuss a completely inelastic collision(保持动量守恒)
 - In $S'(-u) : u, -u \rightarrow 0, 0$
 - In $S : v_x, 0 \rightarrow u, u; \quad v_x = \frac{u + u}{1 + u \frac{u}{c^2}} \quad (9.5.1)$
 - 而 $m \frac{u + u}{1 + \frac{uu}{c^2}} + m \times 0 = 2mu$, 动量守恒不成立.
 - 假定 $m \equiv m(v), m_0 \equiv m(0)$, 有

$$\begin{aligned}m(v_x) + m_0 &= m_{total}(u) \\m(v_x) \cdot v_x + m_0 \cdot 0 &= m_t(u)u \\&= [m(v_x) + m_0]u \\求得 m(v_x) &= \frac{m_0}{\frac{v_x}{u} - 1}\end{aligned}$$

由 (9.5.1), $\frac{v_x}{u} - 1 = \sqrt{1 - \beta^2}$, 则 $m(v) = \gamma m_0$. 于是

$$\begin{aligned}p &= \gamma m_0 v \\E_k &= \int F \cdot dx = \int \frac{d}{dt}(mv) \cdot dx = \int v \cdot d(mv) \\而 d(mv) &= v dm + m dv \\则 E_k &= \int (v^2 dm + m v dv)\end{aligned}$$

考虑 $m^2(1 - \frac{v^2}{c^2}) = m_0^2, m^2(c^2 - v^2) = m_0^2 c^2$, 两边微分得

$$\begin{aligned}c^2 2m dm - v^2 2m dm - m^2 2v dv &= 0, \\c^2 dm - v^2 dm - m dv &= 0, c^2 dm = v^2 dm + m dv\end{aligned}$$

于是

$$\begin{aligned}
 E_k &= \int c^2 dm = mc^2 - m_0 c^2 \\
 &= m_0 c^2 \left[\frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} - 1 \right] \\
 &= (\gamma - 1) m_0 c^2
 \end{aligned}$$

- 讨论
 - 牛顿力学中

$$E_k = \int \mathbf{v} \cdot d(m\mathbf{v}) = \int m\mathbf{v} \cdot d\mathbf{v} = \frac{1}{2}mv^2$$

- ◦ 相对论中, mass-energy $E = mc^2 = E_k + m_0 c^2$
- ◦ 已知动能求速度: $\gamma = \frac{E_k}{m_0 c^2} + 1$
- 相对论能量-动量关系
 - $E = \sqrt{c^2 p^2 + m_0^2 c^4}$
 - 若 $m_0 = 0$, $E = cp$, $p = \frac{E}{c}$
 - 若 $cp \ll m_0 c^2$, 泰勒展开后得到牛顿力学.

期末考试大致内容

- 相对论运动学: 速度的变换
- 理想气体(或给定气体的状态方程) 等温膨胀, 绝热等过程, 功和热, 内能等
- 理想气体的性质: 速度, 平均动能等
- 过程中温度的变化, 熵的变化
- 过程中 **亥姆霍兹自由能变**, 求平衡态(可能有数学上求导等)
- 比热容, 温度.
- 相变 三相点.

Project Proposal

- structure
 - Template
 - Guideline
- how and where
- basics of thesis writing
- deadline

第十章 温度

10.1 Equilibrium state

- **System exchange**

isolated ×

| System | exchange |
|--------|---------------|
| closed | energy |
| open | energy&matter |

- Thermodynamic Equilibrium state: 宏观状态不随时间改变,除非外界条件发生变化.
- description of equilibrium state: state variables
 - extensive quantity: $F(n \text{ systems}) = nF(1 \text{ system})$
 - intensive quantity: $F(n \text{ systems}) = F(1 \text{ system})$
- relaxation time τ : 恢复平衡所用时间
- Quasi-static process 准静态过程: $t \gg \tau$, 每一点都是平衡态, 可以在状态图上画出.
- No-dissipative, quasi-static process is reversible. (无耗散准静态过程是可逆的); All natural process(自发过程) is irreversible.
 - 系统和外界同时恢复初态

10.2 Thermal equilibrium and temperature

- The zeroth law of thermodynamics: 热平衡的传递性(热平衡的系统有共同性质)
- 温度: 衡量热平衡的一种物理性质
- 各种温标

