大学物理笔记

多普勒效应

source:v_s, observer:v_O,distance L

issued at $t=0,x=0$, recieved at $t_1',L+v_Ot_1'$

issued at $t=T,x=v_ST$, received at $t_2',L+v_Ot_2'$

由运动学:

$$v_Pt_1'=L+v_Ot_1'$$
$$v_P(t_2'-T)=L+v_Ot_2'-v_ST$$

于是

$$t_1'=\frac{L}{v_P-v_O}$$
$$t_2'=\frac{L}{v_P-v_O}+\frac{v_P-v_S}{v_P-v_O}T$$
$$T'=t_2'-t_1'=\frac{v_P-v_S}{v_P-v_O}T$$
$$\nu'=\frac{v_P-v_O}{v_P-v_S}\nu$$

Discussion:

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

$v_S>v_O$(including $v_O\le 0$):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:$sin\theta=\frac{vP}{vS}$

驻波(stationary wave)

- 推导

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

$$\begin{aligned}u_1&=Acos(kx-\omega t-\phi)\\u_2&=Acos(kx+\omega t)\\&=Acos(k(x+\frac{\omega}{k}t))\\\text{从而}u_1+u_2&=2Acos(kx-\frac{\phi}{2})cos(wt+\frac{\phi}{2})\end{aligned}\tag{1}$$

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 spped 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

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

By the priciple of relativity, we have

$$x = a_{11}(-u)(x' + ut'), \text{带入}(1.1), \text{有}$$

$$t' = f(x, x'(u,t)) = a_{44}t + a_{41}x$$

从而

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

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

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

代入 (1.2)式,有

$$\begin{aligned} e &= \frac{u}{c^2} \\ a &= \frac{1}{\sqrt{1-\beta^2}} = \gamma = \sqrt{1-\frac{v^2}{c^2}} \\ \text{其中}\beta &= \frac{u}{c} \end{aligned}$$

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: $u \to -u$ 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:

$$
\begin{aligned}
\Delta t' &= \frac{2L_0}{c} \\
(\frac{u\Delta t}{2})^2 + L_0^2 &= (\frac{c\Delta t}{2})^2 (\text{用到光速不变}) \\
\Delta t = \frac{2L_0}{\sqrt{c^2 - u^2}} &= \frac{2L_0/c}{\sqrt{1-\beta^2}} = \gamma \Delta t'
\end{aligned}
$$

- 用光速不变推出尺缩:

$$
\begin{aligned}
c\Delta t_1 = L + u\Delta t_1, c\Delta t_2 &= L - u\Delta t_2 \\
\Delta t = \Delta t_1 + \Delta t_2 &= \frac{L}{c+u} + \frac{L}{c-u} = \frac{2L}{c}\frac{1}{1-\beta^2} \\
\Delta t' &= \frac{2L_0}{c} = \gamma \Delta t \\
\frac{2L_0}{c\gamma} &= \frac{2L}{c}\frac{1}{1-\beta^2} \\
\text{于是} L &= \frac{L_0}{\gamma}
\end{aligned}
$$

- 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

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

  为保证先后次序,必须有

$$
\begin{gathered}
1 - \frac{uv_S}{c^2} < 0 \\
\text{则} v_S < c
\end{gathered}
$$

- 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 $S'(-u) : u, -u \to 0, 0$
  - In $S : v_x, 0 \to u, u$;　$v_x = \frac{u+u}{1+u\frac{u}{c^2}}(9.5.1)$
  - 而 $m\frac{u+u}{1+\frac{uu}{c^2}} + m \times 0 \neq 2mu$,动量守恒不成立.
  - 假定 $m \equiv m(v), m_0 \equiv m(0)$,有

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

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

$$p = \gamma m_0 v$$
$$E_k = \int F \cdot dx = \int \frac{d}{dt}(mv) \cdot dx = \int v \cdot d(mv)$$
$$而 d(mv) = vdm + mdv$$
$$则 E_k = \int (v^2 dm + mvdv)$$

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

$$c^2 2mdm - v^2 2mdm - m^2 2vdv = 0,$$
$$c^2 dm - v^2 dm - mdv = 0, c^2 dm = v^2 dm + mdv$$

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

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

-
  - 相对论中,mass-energy $E = mc^2 = E_k + m_0 c^2$
-
  - 已知动能求速度: $\gamma = \dfrac{E_k}{m_0 c^2} + 1$
- 相对论能量-动量关系
  - $E = \sqrt{c^2 p^2 + m_0^2 c^4}$
  - 若 $m_0 = 0, E = cp, p = \dfrac{E}{c}$
  - 若 $cp << m_0 c^2$,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 Equilibruim state

