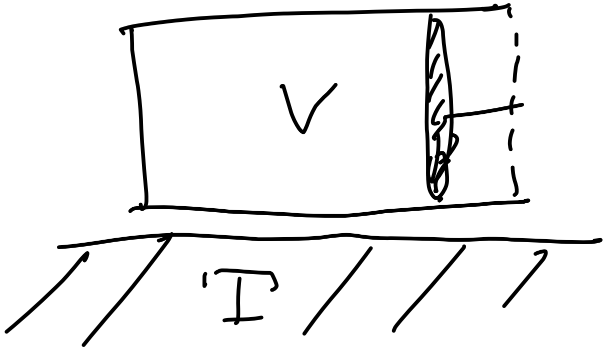
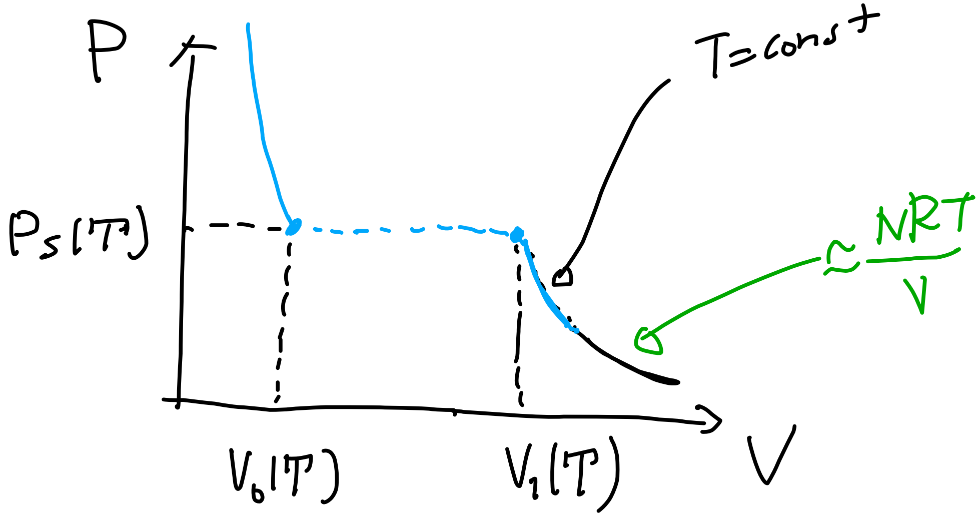
熱力学講義X