10.4 物态方程

- 微分的常见写法 $(\frac{\partial U}{\partial V})_T$, $(\frac{\partial U}{\partial V})_P$. 保持右下标不变
- P, V, T 不独立, $f(P, V, T) = 0 \rightarrow U(T, P) = U(T, V(P, T)) = U(T, V) = 0$
- 等压线膨胀系数 $\alpha_\ell = \frac{1}{L} \frac{\partial L}{\partial T}_P$; $\alpha_V = \frac{1}{V} (\frac{\partial V}{\partial T})_P = \frac{1}{L^3} (\frac{\partial L^3}{\partial T})_P = 3\alpha_\ell$
- 等温线膨胀系数 $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial p}_T$
- 体积变化方程

$$\frac{dV}{V} = \frac{1}{V} (\frac{\partial V}{\partial T})_P dT + \frac{1}{V} (\frac{\partial V}{\partial p})_T dp = \alpha_V(T) dT - \kappa_T(p) dp$$

(全微分)

$$\ln \frac{V}{V_0} = \alpha_V \Delta T - \kappa_T \Delta p$$

$$V = V_0 (1 + \alpha_V \Delta T - \kappa_T \Delta p)$$

- Van der Waal's equation

$$[p + a(\frac{n}{V})^2](V - nb) = nRT$$

推导: 对1mol理想气体:

$$p = \frac{RT}{V_m} \leftarrow \frac{RT}{V_m - b} \text{ (相互作用, 体积减小)}$$

$$\leftarrow \frac{RT}{V_m - b} - \frac{a}{V^2} \text{ (相互作用, 压强减小, 体积越小作用力越大)}$$

第十一章 热力学第一定律

11.1 功,内能和热力学第一定律

- 准静态过程压活塞 $\bar{d}W = -p\bar{d}V$, $W = -\int_{V_i}^{V_f} p dV$ (依赖于 $P - V$ 图上的路径,不是全微分)
- 绝热功: Internal energy function $\Delta U = U_B - U_A \equiv W_{BA} \equiv -W_{AB}$ (用与路径无关的绝热功定义内能变化)
- 非绝热功: $\Delta U = W + Q$ 外界做的功和外界传给内部的热量; 微分 $dU = \bar{d}Q + \bar{d}W$ (功和热不是全微分,与路径有关)

11.3 热容和比热容(Heat capacity and specific heat capacity)

- $C = \lim_{\Delta T \rightarrow 0} \frac{\Delta Q}{\Delta T}$; specific: $C_m = \frac{C}{n}$
 - $C = 0$: 绝热(adiabatic)过程, $\Delta Q = 0$
 - $C = \infty$: 等温(isothermal)过程, $\Delta T = 0$
- $C_V = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta Q}{\Delta T}\right)_V = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$
- $C_P = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta Q}{\Delta T}\right)_p = \lim_{\Delta T \rightarrow 0} \left(\frac{\Delta U + p\Delta V}{\Delta T}\right)_p = \left(\frac{\partial(U + pV)}{\partial T}\right)_p \equiv \left(\frac{\partial H}{\partial T}\right)_p$, $H = U + pV$: enthalpy, 焓
- ratio of specific heat: $\gamma = \frac{C_p}{C_V}$
- heat capacity of ideal gases

| | |
|----------------------------|-----------------------|
| monatomic ideal gas | $C_V = \frac{3}{2}nR$ |
| 双原子 ideal gas | $C_V = \frac{5}{2}nR$ |
| 三原子 ideal gas | $C_V = \frac{6}{2}nR$ |

11.4 Free expansion and internal energy of gas

- Case of free expansion

$$U = U(T, V)$$

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

$$T = T(U, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \left[\left(\frac{\partial T}{\partial U}\right)_V dU + \left(\frac{\partial T}{\partial V}\right)_U dV \right] + \left(\frac{\partial U}{\partial V}\right)_T dV$$

对照左右,得

$$\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial U}\right)_V = 1$$

$$\left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_U = -C_V \left(\frac{\partial T}{\partial V}\right)_U \rightarrow \text{焦耳系数} = 0 (\text{理想气体})$$

故 $U = U(T)$

- 焦耳的实验非常不严谨
- 理想气体:

$$dU(T) = \frac{dU}{dT} dT = C_V dT$$

$$U = U_0 + C_V T$$

$$dQ = dU - dW = C_V dT + p dV$$

理想气体: $d(pV) = d(nRT)$

$$p dV + V dp = nR dT, p dV = nR dT - V dp$$

$$dQ = (C_V + nR) dT - V dp$$

$$C_p = C_V + nR \rightarrow C_V = \frac{nR}{\gamma - 1}, C_p = \frac{\gamma nR}{\gamma - 1}$$

