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van der Waals Equation

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-Critical discussion of the vdW equation

-A new derivation

-Enlarge the applicability

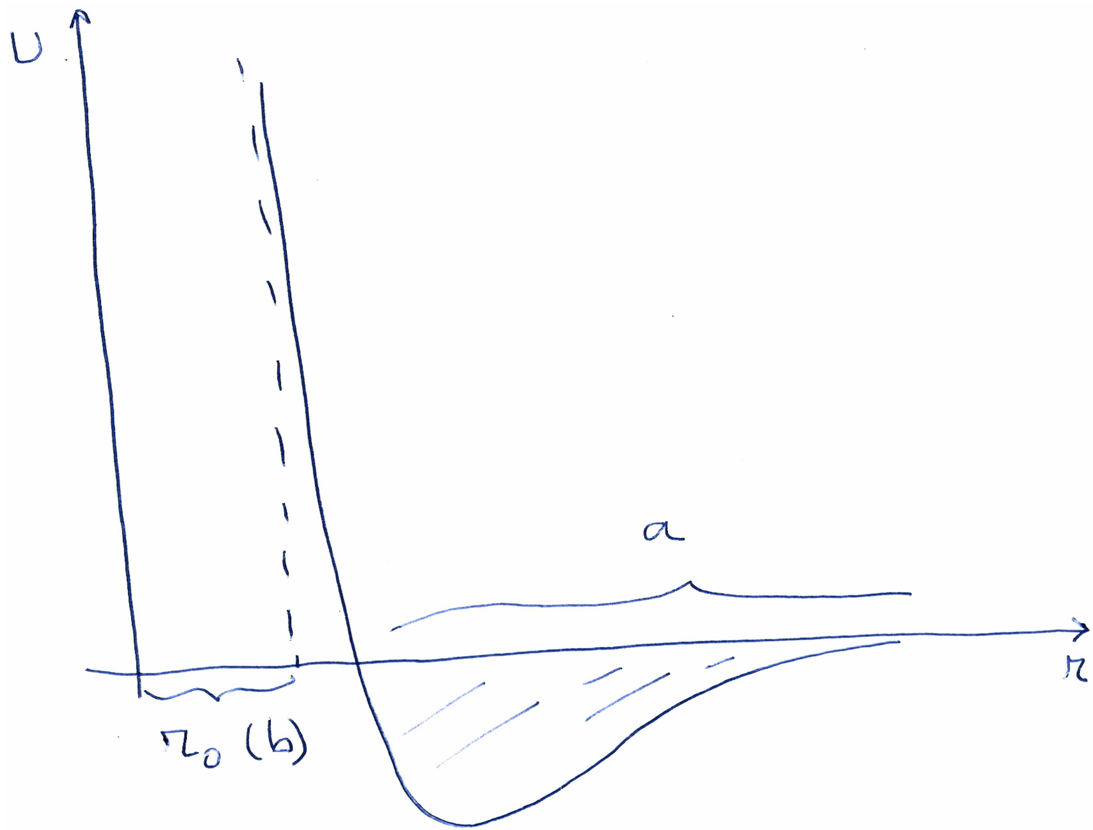
Classical Non-Ideal Gas

N molecules, volume V, temperature T

Interaction

$$E = \frac{1}{2} \sum_{i \neq j} U(\mathbf{r}_i - \mathbf{r}_j)$$

(Equilibrium?)


U
a
r
r_0 (b)

van der Waals's qualitative reasoning, 1873 (1910)

Attractive tail $\Longrightarrow$pressure excess (attractive, interaction, $\sim n^2 = N^2/V^2$)

$$p \longrightarrow p - \frac{N^2}{V^2} a$$

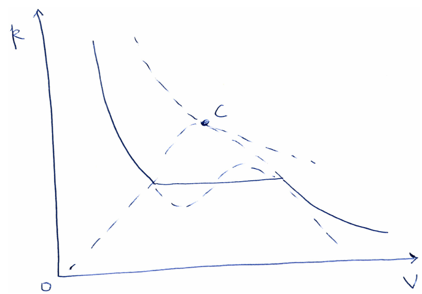
Hard core$\Longrightarrow$excluded volume

$$V \longrightarrow V - Nb$$

van der Waals equation

$$pV = NT \longrightarrow \left(p - \frac{N^2}{V^2}a\right)(V - Nb) = NT$$

vdW isotherms



a, b - phenomenological parameters

Comments

-First-order phase transition (gas-liquid) (Mod Phys Lett **B21** 893 (2007)

-In-between min-max: non-analytical

-Statistical derivation: connection a, b and interaction U (interaction effects)

-Difficulties with standard derivation (Roum J Phys **51** 907 (2006) (Cune, MA)

Standard Derivation (all derivations, Ursell-Mayer cluster exp)

$$\Delta\mathcal{F} = -T \ln\left(\frac{1}{V^N}\int e^{-\beta E} d\mathbf{r}_1 ... d\mathbf{r}_N\right) =$$

$$= -T \ln\left[\frac{1}{V^N}\int \left(e^{-\beta E} - 1\right) d\mathbf{r}_1 ... d\mathbf{r}_N + 1\right]$$

Hypotheses: collisions (collisionless plasma?), single collisions, one at a time (rarefied gas)

"rationale": $\mathcal{F} = N f(T, V/N)$: analytic cont

$$\Delta\mathcal{F} \simeq -T \ln\left[1 - \frac{N^2}{2V^2}\int\left(1 - e^{-\beta U(\mathbf{r}_1-\mathbf{r}_2)}\right) d\mathbf{r}_1 d\mathbf{r}_2\right]$$

$$\Delta\mathcal{F} = -T \ln\left(1 - \frac{N^2}{V}B\right)$$

$$B = \frac{1}{2}\int\left(1 - e^{-\beta U(r)}\right) d\mathbf{r} = b + a/T$$

$$b = 2\pi\int_0^{2r_0} dr \cdot r^2 \ , \ \ a = 2\pi\int_{2r_0} dr \cdot r^2 U(r)$$

Result: (pressure $p = \frac{NT}{V} - \frac{\partial \Delta \mathcal{F}}{\partial V}$)

$$p = \frac{NT}{V} \frac{1 - \frac{N^2}{V} B(1 - 1/N)}{1 - \frac{N^2}{V} B} \simeq$$

$$\simeq \frac{NT}{V} \left(1 + \frac{NB}{V}\right) \simeq \frac{NT}{V - Nb} + \frac{N^2 a}{V^2}$$

valid for $N \ll 1$!