2020/07/15

§ 設定





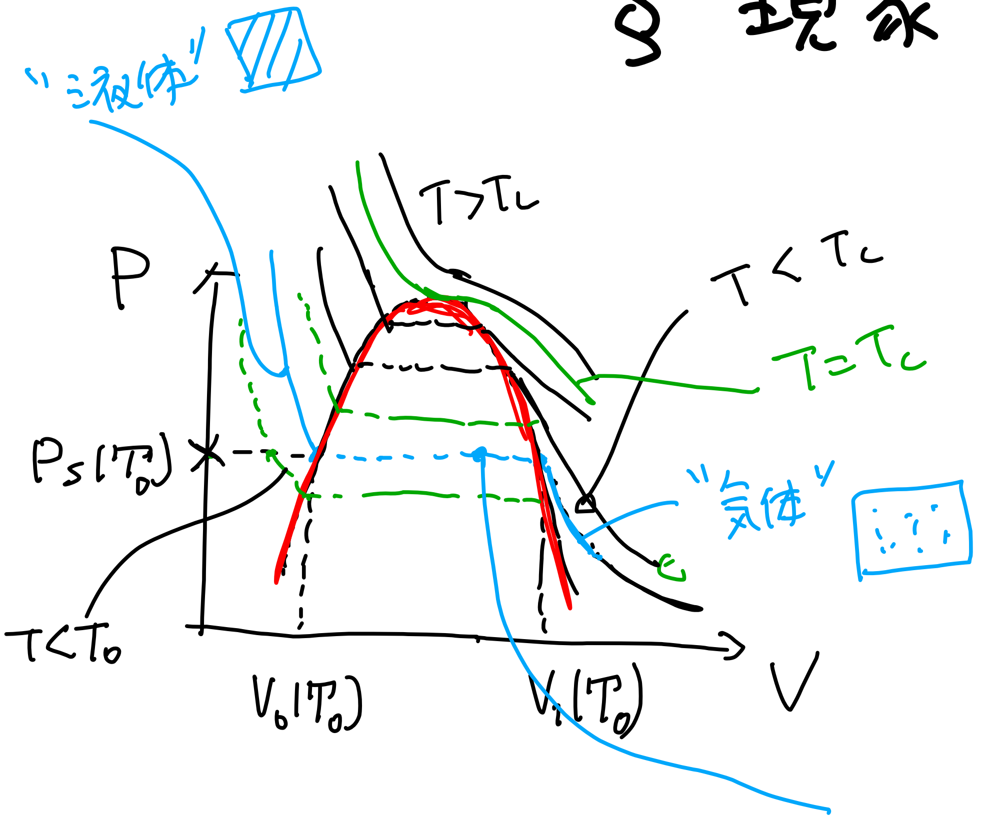
- $V \nearrow$

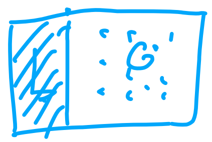
$$P \simeq \frac{NRT}{V}$$

$P_s(T)$: 飽和圧力

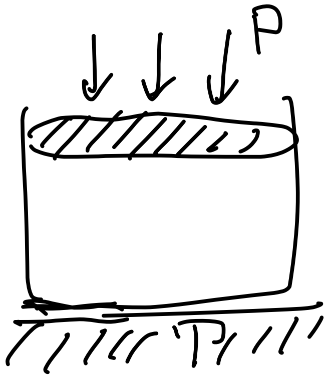
この現象を熱力学として議論する。

§ 現象



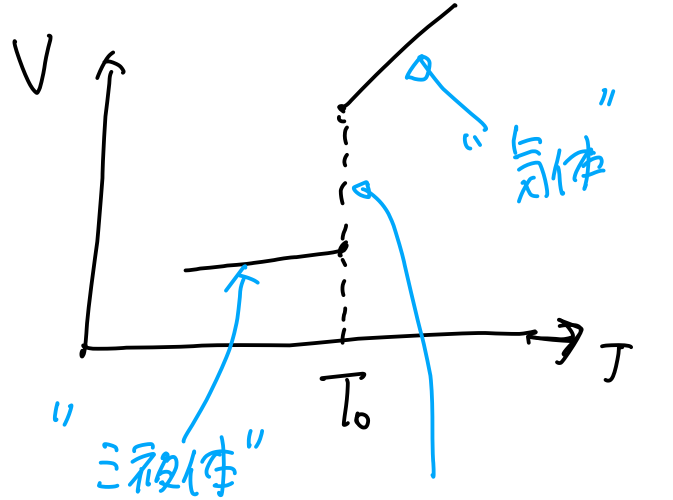


T_c : 臨界温度



$p = \text{const}$

(e.g. $p = P_s(T_0)$)