System	exchange
isolated	$\times$
closed	energy
open	energy&matter
- Thermodynamic Equilibruim state: 宏观状态不随时间改变,除非外界条件发生变化.
- description of equilibruim state: state variables
    - extensive quantity: $F(n\ systems) = nF(1\ system)$
    - intensive quantity: $F(n\ systems) = F(1\ system)$
- relaxation time τ: 恢复平衡所用时间
- Quasi-static process 准静态过程: $t >> \tau$, 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 equilibruim 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
- $P, V, T \text{不独立}, f(P, V, T) = 0 \to U(T, P) = U(T, V(P, T)) = U(T, V) = 0$
- 等压线膨胀系数 $a_\ell = \frac{1}{L}\frac{\partial L}{\partial T}_p$; $\alpha_V = \frac{1}{V}(\frac{\partial V}{\partial T})_P = \frac{1}{L^3}(\frac{\partial L^3}{\partial T})_P = 3\alpha_\ell$
- 等温线膨胀系数 $\kappa_T = -\frac{1}{V}\frac{\partial V}{\partial p}_T$
- 体积变化方程

$$
\begin{aligned}
\frac{dV}{V} &= \frac{1}{V}(\frac{\partial V}{\partial T})_p dT + \frac{1}{V}(\frac{\partial V}{\partial p})_T dp = \alpha_V(T)dT - \kappa_T(p)dp \\
&(\text{全微分}) \\
ln\frac{V}{V_0} &= \alpha_V \Delta T - \kappa_T \Delta p \\
V &= V_0(1 + \alpha_V \Delta T - \kappa_T \Delta p)
\end{aligned}
$$

- Van der Waal's equation

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

推导: 对1mol理想气体:

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

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 $\bar{d}W=-p\bar{d}V$, $W=-\int_{V_i}^{V_f}pdV$ (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)

- $C=\lim_{\Delta T\to 0}\frac{\Delta Q}{\Delta T}$; specific: $C_m=\frac{C}{n}$
  - $C=0$: 绝热(adiabatic)过程, $\Delta Q=0$
  - $C=\infty$: 等温(isothermal)过程,$\Delta T=0$
- $C_V=\lim_{\Delta T\to 0}(\frac{\Delta Q}{\Delta T})_V=\lim_{\Delta T\to 0}(\frac{\Delta U}{\Delta T})_V=\left(\frac{\partial U}{\partial T}\right)_V$
- $C_P=\lim_{\Delta T\to 0}(\frac{\Delta Q}{\Delta T})_p=\lim_{\Delta T\to 0}(\frac{\Delta U+p\Delta V}{\Delta T})_p=\left(\frac{\partial(U+pV)}{\partial T}\right)_p\equiv\left(\frac{\partial H}{\partial T}\right)_p$, $H=U+pV$: 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

$$
\begin{aligned}
U &= U(T,V) \\
dU &= (\frac{\partial U}{\partial T})_V dT + (\frac{\partial U}{\partial V})_T dV \\
T &= T(U,V) \\
dU &= (\frac{\partial U}{\partial T})_V [(\frac{\partial T}{\partial U})_V dU + (\frac{\partial T}{\partial V})_U dV] + (\frac{\partial U}{\partial V})_T dV \\
&\text{对照左右, 得}
\end{aligned}
$$

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

$$
\begin{aligned}
(\frac{\partial U}{\partial V})_T &= -(\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial V})_U = -C_V (\frac{\partial T}{\partial V})_U \rightarrow \text{焦耳系数} = 0(\text{理想气体}) \\
\text{故} U &= U(T)
\end{aligned}
$$

- 焦耳的实验非常不严谨
- 理想气体:

$$
\begin{aligned}
dU(T) &= \frac{dU}{dT} dT = C_V dT \\
U &= U_0 + C_V T \\
dQ &= dU - dW = C_V dT + pdV \\
\text{理想气体}: d(pV) &= d(nRT) \\
pdV + Vdp &= nRdT, pdV = nRdT - Vdp \\
dQ &= (C_V + nR)dT - Vdp \\
C_p &= C_V + nR \rightarrow C_V = \frac{nR}{\gamma - 1}, C_p = \frac{\gamma nR}{\gamma - 1}
\end{aligned}
$$