11.5 Adiabatic equation

$$\begin{aligned} dQ &= dU - dW, \\ &= C_V dT + p dV \end{aligned}$$

$$C_V dT + p dV = 0$$

$$\text{又 } V dp + p dV = nR dT = (\gamma - 1) C_V dT$$

消去 dT , 得

$$V dp + \gamma p dV = 0$$

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0$$

$$\ln p + \gamma \ln V = C$$

$$p V^\gamma = C$$

由 $\gamma > 1$, 绝热线比等温线陡峭

- adiabatic work

$$\begin{aligned}
 W_S &= - \int_{V_1}^{V_2} p dV = -C \int_{V_1}^{V_2} \frac{dV}{V^\gamma} = \frac{C}{\gamma-1} \left(\frac{V_2}{V_2^\gamma} - \frac{V_1}{V_1^\gamma} \right) \\
 &= \frac{1}{\gamma-1} (p_2 V_2 - p_1 V_1) \\
 &= \frac{nR}{\gamma-1} (T_2 - T_1) \\
 &= C_V (T_2 - T_1) = \Delta U
 \end{aligned}$$

- 声音的传播: 绝热

11.6 卡诺循环

- 高温热源 T_1 等温膨胀 → 绝热膨胀 → 低温热源 T_2 等温压缩 → 绝热压缩
- $T_1, U = U(T_1) = \text{const}$ 热机吸热, 做功
- T_2 热机放热
- 整个循环: $\Delta U = 0, \Delta Q_{12} + \Delta Q_{34} - \Delta W = 0$

$$\text{效率 } \eta = \frac{\Delta W}{\Delta Q_{12}} = \frac{\Delta Q_{12} + \Delta Q_{34}}{\Delta Q_{12}} = \frac{Q_1 - Q_2}{Q_1}$$

(考察做功过程中的放热 Q_2 , 放热越多效率越低)

$$\text{等温过程: } Q_1 = \Delta W_{12} = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{nRT_1}{V} dV = nRT_1 \ln \frac{V_2}{V_1}$$

$$Q_2 = -\Delta Q_{34} = nRT_2 \ln \frac{V_3}{V_4}$$

$$\eta = 1 - \frac{T_2 \ln \frac{V_3}{V_4}}{T_1 \ln \frac{V_2}{V_1}}$$

$$2 \rightarrow 3 : T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$4 \rightarrow 1 : T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

要学会将此推导推广到其他热机上

- 可逆过程: 外界不可逆
- 逆卡诺循环: 从低温热源吸热 到高温热源被做功, 放热

第十二章 热力学第二定律

12.1 内容

- No process is possible whose sole result is the absorption of heat from a reservoir and the conversion of this heat into work.
- No process is possible whose sole result is the transfer of heat from a cooler to a hotter body.
- 自发过程具有方向性

12.2 卡诺定理

- 任何热机效率不超过可逆热机

- 证明: 任意热机做功驱动可逆热机的逆过程, 反证法与热二矛盾

12.3 熵与熵原理

- 熵的引入

假设 $Q_2 < 0$ 为放热:

$$\text{效率不大于卡诺热机: } \eta_A = 1 + \frac{Q_2}{Q_1} \leq 1 - \frac{T_2}{T_1}$$

$$\sum_{i=1}^2 \frac{Q_i}{T_i} \leq 0$$

$$\text{一般过程: } \sum_{i=1}^n \frac{Q_i}{T_i} \leq 0 \text{ (系统与很多热源接触)}$$

$$\oint \frac{dQ}{T} \leq 0$$

(取等: 可逆过程, 考虑 $Q_i \rightarrow -Q_i$)

(环路积分)

$$\text{写作全微分: } \frac{\bar{d}Q}{T} \equiv dS$$

$$S_B - S_A = \int_A^B \left(\frac{dQ}{T} \right)_R$$

若环路中包含不可逆过程:

$$\begin{aligned} \oint \left(\frac{dQ}{T} \right) &< 0 \\ \int_A^B \left(\frac{dQ}{T} \right)_{IR} + \int_A^B \left(\frac{dQ}{T} \right)_R &< 0 \\ \int_A^B \left(\frac{dQ}{T} \right)_{IR} - \int_B^A \left(\frac{dQ}{T} \right)_R &< 0 \\ S_B - S_A &> \int_A^B \left(\frac{dQ}{T} \right)_{IR} \\ \int_A^B dS &> \int_A^B \left(\frac{dQ}{T} \right)_{IR} \\ dS &> \left(\frac{dQ}{T} \right)_{IR} \end{aligned}$$

- 熵原理: 任何过程: $dS \geq \frac{dQ}{T}$
 - 绝热过程: $dQ = 0$; 可逆: $dS = 0$, isentropic 等熵过程
 - 孤立系统: $dS \geq 0$; 非平衡趋于平衡: 熵增加; 平衡态: 宏观特征不变, 熵最大
- 热二的另一种形式: The entropy of an isolated system never decreases.