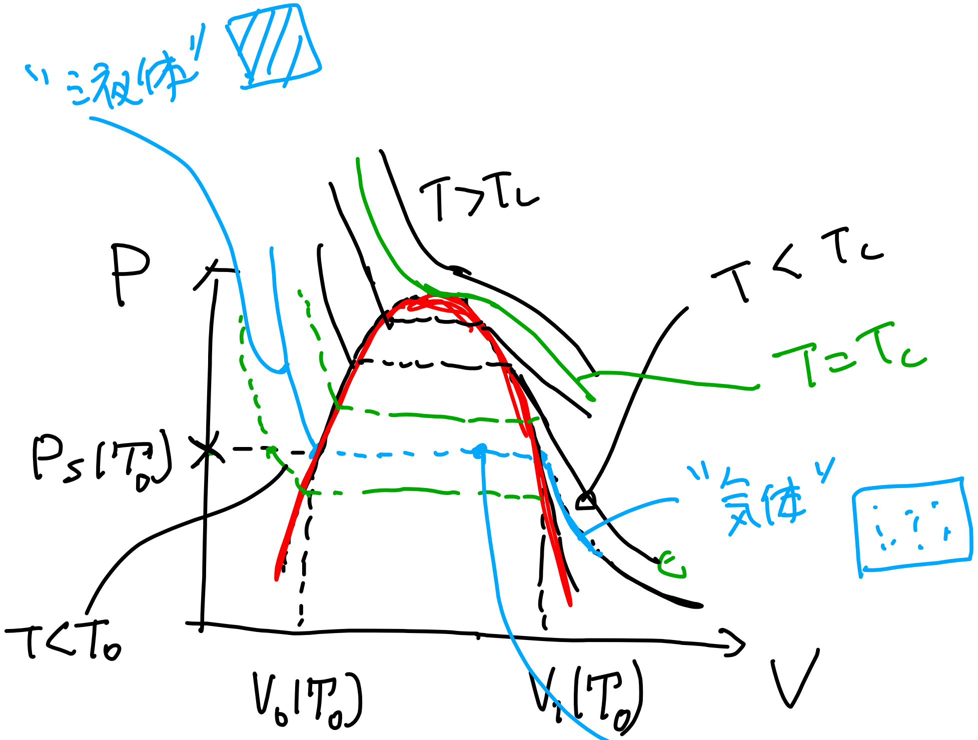
気液転移

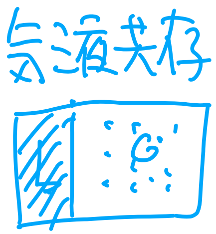
$p = P_s(T_0)$

$\Leftrightarrow T_0 = T_0(p)$
転移温度

~ Intermission ~

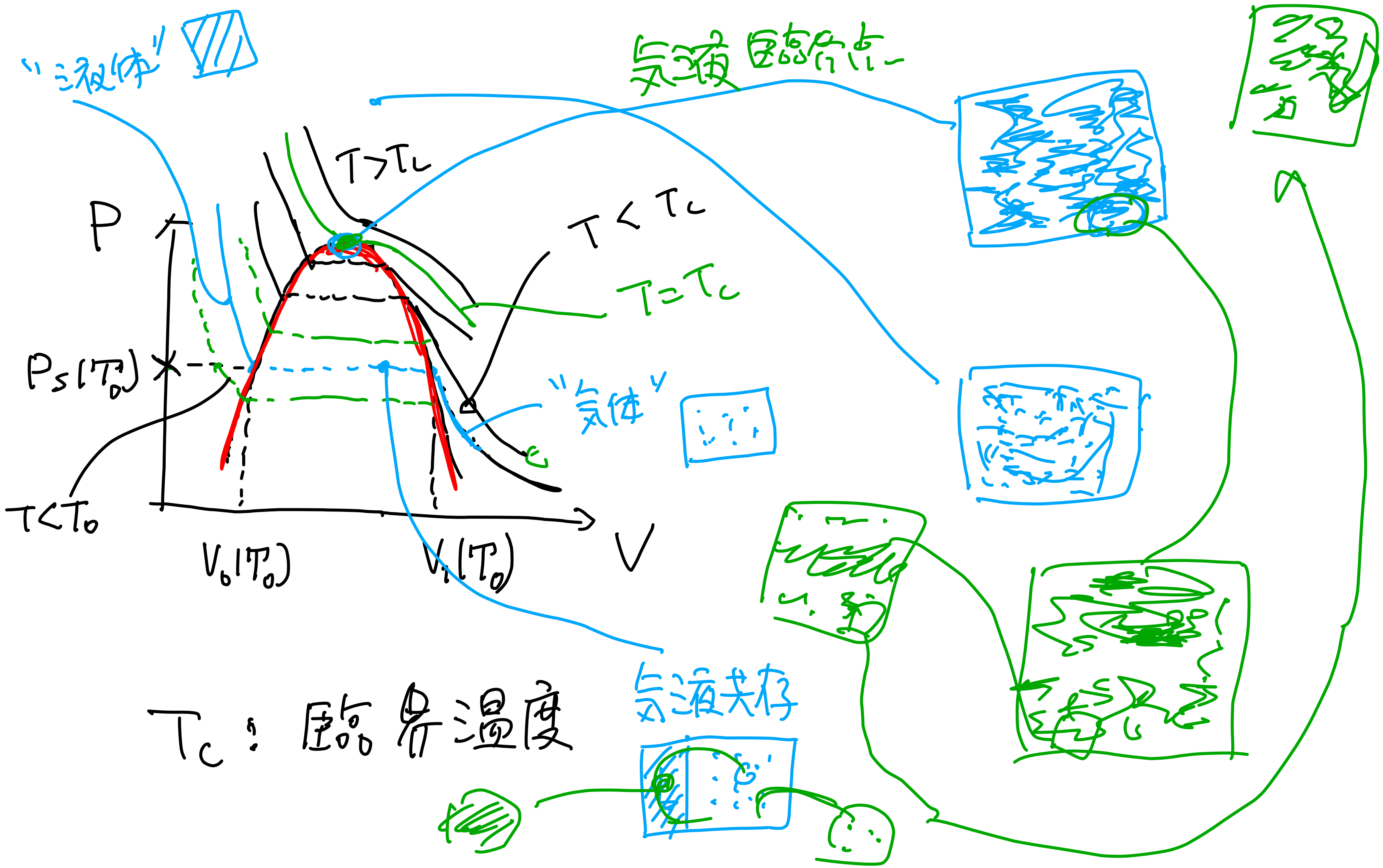
§ 気体と液体の区別？





T_c：臨界温度

§ 臨界点の様子

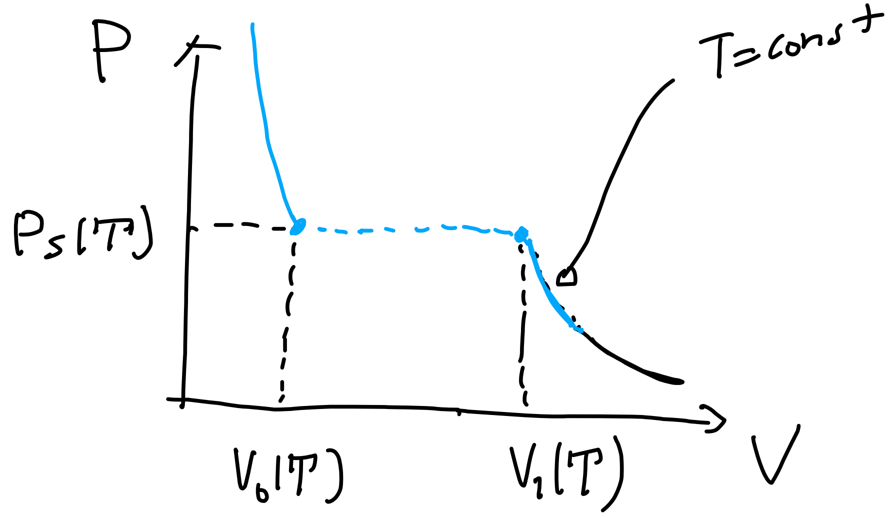


Tc : 臨界温度

