Notes of JU Guoxing TD&SP

hebrewsnabla

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23 Photon

23.1 Classic Thermodynamics of Electromagnetic Radiation

Energy density

$$u = \frac{U}{V} = n\hbar\omega \tag{23.1.1}$$

pressure

$$pV = \frac{1}{3}Nm\langle v^2\rangle \tag{23.1.2}$$

for photon

$$p = \frac{1}{3}nmc^2 \tag{23.1.3}$$

24 Phonon

24.1 Einstein Model

24.2 Debye Model

25 Relativistic Gas

25.1

25.2 Ultrarelativistic Gas

$$E = pc = \hbar kc \tag{25.2.1}$$

single-particle partition function

$$Z_1 = \int_0^\infty \mathrm{e}^{-\beta\hbar kc} g(k)\mathrm{d}k \tag{25.2.2}$$

where

$$g(k)\mathrm{d}k = \frac{Vk^2\mathrm{d}k}{2\pi^2} \tag{25.2.3}$$

Let $x = \beta\hbar kc$

$$Z_1 = \frac{V}{2\pi^2}\left(\frac{1}{\beta\hbar c}\right)^3 \int_0^\infty \mathrm{e}^{-x}\, x^2 \mathrm{d}x = \frac{V}{\pi^2}\left(\frac{1}{\beta\hbar c}\right)^3 \tag{25.2.4}$$

or $Z_1 = \dfrac{V}{\Lambda^3}$

N-particle partition fxn

$$Z_N = \frac{Z_1^N}{N!} \tag{25.2.5}$$

25.3 Adiabatic Expansion

$$VT^3 = Cons. \tag{25.3.1}$$

26 Real Gases

26.1 vdW Gas

$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT \tag{26.1.1}$$

critical point (临界点)

$$\left(\frac{\partial p}{\partial V}\right) = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3} = 0 \tag{26.1.2}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right) = ... \tag{26.1.3}$$

...

critical vol

$$V_c = 3b \tag{26.1.4}$$

critical temp

$$T_c = \frac{8a}{27Rb} \tag{26.1.5}$$

critical pres

$$p_c = \frac{a}{27b^2} \tag{26.1.6}$$

thus

$$\frac{p_c V_c}{RT_c} = \frac{3}{8} \tag{26.1.7}$$

26.2 Dieterici Equation

vdW Eq.

$$
\begin{aligned}
p &= \frac{RT}{V-b} - \frac{a}{V_m^2} \\
&\equiv p_{rep} + p_{attr}
\end{aligned}
\tag{26.2.1}
$$

Dieterici Eq.

$$
p = p_{rep}\,\mathrm{e}^{-\dfrac{a}{RTV}} \tag{26.2.2}
$$

26.3 Virial Expansion

$$
\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots \tag{26.3.1}
$$

B, C, etc., are called virial coefficients.
Try to drive B:

$$
U = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} V(|\mathbf{r}_i - \mathbf{r}_j|) \tag{26.3.2}
$$

$$
Z = \frac{1}{N!h^{3N}} \tag{26.3.3}
$$

...

$$
p = \ldots \tag{26.3.4}
$$

Using hard sphere model

$$
V(r) = \begin{cases} \infty & r < r_0 \\ -\varepsilon\left(\dfrac{r_0}{r}\right)^6 & r > r_0 \end{cases} \tag{26.3.5}
$$

we have

$$
B = b - \frac{a\beta}{N} \tag{26.3.6}
$$

where

$$
a = \ldots \quad b = \ldots \tag{26.3.7}
$$

26.4 The Law of Corresponding States

Def

$$
\tilde{p} = \frac{p}{p_c}, \quad \tilde{V} = \frac{V}{V_c}, \quad \tilde{T} = \frac{T}{T_c} \tag{26.4.1}
$$

thus

$$
\left(\tilde{p} + \frac{3}{\tilde{V}^2}\right) = \frac{8\tilde{T}}{3\tilde{V} - 1} \tag{26.4.2}
$$

27 Cooling Real Gas

27.1 The Joule Expansion

U unchanged. Irreversible.
Joule coefficient

$$\mu_J = \left(\frac{\partial T}{\partial V}\right)_U \tag{27.1.1}$$

thus

$$\mu_J = -\left(\frac{\partial T}{\partial U}\right)_V \left(\frac{\partial U}{\partial V}\right)_T = -\frac{1}{C_V}\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \tag{27.1.2}$$

For ideal gas

$$\mu_J = 0 \tag{27.1.3}$$

For vdW gas

$$\mu_J = -\frac{a}{C_V V^2} \tag{27.1.4}$$

$$\Delta T = \ldots \tag{27.1.5}$$

27.2 Isothermal Expansion

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \tag{27.2.1}$$

$$\Delta U = \int_{V_1}^{V_2} \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] \mathrm{d}V \tag{27.2.2}$$

For ideal gas

$$\Delta U = 0 \tag{27.2.3}$$

For vdW gas

$$\ldots \tag{27.2.4}$$

27.3 Joule-Kelvin Expansion

aka Joule-Thomson expansion.

28 Phase Transitions

28.1 Latent Heat

28.2 Chemical Potential and Phase Changes

Phase equilibrium

$$\mu_1 = \mu_2 \tag{28.2.1}$$

28.3 Clausius-Clapeyron Equation

$$\mu_1(p, T) = \mu_2(p, T) \tag{28.3.1}$$

$$\mathrm{d}\mu_1 = \mathrm{d}\mu_2 \tag{28.3.2}$$

with Gibbs-Duhem Eq.:

$$\mathrm{d}\mu = -s\mathrm{d}T + v\mathrm{d}p \tag{28.3.3}$$

where $s = \dfrac{S}{N},\ v = \dfrac{V}{N}$
thus

$$-s_1\mathrm{d}T + v_1\mathrm{d}p = -s_2\mathrm{d}T + v_2\mathrm{d}p \tag{28.3.4}$$

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{s_2 - s_1}{v_2 - v_1} \tag{28.3.5}$$

Def latent per particle

$$\ell = T\Delta s \tag{28.3.6}$$

thus

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\ell}{T(v_2 - v_1)} \tag{28.3.7}$$

or

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{L}{T(V_2 - V_1)} \tag{28.3.8}$$