11.5 Adiabatic equation

$$
\begin{aligned}
dQ &= dU - dW, \\
&= C_V dT + pdV \\
C_V dT + pdV &= 0 \\
\text{又} Vdp + pdV &= nRdT = (\gamma - 1) C_V dT
\end{aligned}
$$

消去 dT,得

$$
\begin{aligned}
Vdp + \gamma pdV &= 0 \\
\frac{dp}{p} + \gamma \frac{dV}{V} &= 0 \\
lnp + \gamma lnV &= C \\
pV^\gamma &= C
\end{aligned}
$$

由 $\gamma > 1$, 绝热线比等温线陡峭

- adiabatic work

$$
\begin{aligned}
W_S &= -\int_{V_1}^{V_2} pdV = -C\int_{V_1}^{V_2}\frac{dV}{V^\gamma} = \frac{C}{\gamma-1}(\frac{V_2}{V_2^\gamma}-\frac{V_1}{V_1^\gamma}) \\
&= \frac{1}{\gamma-1}(p_2V_2-p_1V_1) \\
&= \frac{nR}{\gamma-1}(T_2-T_1) \\
&= C_V(T_2-T_1) = \Delta U
\end{aligned}
$$

- 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
- $T_1, U=U(T_1)=const$ 热机吸热,做功
- T_2 热机放热
- 整个循环: $\Delta U=0, \Delta Q_{12}+\Delta Q_{34}-\Delta W=0$

$$
\begin{gathered}
\text{效率}\eta = \frac{\Delta W}{\Delta Q_{12}} = \frac{\Delta Q_{12}+\Delta Q_{34}}{\Delta Q_{12}} = \frac{Q_1-Q_2}{Q_1} \\
(\text{考察做功过程中的放热}Q_2\text{，放热越多效率越低})
\end{gathered}
$$

$$
\begin{aligned}
\text{等温过程}: Q_1 = \Delta W_{12} = \int_{V_1}^{V_2} pdV &= \int_{V_1}^{V_2}\frac{nRT_1}{V}dV = nRT_1 ln\frac{V_2}{V_1} \\
Q_2 = -\Delta Q_{34} &= nRT_2 ln\frac{V_3}{V_4} \\
\eta &= 1-\frac{T_2 ln\frac{V_3}{V_4}}{T_1 ln\frac{V_2}{V_1}} \\
2\to 3: T_1V_2^{\gamma-1} &= T_2V_3^{\gamma-1} \\
4\to 1: T_1V_1^{\gamma-1} &= T_2V_4^{\gamma-1} \\
\eta &= 1-\frac{T_2}{T_1}
\end{aligned}
$$

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:

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

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

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

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

$$(\text{取等}: \text{可逆过程}, \text{考虑}Q_i \to -Q_i)$$

$$(\text{环路积分})$$

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

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

若环路中包含不可逆过程:

$$\oint\left(\frac{dQ}{T}\right) < 0$$

$$\int_A^B\left(\frac{dQ}{T}\right)_{IR} + \int_A^B\left(\frac{dQ}{T}\right)_R < 0$$

$$\int_A^B\left(\frac{dQ}{T}\right)_{IR} - \int_B^A\left(\frac{dQ}{T}\right)_R < 0$$

$$S_B - S_A > \int_A^B\left(\frac{dQ}{T}\right)_{IR}$$

$$\int_A^B dS > \int_A^B\left(\frac{dQ}{T}\right)_{IR}$$

$$dS > \left(\frac{dQ}{T}\right)_{IR}$$

- 熵原理: 任何过程: $dS \ge \dfrac{dQ}{T}$
  - 绝热过程: $dQ=0$; 可逆: $dS=0$, isentropic 等熵过程
  - 孤立系统: $dS\ge 0$; 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: $\Delta S = \dfrac{\Delta Q}{T} = \dfrac{-Q}{T} < 0$,矛盾!
  - 两热源 $T_1 > T_2$, T_1吸热, T_2放热: $\Delta S = \dfrac{Q}{T_1} - \dfrac{Q}{T_2} < 0$, 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
  - $T_0 \to T_i$之间加上卡诺热机
  - $T_0 \to Q_{0i}$
  - 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

$$\begin{aligned} dS &= \frac{1}{T}(dU + pdV)(\text{第一定律}) \\ &= C_V \frac{dT}{T} + nR\frac{dV}{V}(\text{第二类曲线积分}) \\ S_f - S_i &= C_v ln\frac{T_f}{T_i} + nRln\frac{V_f}{V_i} \\ S &= C_v lnT + nRlnV + S_0 \\ \text{状态函数}: S(T,V) &= C_v lnT + nRlnV + S_0 \end{aligned}$$