- 自己相似形
- フラクタル

~ Intermission ~

§ クラペイロンの式



例：

水 → 水蒸気

1気圧 → 373 K

1500m の山
1気圧 −150 hPa → 368 K

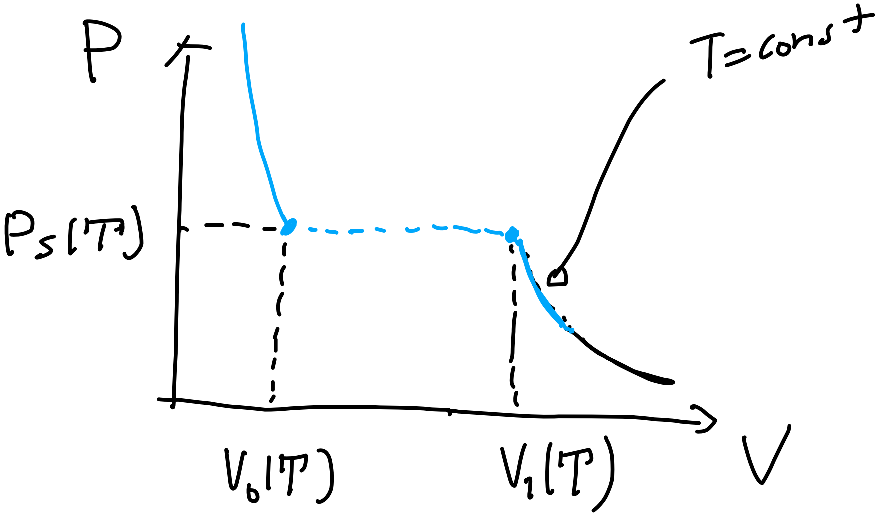
$$T_0 = T_0(p)$$

$$\Longleftrightarrow \quad P_s = P_s(T)$$

$$\left(\frac{dT_0(p)}{dp}\right)^{-1} = \frac{dP_s(T)}{dT} = \frac{L}{T(V_1 - V_0)}$$