Difficulty taken over in the virial expansion (series in powers of n), BBGK hierarchy, ...

Cause of difficulties: interaction

We must solve first for the interaction effects, then do statistics!

Correct derivation

$$\Phi(\mathbf{r}_i) = \sum_j{}' U(\mathbf{r}_i - \mathbf{r}_j)$$

$j \neq i$! (self-interaction!)

Total int energy

$$E = \frac{1}{2}\sum_i \Phi(\mathbf{r}_i)$$

Correction to free energy

$$\Delta\mathcal{F} = -T \ln\left(\frac{1}{V^N}\int' e^{-\beta E} d\mathbf{r}_1 \ldots d\mathbf{r}_N\right)$$

Note: 1) the prime, 2) all $\mathbf{r}_i$!

The prime: integration over $V - Nb$, $b = \frac{1}{2} \cdot 4\pi(2r_0)^3/3$;
1/2 independent integration

Interaction: single-prtcl excs

Mean field

$$\Phi = \sum_j{}' U(\mathbf{r}_j) = \frac{N}{V}\int_{2r_0} d\mathbf{r}U(\mathbf{r}) = \frac{2Na}{V}$$

Not necessarily the same cutoff! (1st extension; plasma)

What we get?

$$\Delta\mathcal{F} = -T\ln\left(\frac{(V-Nb)^N}{V^N}e^{-\frac{1}{2}\beta N\Phi}\right) =$$

$$= \frac{1}{2}N\Phi - NT\ln\left(1-\frac{Nb}{V}\right) = \frac{N^2a}{V} - NT\ln\left(1-\frac{Nb}{V}\right)$$

The pressure

$$p = \frac{NT}{V} + \frac{N^2 a}{V^2} + NT \frac{Nb/V^2}{1 - Nb/V} =$$

$$= \frac{NT}{V}\left(1 + \frac{Nb/V}{1 - Nb/V}\right) + \frac{N^2 a}{V^2} = \frac{NT}{V - Nb} + \frac{N^2 a}{V^2}$$

(vdW equation)

2nd extension: external potential

Int energy

$$E = \sum_i \varphi(\mathbf{r}_i) + \frac{1}{2} N \Phi$$

$$\Delta\mathcal{F} = -T \ln \left(\frac{1}{V^N} \int' e^{-\beta \sum_i \varphi(\mathbf{r}_i) - \frac{1}{2} N \Phi} d\mathbf{r}_1 \ldots d\mathbf{r}_N \right) =$$

$$= -T \ln \left[\left(\frac{1}{V} \int' e^{-\beta \varphi(\mathbf{r})} d\mathbf{r} \right)^N e^{-\frac{1}{2} \beta N \Phi} \right] =$$

$$= -NT \ln \left(\frac{1}{V} \int' e^{-\beta \varphi(\mathbf{r})} d\mathbf{r} \right) + \frac{1}{2} N \Phi$$

Attention: excluded volume!

$$\int' e^{-\beta\varphi(\mathbf{r})} d\mathbf{r} = \int e^{-\beta\varphi(\mathbf{r})} d\mathbf{r} - b \sum_i e^{-\beta\varphi(\mathbf{r}_i)} =$$

$$= \int e^{-\beta\varphi(\mathbf{r})} d\mathbf{r} - \frac{Nb}{V} \int e^{-\beta\varphi(\mathbf{r})} d\mathbf{r} = \left(1 - \frac{Nb}{V}\right) \int e^{-\beta\varphi(\mathbf{r})} d\mathbf{r}$$

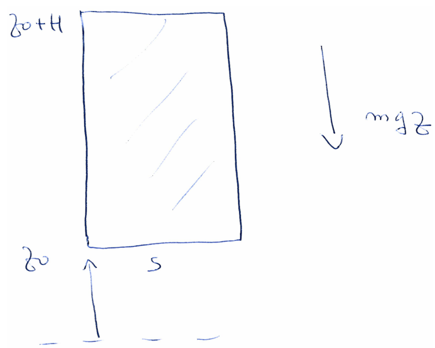
$$\Delta\mathcal{F} = -NT \ln\left(1 - \frac{Nb}{V}\right) + \frac{1}{2} N\Phi - NT \ln\left(\frac{1}{V} \int e^{-\beta\varphi(\mathbf{r})} d\mathbf{r}\right)$$

Correction - external field (exact result!)

$$I = \frac{1}{V} \int e^{-\beta \varphi(\mathbf{r})} d\mathbf{r}$$

$$p = \frac{NT}{V-Nb} + \frac{N^2 a}{V^2} + NT \frac{\partial \ln I}{\partial V}$$

Gravitational field - barometric formula (surface effects)



$$\varphi = mgz \;,\;\; I = \frac{e^{-\beta mgz_0}}{\beta mgV}\left(1 - e^{-\beta mgH}\right)$$

Hydrostatic pressure

$$\Delta p_0 = -\Delta p_H \simeq \frac{NmgH}{2V}$$