Thermodynamics & Statistical Physics

Chapter 2. Thermodynamical properties of uniform medium

Yuan-Chuan Zou
zouyc@hust.edu.cn

School of Physics, Huazhong University of Science and Technology

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Maxwell relations App 1

- Comparing the two expressions above,
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- For van der Waals gas ($(p + \frac{a}{V_m^2})(V_m - b) = RT$),
- $\left(\frac{\partial U_m}{\partial V_m}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_{V_m} - p = T\frac{R}{V_m - b} - p = \frac{a}{V_m^2}$.

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- App 2: Choose (T, p) as free parameters for H,
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  $$= T\left[\left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p\right] + V\mathrm{d}p$$
  $$= T\left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]\mathrm{d}p.$$

Maxwell relations App 2

- App 2: Choose (T, p) as free parameters for H,
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- $\therefore C_p = \left(\frac{\partial H}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p,$
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- $\xrightarrow{\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p} \left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V,$
  where $\left(\frac{\partial V}{\partial T}\right)_p$ can be taken from the EOS.

Maxwell relations Apps 1 & 2

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- For general case, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$, $\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$,
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  $C_p - C_V = T \cdot \beta p \cdot \alpha V = \alpha\beta p V T$, or $= \frac{\alpha^2 V T}{\kappa_T}$.

Jacobian determinant

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$$\frac{\partial(u,v)}{\partial(x,y)} \equiv \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x}\frac{\partial v}{\partial y} - \frac{\partial u}{\partial y}\frac{\partial v}{\partial x}.$$

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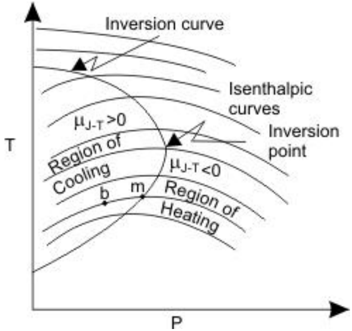

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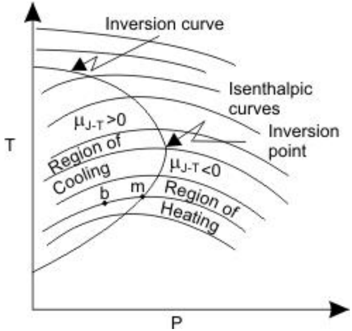

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$= \frac{V}{C_p}\left(-\frac{p}{RT}B + \frac{nT}{V}\frac{\mathrm{d}B}{\mathrm{d}T}\right) = \frac{n}{C_p}\left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right).$
- $B<0$, attractive; $B>0$, repulsive. $\frac{\mathrm{d}B}{\mathrm{d}T}>0$ (Fig 1.3).

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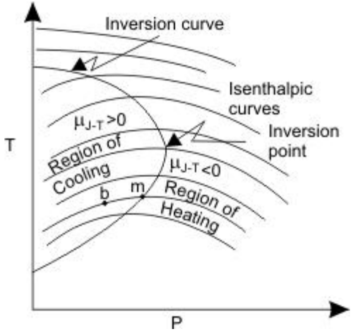

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- $B<0$, attractive; $B>0$, repulsive. $\frac{\mathrm{d}B}{\mathrm{d}T}>0$ (Fig 1.3).
- Low T, attractive, $B<0$, $\mu>0$, cooling; higher T, $B>0$, it is possible $\mu<0$, heating.

Adiabatic process

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- Expansion(V increasing) makes T dropping. ...

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3. $$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V = \frac{C_V}{T}\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_V \mathrm{d}V,$$

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  where $\varphi(T) = \frac{H_{m,0}}{RT} - \int \frac{1}{RT^2}\mathrm{d}T\int C_{p,m}\mathrm{d}T - \frac{S_{m,0}}{R}$.