-
  -
    - Free expansion from $V \to 2V(T = const)$:用熵作为状态函数来求: $\Delta S = nRln2 > 0$, irreversible
  - 热库reservior $\Delta S = \int \frac{dQ}{T} = \frac{\Delta Q}{T}$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) $\Delta S = \frac{1}{T} \int pdV = nRln\frac{V_f}{V_i}$
  - 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⇒耗散功; 只要有耗散,就不可逆

- 熵的微观解释: $S = k_B lnW, W$: 微观状态数
  - 自由膨胀到两倍体积: N个粒子, $W = 2^N W_0,\ \Delta S = k_B Nln2$
  - 熵: 广延量: 微观状态用乘法原理计算, lnW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

$$
\begin{aligned}
&dQ = TdS \\
&dU = TdS - pdV + \mu dn \\
&\quad (fundamental\ equation\ of\ thermodynamics) \\
&\quad (\mu dn\text{代表与外界的物质交换, }\mu\text{指化学势})
\end{aligned}
$$

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

U是广延量：

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

两边对λ求导数：

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

令$\lambda = 1$：

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

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

$$
\begin{aligned}
f(\lambda x_1, \lambda x_2, \cdots, \lambda x_n) &= \lambda^k f(x_1, x_2, \cdots, x_n) \\
\sum_{n=1}^{n} \frac{\partial f}{\partial(\lambda x_i)} \frac{\partial(\lambda x_i)}{\partial \lambda} &= k\lambda^{k-1} f(x_1, x_2, \cdots, x_n) \\
\text{令}\lambda = 1,\text{得}& \\
\sum_{n=1}^{n} \frac{\partial f}{\partial x_i} x_i &= kf(x_1, x_2, \cdots, x_n)
\end{aligned}
$$

- 其他热力学势的引入

$$
\begin{aligned}
dU &= TdS - pdV - Vdp + Vdp + \mu dn \\
d(U + pV) &= TdS + Vdp + \mu dn \equiv dH \\
&(\sim reaction\ heat, enthopy) \\
dU &= TdS - pdV + \mu dn - TdS - SdT \\
d(U - TS) &= -SdT - pdV + \mu dn \equiv dF \\
&(\sim useful\ work,\ Helmholtz\ free\ energy) \\
d(U - TS + pV) &= -SdT + Vdp + \mu dn \equiv dG \\
&(Gibbs\ free\ energy) \\
&G = F + pV = H - TS(free\ enthopy) \\
&F = U - TS
\end{aligned}
$$

Legendre变换:

$$
\begin{aligned}
df &= udx + vdy,\ \text{是}x\text{与}y\text{的函数} \\
g &= f - ux \\
dg &= df - udx - xdu \\
&= udx + vdy - udx - xdu \\
&= -xdu + vdy, \text{是}u\text{与}y\text{的函数}
\end{aligned}
$$

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

$$\begin{aligned} G &= (\frac{\partial G}{\partial n})_{T,p} n = \mu n \\ dG &= nd\mu + \mu dn \\ nd\mu &= -SdT + Vdp \\ d\mu &= -S_m dT + V_m dp \\ &(S_m：摩尔熵, V_m：摩尔体积) \end{aligned}$$

- 麦克斯韦关系

$$\begin{aligned} U(S,V,n) &= TS - pV + \mu n \\ \frac{\partial}{\partial p}(\frac{\partial G}{\partial T}) &= \frac{\partial}{\partial T}(\frac{\partial G}{\partial p}) = \frac{\partial^2 G}{\partial T \partial p} \\ -(\frac{\partial S}{\partial p})_{T,n} &= (\frac{\partial V}{\partial T})_{p,n} \\ &(也可从全微分理解) \\ dU &= TdS - pdV \\ &= T\Big[(\frac{\partial S}{\partial T})_V dT + (\frac{\partial S}{\partial V})_T dV - pdV\Big] \\ 由 dF = -SdT - pdV, 结合麦克斯韦关系： \\ &= T\Big[(\frac{\partial S}{\partial T})_V dT + (\frac{\partial p}{\partial T})_V dV - pdV\Big] \\ 考虑 C_V = T(\frac{\partial S}{\partial T})_V： \\ &= C_V dT + T(\frac{\partial p}{\partial T})_V dV - pdV \\ (\frac{\partial U}{\partial V})_T &= T(\frac{\partial p}{\partial T})_V - p \end{aligned}$$