- 从单一热源吸热的熵变: $\Delta S = \frac{\Delta Q}{T} = \frac{-Q}{T} < 0$, 矛盾!
- 两热源 $T_1 > T_2$, T_1 吸热, T_2 放热: $\Delta S = \frac{Q}{T_1} - \frac{Q}{T_2} < 0$, 矛盾!

- 克劳修斯不等式的证明: 考虑多热源与单一热源 T_0 由多个卡诺机联合:

- 系统作循环过程, 分别与热源 T_i 交换 Q_i 的热量
- $T_0 \rightarrow T_i$ 之间加上卡诺热机
- $T_0 \rightarrow Q_{0i}$
- Carnot engines: $\frac{Q_{0i}}{T_0} = \frac{Q_i}{T_i}$
- 对整个辅助系统: T_i 系统, 热机不变, 热源 T_0 放热, 对外做功. 第一定律: $\sum_{n=1}^n Q_{0i} = \sum_{n=1}^n W_i$
- 第二定律: 没有真正做功 $\sum_{n=1}^n Q_{0i} = T_0 \sum_{n=1}^n \frac{Q_i}{T_i} = \sum_{n=1}^n W_i \leq 0$

- 求熵变

- 理想气体

$$dS = \frac{1}{T}(dU + pdV) \text{ (第一定律)}$$

$$= C_V \frac{dT}{T} + nR \frac{dV}{V} \text{ (第二类曲线积分)}$$

$$S_f - S_i = C_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

$$S = C_v \ln T + nR \ln V + S_0$$

$$\text{状态函数: } S(T, V) = C_v \ln T + nR \ln V + S_0$$

- ◦ ◻ Free expansion from $V \rightarrow 2V (T = \text{const})$: 用熵作为状态函数来求: $\Delta S = nR \ln 2 > 0$, irreversible
- 热库 reservoir $\Delta S = \int \frac{dQ}{T} = \frac{\Delta Q}{T}$ 吸热熵增, 放热熵减
- 由准静态过程连接的状态: $\Delta S = \int_i^f \frac{dQ}{T}$, $dQ = C_p dT / C_v dT$
- 由不可逆过程联系的: 找到相应的可逆过程 (如不可逆的自由膨胀转化为等温过程) $\Delta S = \frac{1}{T} \int p dV = nR \ln \frac{V_f}{V_i}$
- 混合: $\Delta S = \int_{T_1}^{T_f} \frac{m_1 c_1 dT}{T} + \int_{T_2}^{T_f} \frac{m_2 c_2 dT}{T}$
 - ◻ 吉布斯佯谬: 相同气体混合

- 再探功与热

- 做功: 有广义距离: 电热丝, 搅拌, 微波炉等;
- 但这些功只能转化为热, 熵也就增加了 \Rightarrow 耗散功; 只要有耗散, 就不可逆

- 熵的微观解释: $S = k_B \ln W$, W : 微观状态数

- 自由膨胀到两倍体积: N 个粒子, $W = 2^N W_0$, $\Delta S = k_B N \ln 2$
- 熵: 广延量: 微观状态用乘法原理计算, $\ln W$ 可加
- 习题 (12.9): 棋盘密度最大: 平衡状态

12.4 热力学势

- 内能的计算

$$dQ = TdS$$

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

(*fundamental equation of thermodynamics*)

(μdn 代表与外界的物质交换, μ 指化学势)

$$\left(\frac{\partial U}{\partial S}\right)_{V,n} = T, \left(\frac{\partial U}{\partial V}\right)_{S,n} = -p, \left(\frac{\partial U}{\partial n}\right)_{S,V} = \mu$$

U 是广延量:

$$U(\lambda S, \lambda V, \lambda n) = \lambda U(S, V, n)$$

两边对 λ 求导数:

$$\left(\frac{\partial U}{\partial(\lambda S)}\right)S + \left(\frac{\partial U}{\partial(\lambda V)}\right)V + \left(\frac{\partial U}{\partial(\lambda n)}\right)n = U$$

