5.62 Physical Chemistry II
Spring 2008

5.62 Lecture #20: Virial Equation of State

Goal: Derive Virial Eqn. of State

$$p = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

pressure

$$Q = \frac{(2\pi mkT)^{3N/2}}{N!h^{3N}} Z(N,V,T) = \frac{(2\pi mkT)^{3N/2}}{N!h^{3N}} V^N \exp\left[\frac{N\beta}{2}\left(\frac{N}{V}\right)\right]$$

$$\ln Q = \ln\left[\frac{(2\pi mkT)^{3N/2}}{N!h^{3N}}\right] + N\ln V + \frac{N\beta}{2}\left(\frac{N}{V}\right)$$

Plugging ln Q into equation for p …

$$p = kT\left[\frac{\partial(\text{constants})}{\partial V} + \frac{N\partial \ln V}{\partial V} + \frac{\partial\left(N^2\beta/2V\right)}{\partial V}\right]$$

$$= kT\left[0 + \frac{N}{V} - \frac{\beta N^2}{2V^2}\right] = \frac{NkT}{V} - \frac{N^2kT\beta}{2V^2}$$

$$Nk = nR,\ nN_a = N$$

$$pV = nRT - \frac{N_a n\beta}{2}\left(\frac{nRT}{V}\right) \qquad \frac{pV}{n} \equiv p\bar{V} = RT - \frac{N_a\beta}{2}\left(\frac{RT}{\bar{V}}\right) \equiv RT + \boxed{B_2(T)}\left(\frac{RT}{\bar{V}}\right)$$

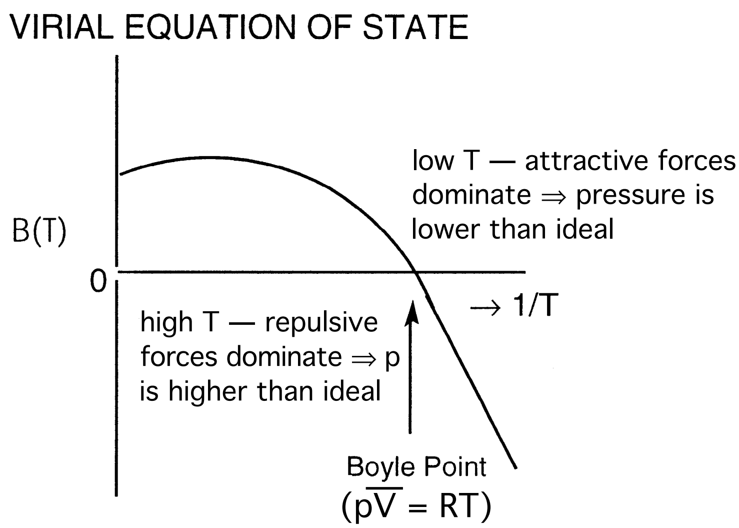
units Volume/mol.

$$p\bar{V} = RT + B_2(T)\left(\frac{RT}{\bar{V}}\right) \qquad \text{Virial Equation of State}$$

$$B_2(T) = -\frac{N_a\beta}{2} = -2\pi N_a\int_0^\infty dr\, r^2[e^{-u(r)/kT} - 1] \qquad \text{2nd VIRIAL COEFFICIENT}$$

[The 1st VIRIAL COEFFICIENT, $B_1(T)$, is 1!]

As $T \to \infty, B_2(T) \to 0$ because $\left[e^{-u(r)/kT} - 1\right] \to 0$
At finite high T, $B_2(T) > 0$
At low T, $B_2(T) < 0$



Typical Values of B_2(T) … in cm^3 mol^{-1}

	500K	400K	300K	200K
Ar	+7	–1.0	–15.5	–47.4
C_2H_6	–52	–96	–182	–410

For $\rho = \frac{n}{V} = 4.46 \times 10^{-5}$ mol cm^{-3}

		$\boxed{\text{Ar}}$		$\boxed{C_2H_6}$	
T(K)	p_{ideal} (atm)	p_{actual}	% dif	p_{actual}	% dif
500	1.8299	1.83047	+0.03	1.8258	–0.2
400	1.4639	1.4638	–0.003	1.4576	–0.4
300	1.0979	1.0971	–0.07	1.0889	–0.8
200	0.7320	0.7304	–0.2	0.7186	–1.82
		$\frac{\varepsilon}{k} = 124K$ [ε is well depth. We will see this later.]		$\frac{\varepsilon}{k} \cong 200K$	

Trend is toward too low p at low T and too high p at high T. There is a difference between Ar and benzene in the sense that benzene seems always to have too low p. If we include more terms in Z …

$$p\overline{V} = RT + \underbrace{B_2(T)}_{\text{2nd VIRIAL COEFF}}\left(\frac{RT}{\overline{V}}\right) + \underbrace{B_3(T)}_{\text{3rd VIRIAL COEFF}}\left(\frac{RT}{\overline{V}^2}\right) + \cdots = \sum_{n=1} B_n(T)RT\overline{V}^{1-n} \qquad [B_1(T) \equiv 1]$$