L：気化熱

§ 気化熱



$$L = Q\left[(T, V_0(T)) \xrightarrow{q.s.} (T, V_1(T))\right]$$

$$= T\left[S(T, V_1(T)) - S(T, V_0(T))\right]$$

分子間エネルギー ↑

分子の運動エネルギー →

"熱"を吸収

$$\boxed{dF = -S\,dT - p\,dV}$$

§ 導出

$$F(T, V_1(T)) - F(T, V_0(T)) = -P_s(T)\left(V_1(T) - V_0(T)\right)$$

Tで微分

$$\underbrace{\left(\frac{\partial F}{\partial T}\right)_V\Big|_{V_1(T)}}_{-S(T, V_1(T))} + \underbrace{\left(\frac{\partial F}{\partial V}\right)_T\Big|_{V_1(T)}\frac{dV_1}{dT}}_{-P_s(T)\frac{dV_1}{dT}} - \left(\frac{\partial F}{\partial T}\right)_V\Big|_{V_0(T)} - \left(\frac{\partial F}{\partial V}\right)_T\Big|_{V_0(T)}\frac{dV_0}{dT}$$

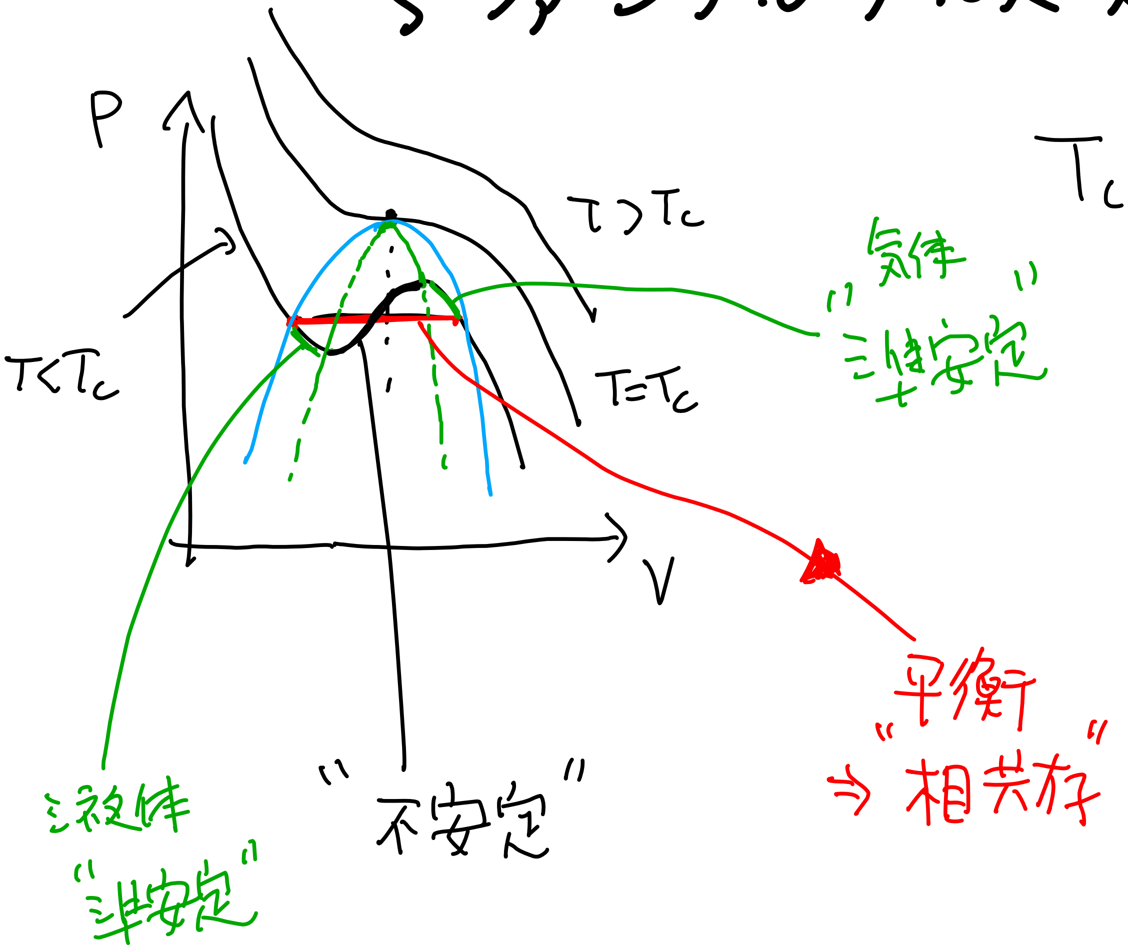
$$= -\frac{dP_s(T)}{dT}\left(V_1(T) - V_0(T)\right) - P_s(T)\left[\frac{dV_1(T)}{dT} - \frac{dV_0(T)}{dT}\right]$$

