Thermodynamics & Statistical Physics

Chapter 2. Thermodynamical properties of uniform medium

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Table of contents

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Table of contents

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$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p = \frac{\partial^2 H}{\partial S \partial p},$$
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- App 1. Choose (T, V) as free parameters for U:
- $$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V, \ \ldots(1)$$

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  $= T\left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] \mathrm{d}V$. ...(2)

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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Maxwell relations App 2

- App 2: Choose (T, p) as free parameters for H,
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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.

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  $C_p - C_V = T \cdot \beta p \cdot \alpha V = \alpha\beta p V T$, or $= \frac{\alpha^2 V T}{\kappa_T}$.

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Table of contents

§2.3 Throttling process and adiabatic expansion

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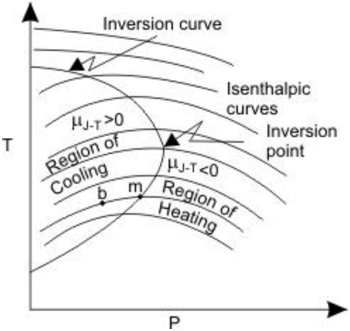

- $\therefore \mu = \frac{V}{C_p}(T\alpha - 1) = \frac{V}{C_p}\left(1 - \frac{p}{RT}B + \frac{nT}{V}\frac{\mathrm{d}B}{\mathrm{d}T} - 1\right)$
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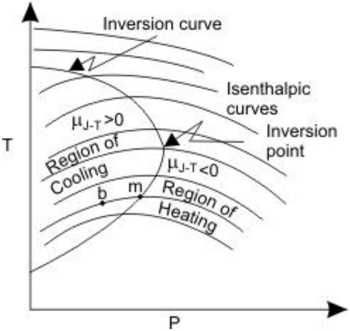

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$$= \frac{V}{C_p}\left(-\frac{p}{RT}B + \frac{nT}{V}\frac{\mathrm{d}B}{\mathrm{d}T}\right) = \frac{n}{C_p}\left(T\frac{\mathrm{d}B}{\mathrm{d}T} - B\right).$$
- $B<0$, attractive; $B>0$, repulsive. $\frac{\mathrm{d}B}{\mathrm{d}T}>0$ (Fig 1.3).

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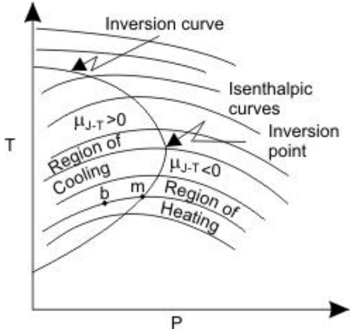

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- $B < 0$, attractive; $B > 0$, repulsive. $\frac{\mathrm{d}B}{\mathrm{d}T} > 0$ (Fig 1.3).
- Low T, attractive, $B < 0$, $\mu > 0$, cooling; higher T, $B > 0$, it is possible $\mu < 0$, heating.

Adiabatic process

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

Table of contents

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

Table of contents

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Table of contents

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

Radiation flux density

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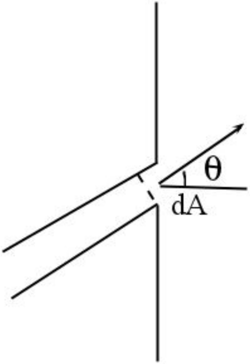

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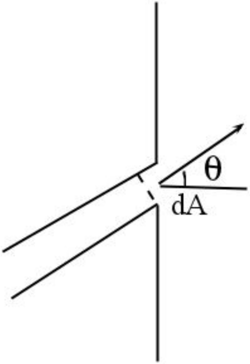

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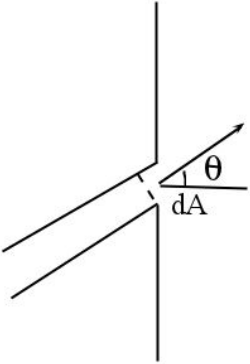

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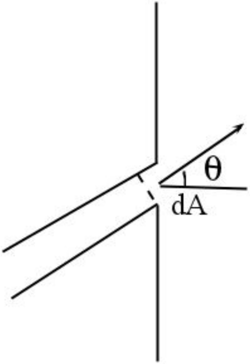

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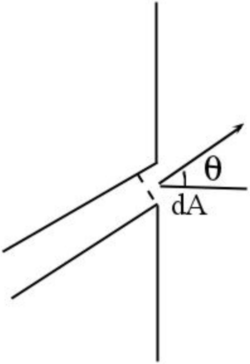

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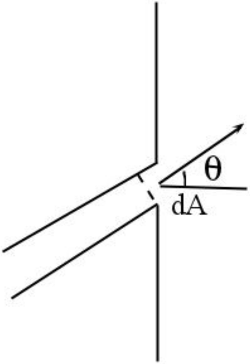

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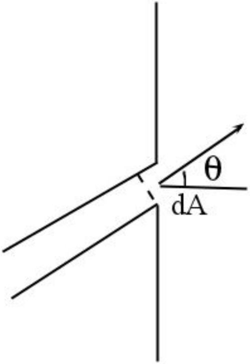

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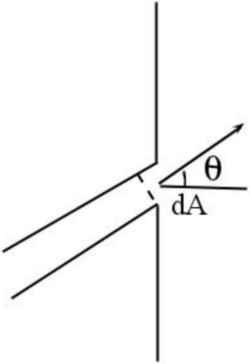

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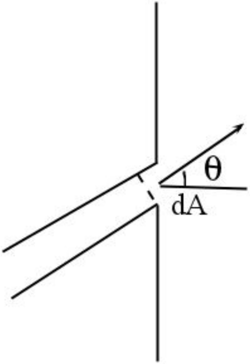

1. In unit time, in the direction θ, through area $\mathrm{d}A$, the energy $u_\theta c \mathrm{d}A\cos\theta$. $(u\mathrm{d}V = uc\mathrm{d}t(\mathrm{d}A\cos\theta))$
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3. Integrate for all directions: $J_u\mathrm{d}A = \int_0^{2\pi} uc\mathrm{d}A\cos\theta\frac{\mathrm{d}\Omega}{4\pi}$.

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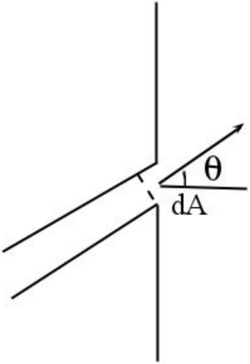

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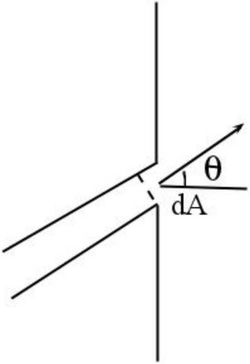

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Example of blackbody:
tiny window of the cavity in equilibrium.

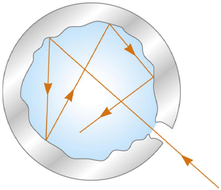

Table of contents

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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.

Thermodynamics of magnetic medium: entropy

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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:

Thermodynamics of magnetic medium: general

- 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:
  $đW = -\mu_0 m \mathrm{d}\mathscr{H}$.

Table of contents