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  $\Rightarrow \mathrm{d}F = -S\mathrm{d}T + \sigma \mathrm{d}A$.
- 2nd, $\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_A$, $\sigma = \left(\frac{\partial F}{\partial A}\right)_T$.
  Experiments $\rightarrow \sigma(T)$ does not depend on A.
  $F = \sigma A + F_0 = \sigma A$, (as $A \rightarrow 0, F \rightarrow 0$)
  $S = -\left(\frac{\partial F}{\partial T}\right)_A = -A\left(\frac{\partial \sigma}{\partial T}\right)_A = -A\frac{\mathrm{d}\sigma(T)}{\mathrm{d}T}$,
  $U = F + TS = \sigma A - TA\frac{\mathrm{d}\sigma(T)}{\mathrm{d}T}$.

Eg. Thermodynamical functions of the surface system.

- 1st, find the characteristic function. Surface system, mechanical parameter σ, geometrical parameter A .
  EOS: $f(\sigma, A, T) = 0$.
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  $\sigma(T)$ (EOS) is only the quantity needed to be measured.

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  Properties: uniform, isotropic, $u_\nu(T)$. *(prove)*

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  $= \frac{4}{3}a\mathrm{d}(VT^3) \Rightarrow S = \frac{4}{3}aT^3V + S_0$. $S_0 = 0$ as when $V = 0$ the radiation field does not exist.

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- $J_u = \frac{1}{4}cu$.

Radiation flux density

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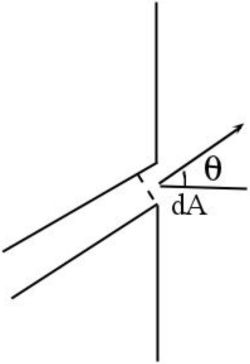

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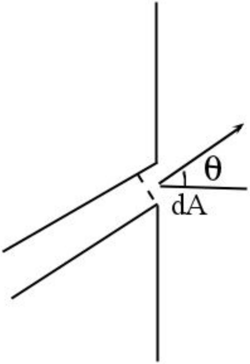

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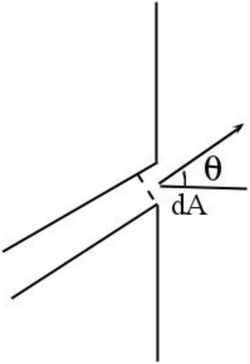

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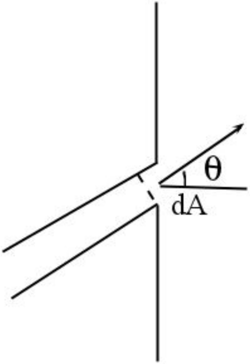

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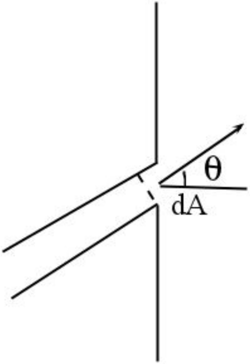

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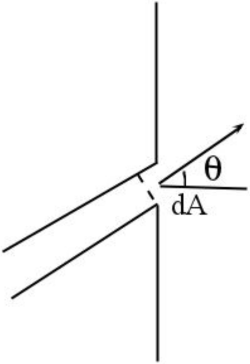

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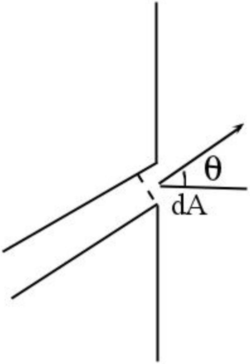

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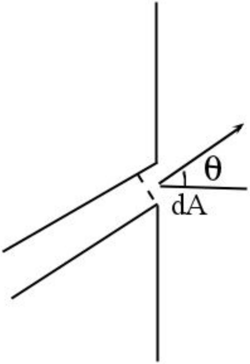

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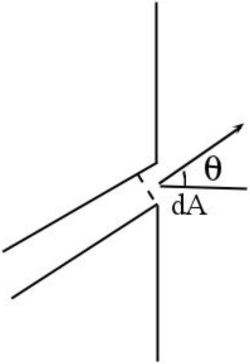