令 $\lambda = 1$:

$$U = TS - pV + \mu n$$

欧拉齐次函数定理:设 $f(x_1, x_2, \dots, x_n)$ 是 k 次函数,

$$f(\lambda x_1, \lambda x_2, \dots, \lambda x_n) = \lambda^k f(x_1, x_2, \dots, x_n)$$

$$\sum_{n=1}^n \frac{\partial f}{\partial(\lambda x_i)} \frac{\partial(\lambda x_i)}{\partial \lambda} = k \lambda^{k-1} f(x_1, x_2, \dots, x_n)$$

令 $\lambda = 1$, 得

$$\sum_{n=1}^n \frac{\partial f}{\partial x_i} x_i = k f(x_1, x_2, \dots, x_n)$$

- 其他热力学势的引入

$$dU = TdS - pdV - Vdp + Vdp + \mu dn$$

$$d(U + pV) = TdS + Vdp + \mu dn \equiv dH$$

(\sim *reaction heat, enthalpy*)

$$dU = TdS - pdV + \mu dn - TdS - SdT$$

$$d(U - TS) = -SdT - pdV + \mu dn \equiv dF$$

(\sim *useful work, Helmholtz free energy*)

$$d(U - TS + pV) = -SdT + Vdp + \mu dn \equiv dG$$

(*Gibbs free energy*)

$$G = F + pV = H - TS(\text{free enthalpy})$$

$$F = U - TS$$

Legendre变换:

$df = udx + vdy$, 是 x 与 y 的函数

$$g = f - ux$$

$$dg = df - udx - xdu$$

$$= udx + vdy - udx - xdu$$

$$= -xdu + vdy, \text{是} u \text{与} y \text{的函数}$$

- 化学势的求法: $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p}$, 摩尔吉布斯自由能

$$G = \left(\frac{\partial G}{\partial n}\right)_{T,p} n = \mu n$$

$$dG = n d\mu + \mu dn$$

$$n d\mu = -S dT + V dp$$

$$d\mu = -S_m dT + V_m dp$$

(S_m : 摩尔熵, V_m : 摩尔体积)

- 麦克斯韦关系

$$U(S, V, n) = TS - pV + \mu n$$

$$\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial T} \right) = \frac{\partial}{\partial T} \left(\frac{\partial G}{\partial p} \right) = \frac{\partial^2 G}{\partial T \partial p}$$

$$-\left(\frac{\partial S}{\partial p}\right)_{T,n} = \left(\frac{\partial V}{\partial T}\right)_{p,n}$$

(也可从全微分理解)

$$dU = T dS - p dV$$

$$= T \left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV - p dV \right]$$

由 $dF = -S dT - p dV$, 结合麦克斯韦关系:

$$= T \left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial T}\right)_V dV - p dV \right]$$

考虑 $C_V = T \left(\frac{\partial S}{\partial T}\right)_V$:

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_V - p$$

- Criteria of thermodynamics equilibrium

$$\Delta S_t = \Delta S + \Delta S_0 = \Delta S - \frac{\Delta Q}{T_0}$$

where Q is released to the system

$$= \Delta S - \frac{\Delta U - \Delta W - \mu \Delta n}{T_0} \geq 0$$

$$\Delta U \leq T_0 \Delta S + \Delta W + \mu \Delta n$$

$$(\Delta U)_{S,V,n} \leq 0$$

$$\Delta F = \Delta(U - TS) \leq -S \Delta T - p \Delta V + \mu \Delta n$$

$$(\Delta F)_{T,V,n} \leq 0$$

$$\Delta G = \Delta(F - pV) \leq -S \Delta T + V \Delta p + \mu \Delta n$$

$$(\Delta G)_{T,p,n} \leq 0$$

- 热力学势的物理意义

- $(\Delta H)_p = \Delta U + p \Delta V = \Delta Q$, 化学反应中等压过程的反应热. $\Delta H > 0$: endothermic 吸热; $\Delta H < 0$: exothermic 放热

- 等温最大功与亥姆霍兹自由能

$$\begin{aligned}\Delta S_t &= \Delta S + \Delta S_r \\ &= \Delta S - \frac{\Delta Q}{T_0} \geq 0\end{aligned}$$

$$\Delta Q = \Delta U - \Delta W$$

$$\Delta W \geq \Delta U - T_0 \Delta S = \Delta F$$

$$\Delta W_{\text{对外}} = -\Delta W \leq -\Delta F$$

- ◦ 额外功与吉布斯自由能