- Criteria of thermodynamics equilibrium

$$\begin{aligned} \Delta S_t &= \Delta S + \Delta S_0 = \Delta S - \frac{\Delta Q}{T_0} \\ &where\ Q\ is\ released\ to\ the\ system \\ &= \Delta S - \frac{\Delta U - \Delta W - \mu \Delta n}{T_0} \geq 0 \\ \Delta U &\leq T_0 \Delta S + \Delta W + \mu \Delta n \\ (\Delta U)_{S,V,n} &\leq 0 \\ \Delta F &= \Delta(U - TS) \leq -S\Delta T - p\Delta V + \mu \Delta n \\ (\Delta F)_{T,V,n} &\leq 0 \\ \Delta G &= \Delta(F = pV) \leq -S\Delta T + V\Delta p + \mu \Delta n \\ (\Delta G)_{T,p,n} &\leq 0 \end{aligned}$$

- 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 设想系统与reservoir T_0接触,这是等温过程

$$
\begin{aligned}
\Delta S_t &= \Delta S + \Delta S_{reservoir} \\
&\text{(热源损失}\Delta Q\text{的热量)} \\
&= \Delta S - \frac{\Delta Q}{T_0} \geq 0 \\
&\text{对系统：} \\
\Delta Q &= \Delta U - \Delta W_{to\ system} \\
\Delta W_{to\ system} &\geq \Delta U - T_0 \Delta S = \Delta F \\
\Delta W_{by\ system} &= -\Delta W \leq -\Delta F
\end{aligned}
$$

- - 额外功与吉布斯自由能

等温等压过程/ isothermal isobaric:

$$
\begin{aligned}
\Delta W &= -p\Delta V + \Delta W_{other}(non-expansion\ work) \\
\Delta W &\geq \Delta U - T_0 \Delta S \\
-\Delta W_{other} &\leq \Delta(U - TS + pV) \equiv -\Delta G
\end{aligned}
$$

- 平衡条件: 温度,压强,化学势

第十三章 理想气体的微观模型

Microscopic Model for Ideal gas

13.1 理想气体

- Microscopic description
  - It contains of N identical molecules
  - The molecules obey Newton's law
  - The average spacing $>> r$(相互作用不产生内能的改变)
  - Collisions are elastic and are of negligible duration.
- Microscopic meaning of **pressure**

考虑粒子撞壁运动

$$\Delta p_x = p_f - p_i = -2mv_x$$
$$\Delta t = \frac{2\ell}{v_x}\text{撞击频率}$$
$$\bar{F} = -\frac{\Delta p_x}{\Delta t}(the\ force\ on\ wall)$$
$$= \frac{2mv_x}{\frac{2\ell}{v_x}} = \frac{mv_x^2}{\ell}$$
$$p = \frac{1}{\ell^2}\sum_{n=1}^{N}\bar{F}_n = \frac{m}{\ell^3}(v_{x1}^2 + v_{x2}^2 + \cdots)$$
$$= \frac{Nm}{\ell^3}\frac{(v_{x1}^2 + v_{x2}^2 + \cdots)}{N}$$
$$= \frac{Nm}{\ell^3}\bar{v_x^2}$$
$$= \frac{Nm}{3V}\bar{v^2}(isotropic\ \text{各向同性})$$
$$= \frac{1}{3}\rho\bar{v^2}$$

定义方均根速率 $v_{rms} = \sqrt{\bar{v^2}} = \sqrt{\frac{3p}{\rho}}$

- Microscopic interpretation of T and U

$$pV = \frac{2}{3}N(\frac{1}{2}m\bar{v^2})$$
$$nRT = \frac{2}{3}N(\frac{1}{2}m\bar{v^2})$$
$$\frac{1}{2}m\bar{v^2} = \frac{3}{2}\frac{nR}{N}T = \frac{3}{2}\frac{R}{N_A}T = \frac{3}{2}k_BT$$
$$k_B:\text{玻尔兹曼常数 联系宏观温度与微观速度}$$
$$LHS:\text{单个粒子内能}$$

- 理想气体定体积热容 C_V
  - monatomic: 只有平动自由度 $U = (3\times\frac{1}{2}k_BT)N = \frac{3}{2}k_BNT = \frac{3}{2}nRT$, 对 T求导即得 C_V
  - diatomic: 多两个转动自由度
  - ployatomic: 多三个转动自由度

13.2 Equilibrium distributions

$$\bar{v^2} = \frac{n_1v_1'^2 + n_2v_2'^2 + \cdots}{N}$$
$$= \int v^2\frac{dn}{N}$$