$$\Rightarrow \quad S(T, V_1(T)) - S(T, V_0(T)) = \frac{dP_s(T)}{dT}\left(V_1(T) - V_0(T)\right)$$

$$\therefore \quad \frac{dP_s(T)}{dT} = \frac{L}{T\left[V_1(T) - V_0(T)\right]} \quad //$$

~ Intermission ~

§ ファンデルワールス気体



$$T_c = \frac{8a}{27bR}$$

ファンデルワールス気体
状態方程式

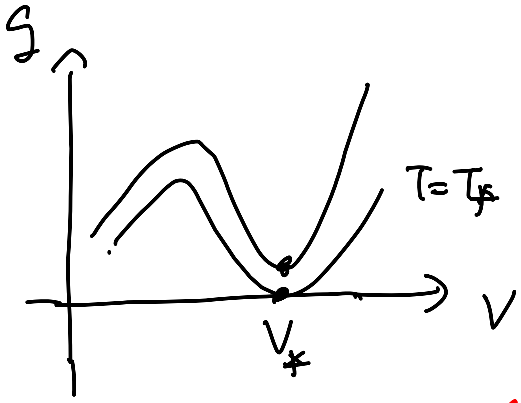
⇓

相共存？

・熱力学変分原理

§計算

$$P = \frac{NRT}{V-Nb} - \left(\frac{N}{V}\right)^2 a$$



$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{NRT}{(V-Nb)^2} + 2\frac{N^2}{V^3}a = 0$$

$$\begin{cases} g(V) \equiv NRT\,V^3 - 2N^2a\,(V-Nb)^2 = 0 \\ g'(V) = 3NRTV^2 - 4N^2a\,(V-Nb) = 0 \end{cases}$$

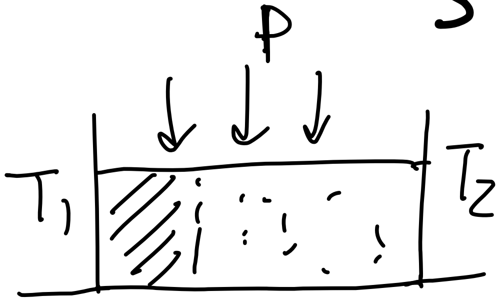
$$NRTV^3 - 2N^2a\,\cancel{(V-Nb)^2} - \frac{3}{2}NRTV^2(V-Nb) + 2N^2a\,\cancel{(V-Nb)^2} = 0$$

$$V - \frac{3}{2}(V-Nb) = 0 \qquad \underline{V_* = 3Nb}$$

$$T_* = \frac{2N^2a}{NRV_*^3}(V_*-Nb)^2 = \frac{8N^2a(Nb)^2}{27NR(Nb)^3}$$

$$= \frac{8a}{27Rb} \quad //$$

§ 最近の話題



$T_1 < T_0(p) < T_2$

熱伝導下相共存

e.g. 水

$T_1 = 95\ ^\circ\mathrm{C}$

$T_2 = 105\ ^\circ\mathrm{C}$

p : 1気圧

$\Downarrow$

界面の温度 $\simeq 96^\circ\mathrm{C}$

(理論的予言)

cf. Global thermodynamics for heat conduction systems
J. Stat. Phys. **177** (2019)

§ レポート