1. In unit time, in the direction θ, through area $\mathrm{d}A$, the energy $u_\theta c\mathrm{d}A\cos\theta$. $(u\mathrm{d}V = uc\mathrm{d}t(\mathrm{d}A\cos\theta))$
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3. Integrate for all directions: $J_u\mathrm{d}A = \int_0^{2\pi} uc\mathrm{d}A\cos\theta\frac{\mathrm{d}\Omega}{4\pi}$.

$$\Rightarrow J_u = \frac{uc}{4\pi}\int_0^{2\pi}\cos\theta\mathrm{d}\Omega = \frac{uc}{4\pi}\int_0^{2\pi}\mathrm{d}\varphi\int_0^{\pi/2}\cos\theta\sin\theta\mathrm{d}\theta$$
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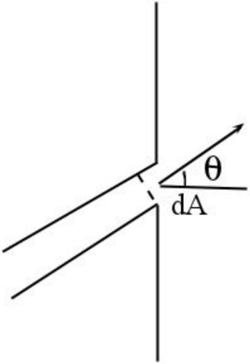

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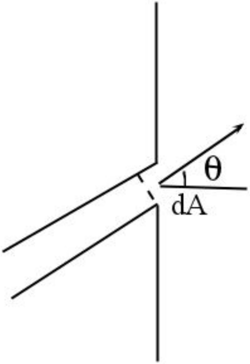

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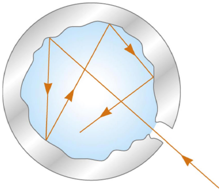
Example of blackbody:
tiny window of the cavity in equilibrium.



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  $\Rightarrow \left(\frac{\partial S}{\partial \mathscr{H}}\right)_T = \mu_0 \left(\frac{\partial m}{\partial T}\right)_{\mathscr{H}}$, Maxwell's relation for magnetic medium.

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  Cooling by decreasing $\mathscr{H}$.

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  $G = U - TS + pV - \mu_0 \mathscr{H} m$,
  $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p - \mu_0 m \mathrm{d}\mathscr{H}$,
  $V = \left(\frac{\partial G}{\partial p}\right)_{T,\mathscr{H}}$, $-\mu_0 m = \left(\frac{\partial G}{\partial \mathscr{H}}\right)_{T,p}$, $\frac{\partial^2 G}{\partial \mathscr{H} \partial p} = \frac{\partial^2 G}{\partial p \partial \mathscr{H}}$,
  $\Rightarrow \left(\frac{\partial V}{\partial \mathscr{H}}\right)_{T,p} = -\mu_0 \left(\frac{\partial m}{\partial p}\right)_{T,\mathscr{H}}$.
- 3°. In non-uniform magnetic field, potential energy change:

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- 2°. Considering the volume change:
  $đW = \mu_0 \mathscr{H} \mathrm{d}m - p\mathrm{d}V$.
- $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu_0 \mathscr{H} \mathrm{d}m$,
  $G = U - TS + pV - \mu_0 \mathscr{H} m$,
  $\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p - \mu_0 m \mathrm{d}\mathscr{H}$,
  $V = \left(\frac{\partial G}{\partial p}\right)_{T,\mathscr{H}}$, $-\mu_0 m = \left(\frac{\partial G}{\partial \mathscr{H}}\right)_{T,p}$, $\frac{\partial^2 G}{\partial \mathscr{H} \partial p} = \frac{\partial^2 G}{\partial p \partial \mathscr{H}}$,
  $\Rightarrow \left(\frac{\partial V}{\partial \mathscr{H}}\right)_{T,p} = -\mu_0 \left(\frac{\partial m}{\partial p}\right)_{T,\mathscr{H}}$.
- 3°. In non-uniform magnetic field, potential energy change:
  $đW = -\mu_0 m \mathrm{d}\mathscr{H}$.

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