在引入的速度空间内 dn is the number of modules in $v_x \to v_x + dv_x, y, z$亦然, i.e. $\frac{dn}{N}$ is the probability that one molecule near v. It's proportional to dv_x. Let us suppose

$$
\begin{aligned}
\frac{dn(v_x,v_y,v_z)}{N} &= f(v_x)dv_x f(v_y)dv_y f(v_z)dv_z \\
\text{速度各向同, 与方向无关}: \\
f(v_x)f(v_y)f(v_z) &= \phi(v^2) = \phi(v_x^2+v_y^2+v_z^2) \\
Simplest\ solution: \\
f(v_x) &= Cexp(-\frac{v_x^2}{\alpha^2}) \\
probability\ satisfies\ normalization: \\
1 &= \int \frac{dn}{N} \\
&= \int (f(v_x)dv_x)^3 \\
&= C\int exp(-\frac{v_x^2}{\alpha^2})dv_x \\
C &= \frac{1}{\int_{-\infty}^{\infty} exp(-\frac{v_x^2}{\alpha^2})dv_x} \\
&= \frac{1}{\alpha\int_{-\infty}^{\infty} exp(-\frac{v_x^2}{\alpha^2})d\frac{v_x}{\alpha}} \\
&= \frac{1}{\alpha\sqrt{\pi}}
\end{aligned}
$$

于是

$$
\begin{aligned}
\frac{dn(v_x,v_y,v_z)}{N} &= (\frac{1}{\alpha\sqrt{\pi}})^3 exp\Big[-\frac{v_x^2+v_y^2+v_z^2}{\alpha^2}\Big] \\
&= (\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_x^2}{\alpha^2}}dv_x(\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_y^2}{\alpha^2}}dv_y(\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_z^2}{\alpha^2}}dv_z \\
\bar{v^2} &= \int (v_x^2+v_y^2+v_z^2)\frac{dn(v_x,v_y,v_z)}{N} \\
&= 3\int_{-\infty}^{\infty} v_x^2(\frac{1}{\alpha\sqrt{\pi}})e^{-\frac{v_x^2}{\alpha^2}}dv_x(v_x\text{对}dv_y\text{积分得}1) \\
&= 3\times\frac{2\alpha^2}{\sqrt{\pi}}\int_0^{\infty} y^2e^{-y^2}dy \\
&= 3\times\frac{2\alpha^2}{\sqrt{\pi}}\frac{1}{2}\Gamma(\frac{3}{2}) = 3\times\frac{2\alpha^2}{\sqrt{\pi}}\frac{1}{4}\Gamma(\frac{1}{2}) = 3\times\frac{2\alpha^2}{\sqrt{\pi}}\frac{1}{4}\sqrt{\pi} \\
&= \frac{3}{2}\alpha^2 \\
\alpha^2 &= 2k_BT/m
\end{aligned}
$$

从而有Maxwell velocity distribution:

$$
\begin{aligned}
\frac{dn(v_x,v_y,v_z)}{N} &= (\frac{m}{2\pi k_BT})^{\frac{3}{2}}exp\Big[-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}\Big]dv_xdv_ydv_z \\
dn(v_x,v_y,v_z) &= n_0(\frac{m}{2\pi k_BT})^{\frac{3}{2}}exp\Big[-\frac{m(v_x^2+v_y^2+v_z^2)}{2k_BT}\Big]dv_xdv_ydv_z
\end{aligned}
$$

Maxwell speed distribution: 将速度空间的体积元换为速率空间的球壳

$$
\begin{aligned}
dv_x dv_y dv_z &\to 4\pi v^2 dv \\
dn(v) &= n_0(\frac{m}{2\pi k_B T})^{\frac{3}{2}} exp\Big[-\frac{\frac{1}{2}mv^2}{k_B T}\Big]4\pi v^2 dv \\
&= f(v)dv \\
\frac{d}{dv}f(v) &= 0, \text{知} \\
v_m &= \sqrt{\frac{2k_B T}{m}} \\
Maxwellian\ can\ be\ written\ as\ &: \\
\frac{dn(v)}{N} &= 4\pi(\frac{1}{\pi v_m^2})^{\frac{3}{2}} exp(-\frac{v^2}{v_m^2})v^2 dv
\end{aligned}
$$

The average speed

- Gaussian intergral using Gamma function:

$$
\begin{aligned}
I &= \int_0^\infty e^{-x^2} dx \\
\Gamma(v) &= \int_0^\infty e^{-t} t^{v-1} dt \\
I &= \int_0^\infty e^{-y} \frac{1}{2\sqrt{y}} dy \\
&= \frac{1}{2}\Gamma(\frac{1}{2}) \\
&= \frac{\sqrt{\pi}}{2} \\
I_n &= \int_0^\infty x^n e^{-x^2} dx = \frac{1}{2}\Gamma(\frac{n+1}{2})
\end{aligned}
$$

13.3 Equipartition theorem

第十四章 相变 Phase Transition

14.1 范德瓦尔斯方程

- $p = \dfrac{nRT}{V-nb} - a(\dfrac{n}{V})^2$.第二项:吸引力;第一项:最小体积(斥力).高温低密度:趋于理想气体
- Critical point临界点.求临界状态:

$$
\begin{aligned}
(\frac{\partial p}{\partial V})_T &= 0 \\
(\frac{\partial^2 p}{\partial V^2})_T &= 0 \\
\text{求出} p_C, V_C, T_C
\end{aligned}
$$

- $p-V$图的稳定性分析
- 一摩尔物质isotherms: $dG = Vdp, g = \int vdp$

- 确定临界点.$C-G$:气液共存

$$
\begin{aligned}
0 &= g_G - g_C \\
&= \int_{pC}^{pG} v(p)dp \\
&= (\int_C^D + \int_D^E + \int_E^F + \int_F^G)v(p)dp \\
&= (\int_C^D - \int_E^D) - (\int_F^E - \int_F^G)v(p)dp \\
&= A_{CDEC} - A_{EFGE} \\
&(Maxwell\ equal\ area\ construction)
\end{aligned}
$$

- $v = xv_g + (1-x)v_\ell$,求摩尔分数

14.2 Phase and Phase Diagrams

- A:三相点 ; C:临界点: $p-V$图那条线的极大值点.临界温度以上,无法区分气体与液体,Supercritical fluid
- 线:相平衡曲线

14.3 克拉伯龙方程

- 相平衡:化学势相等.共存曲线

$$
\mu^I(T,p) = \mu^{II}(T,p)
$$

According to Gibbs-Duheim equation:

$$
\begin{aligned}
d\mu^I &= d\mu^{II} \\
-S_m^I dT + V_m^I dp &= -S_m^{II} dT + V_m^{II} dp \\
(\frac{\partial p}{\partial T})_{CO} &= \frac{S_m^I - S_m^{II}}{V_m^I - V_m^{II}} \\
&= \frac{T\Delta S_m}{T\Delta V_m} \\
\Delta G = \Delta H - T\Delta S = 0: \\
&= \frac{\Delta H_m}{T\Delta V_m} = \frac{\ell}{T\Delta V_m}(latent\ heat)
\end{aligned}
$$

汽化过程的斜率: $\dfrac{dp}{dT} = \dfrac{\ell_V p}{RT^2}$

- 沿冰线:

$$
\begin{aligned}
\Delta T &= T - T_t r \\
&= \frac{T(V_{mw} - V_{mi})}{\ell_F}\Delta p
\end{aligned}
$$

习题课

9.3

- Known $x=0, x'=-200m$, to find t:

$$x' = \gamma(x-ut)$$

或用尺缩

- To find t':

$$x = \gamma(x'+ut')$$

9.16

- Conservation of mass-energy:

$$m_{n0}c^2 = m_{p0}c^2 + m_ec^2 + E_\nu$$

- Conservation of 动量:

$$\begin{aligned} p_e + p_\nu &= 0 \\ E_\nu &= cp_\nu \\ E_e^2 &= p_e^2c^2 + E_0^2 \\ \frac{1}{c}\sqrt{E_e^2 - E_0^2} &= \frac{E_\nu}{c} \end{aligned}$$

11.9

$$\begin{aligned} \eta &= \frac{W}{\Delta Q_{BC}} \\ &= \frac{\Delta Q_{BC} - \Delta Q_{AD}}{\Delta Q_{BC}} \\ &= 1 - \frac{\Delta Q_{AD}}{\Delta Q_{BC}} \\ &= 1 - \frac{T_D - T_A}{T_C - T_B} \end{aligned}$$

12.8

$$\Delta S = (\int_{333K}^{T_f} + \int_{T_f}^{288})\frac{mcdT}{T} + \frac{\Delta Q_s}{T_s}$$

12.12

show that

$$(\frac{\partial\mu}{\partial V_m})_T = V_m(\frac{\partial p}{\partial V_m})_T$$

$$\begin{aligned}
d\mu &= -sdT + vdp \\
(\frac{\partial\mu}{\partial v})_T &= (\frac{\partial\mu}{\partial p})_T(\frac{\partial p}{\partial v})_T = v(\frac{\partial p}{\partial v})_T \\
or &: \\
d\mu &= -sdT + v[(\frac{\partial p}{\partial T})_v dT + (\frac{\partial p}{\partial v})_T dv] \\
&=
\end{aligned}$$

12.13

show that

$$\begin{aligned}
TdS &= C_p dT - TV\alpha dp \\
TdS &= C_V dT + T\frac{\alpha}{\kappa}dV
\end{aligned}$$

$$\begin{aligned}
dH &= TdS + Vdp \\
&= T(\frac{\partial S}{\partial T})_p dT + [T(\frac{\partial S}{\partial p})_T + V]dp \\
C_p &= (\frac{\partial H}{\partial T})_p = T(\frac{\partial S}{\partial T})_p \\
(\frac{\partial H}{\partial p})_T &= T(\frac{\partial S}{\partial p})_T + V = -T(\frac{\partial V}{\partial T})_p + V
\end{aligned}$$

Thus

$$\begin{aligned}
TdS &= T(\frac{\partial S}{\partial T})_p dT + T(\frac{\partial S}{\partial p})_T dp \\
&= C_p dT - T(\frac{\partial V}{\partial T})_p dp \\
&= C_p dT - TV\alpha dp
\end{aligned}$$

and

$$
\begin{aligned}
TdS &= T(\frac{\partial S}{\partial T})_V dT + T(\frac{\partial S}{\partial V})_T dV \\
&= C_V dT + T(\frac{\partial p}{\partial T})_V dV
\end{aligned}
$$

$$
Cyclic\ chain\ rule:
$$

$$
\begin{aligned}
&= C_V dT - T\frac{(\frac{\partial V}{\partial T})_p}{(\frac{\partial V}{\partial p})_T} dV \\
&= C_V dT + T\frac{\alpha}{\kappa} dV
\end{aligned}
$$

12.11

show that

$$
\begin{aligned}
(\frac{\partial C_V}{\partial V})_T &= T(\frac{\partial^2 p}{\partial T^2})_V \\
(\frac{\partial C_p}{\partial V})_T &= T(\frac{\partial^2 V}{\partial T^2})_p
\end{aligned}
$$

$$
\begin{aligned}
(\frac{\partial C_V}{\partial V})_T &= T(\frac{\partial(\frac{\partial S}{\partial T})_V}{\partial V})_T \\
&= T(\frac{\partial(\frac{\partial S}{\partial V})_T}{\partial T})_V \\
&= T(\frac{\partial(\frac{\partial p}{\partial T})_V}{\partial T})_V \\
&= T(\frac{\partial^2 p}{\partial T^2})_V
\end{aligned}
$$

show

$$
\frac{\kappa_T}{\kappa_S} = \frac{C_p}{C_V}
$$

$$
TdS = (\frac{\partial U}{\partial p})_V dp + [(\frac{\partial U}{\partial V})_p + p]dV
$$

Let $dS = 0$,we have

$$
\begin{aligned}
(\frac{\partial V}{\partial p})_S &= -\frac{(\frac{\partial U}{\partial p})_V}{(\frac{\partial U}{\partial V})_p + p} \\
(\frac{\partial U}{\partial p})_V &= (\frac{\partial U}{\partial T})_V (\frac{\partial T}{\partial p})_V \\
&= C_V (\frac{\partial T}{\partial p})_V \\
(\frac{\partial U}{\partial V})_p &= (\frac{\partial U}{\partial T})_p (\frac{\partial T}{\partial V})_p \\
(\frac{\partial U}{\partial V})_p + p &= \left[(\frac{\partial U}{\partial T})_p + p(\frac{\partial V}{\partial T})_p\right] (\frac{\partial T}{\partial V})_p \\
&= C_p (\frac{\partial T}{\partial V})_p
\end{aligned}
$$

Therefore,

$$
\begin{aligned}
(\frac{\partial V}{\partial p})_S &= -\frac{(\frac{\partial U}{\partial p})_V}{(\frac{\partial U}{\partial V})_p + p} \\
&= -\frac{C_V}{C_p} \frac{(\frac{\partial T}{\partial p})_V}{(\frac{\partial T}{\partial V})_p} \\
&= \frac{C_V}{C_p} (\frac{\partial V}{\partial p})_T
\end{aligned}
$$

移项得证.