<u>Calculate $B_2(T)$ for Hard Sphere Potential</u>

$$\text{Hard sphere potential: } u(r) = \begin{cases} \infty & r<\sigma \\ 0 & r \geq \sigma \end{cases}$$

where $\sigma \equiv$ sum of two atomic radii

$$B_2(T) = \frac{-N_a}{2}\beta \qquad \beta = 4\pi\int_0^\infty dr\, r^2\left[e^{-u(r)/kT} - 1\right]$$

$$\beta = 4\pi\int_0^\sigma dr\, r^2\left(e^{-\infty} - 1\right) + 4\pi\int_\sigma^\infty dr\, r^2\left(e^{-0} - 1\right)$$

$$\beta = -4\pi \int_0^{\sigma} r^2 dr + 4\pi \cdot 0$$

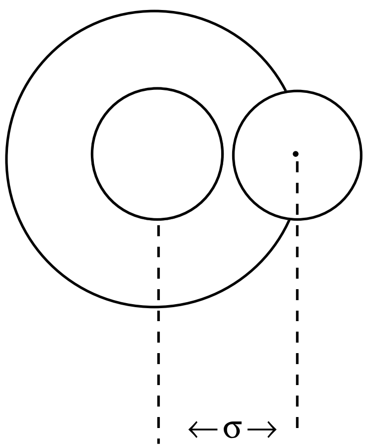
$$\beta = \frac{-4\pi}{3}\sigma^3 \Rightarrow \qquad B_2(T) = \frac{2\pi}{3}\sigma^3 N_a$$

INDEPENDENT OF TEMPERATURE

What is physical significance of B_2 for hard sphere potential?

IT IS THE EXCLUDED VOLUME

Simple geometric argument independent of statistical mechanics:



a volume $\frac{4\pi}{3}\sigma^3$

$$\underbrace{\frac{N_a}{2}}_{\text{each “volume” includes 2 atoms}}\frac{4\pi}{3}\sigma^3 = N_a\underbrace{\frac{2\pi\sigma^3}{3}}_{\text{same as } B_2 \text{ calculated from stat. mech.}}$$

Hard-sphere equation of state, correct through $B_2(T)$, is

$$p\bar{V} = RT + B_2\frac{RT}{\bar{V}} \approx RT + B_2 p \quad \text{because} \quad \left[\frac{RT}{\bar{V}} = p - \underbrace{B_2\frac{RT}{\bar{V}^2}}_{\text{small}} \approx p\right]$$

$$p\left(\bar{V} - B_2\right) = RT$$

$$p\left(\bar{V} - \underbrace{N_a\frac{2\pi\sigma^3}{3}}_{\text{excluded volume}}\right) = RT$$

Compare to van der Waals eqn. of state:

$$\left(p + \frac{a}{\overline{V}^2}\right)\left(\overline{V} - \underbrace{b}_{\text{excluded volume}}\right) = RT$$

(The true molar volume $\overline{V}$ is reduced by b. A volume $\overline{V}$ + b is required to give values of p, R, T that are consistent with the ideal gas law.)

So far we have considered only the repulsive part of the potential.

Now include attractions: e.g., square well, Sutherland, or Lennard-Jones.

Square well potential: $u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon_b & \sigma \le r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$

See Non-Lecture: Result is excluded volume + term of opposite sign.

Sutherland potential: $u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon\left(\dfrac{\sigma}{r}\right)^6 & r \ge \sigma \end{cases}$ [goal is to express β in terms of σ, ε]

$$\beta = 4\pi\int_0^\infty dr\, r^2\left[e^{-u(r)/kT} - 1\right]$$

$$= 4\pi\int_0^\sigma dr\, r^2\left(e^{-\infty} - 1\right) + 4\pi\int_\sigma^\infty dr\, r^2\left(\underbrace{e^{\varepsilon\sigma^6/r^6kT}}_{\text{expand}} - 1\right)$$

$$-\frac{4}{3}\pi\sigma^3 \qquad 4\pi\int_\sigma^\infty dr\, r^2\left(1 + \varepsilon\sigma^6/r^6kT - 1\right)$$ for modest (i.e.,not too small) kT (weak attraction)

$$4\pi\varepsilon\sigma^6/kT\int_\sigma^\infty dr\, r^{-4} = \frac{4}{3}\pi\sigma^3\frac{\varepsilon}{kT}$$

If T is too small, must keep more terms in the expansion.

$$\beta = \frac{4}{3}\pi\sigma^3\left(\frac{\varepsilon}{kT} - 1\right)$$ β is T-dependent and can be positive at low-T and negative at high-T

$$B_2(T) = -\frac{N_a}{2}\beta(T) = \underbrace{\frac{2}{3}\pi\sigma^3 N_a}_{\text{hard sphere}} - \underbrace{\frac{2}{3}\pi\sigma^3 N_a\,\varepsilon/kT}_{\text{from attractive part of u(r)}}$$

High T: T-independent, excluded volume repulsion dominates

Low T: linear variation of $B_2(T)$ vs. 1/T. Use this to determine ε.

Equation of state:

$$p\overline{V} = RT + B_2\frac{RT}{\overline{V}} \approx RT + B_2 p$$

$$p\left(\overline{V} - B_2\right) = RT \quad \longleftarrow \boxed{\text{insert the 2 terms of } B_2(T)}$$

$$p\left(\overline{V} - N_a\frac{2\pi\sigma^3}{3}\right) + p\cdot\frac{2}{3}\pi\sigma^3 N_a\,\varepsilon/kT = RT \quad \longleftarrow \boxed{\text{replace p/kT in second term}}$$

$$\frac{p}{kT} = \frac{p}{pV/N} = \frac{nN_a}{V} = \frac{N_a}{\overline{V}}$$

$$p\left(\overline{V} - N_a\frac{2\pi\sigma^3}{3}\right) + \frac{2}{3}\pi\sigma^3 N_a^2\,\varepsilon/\overline{V} = RT$$

Define $b = N_a\dfrac{2\pi\sigma^3}{3}$, $a = \dfrac{2}{3}\pi\sigma^3 N_a^2\varepsilon$

$$p\left(\overline{V} - b\right) + a/\overline{V} \approx \left(p + a/\overline{V}^2\right)\left(\overline{V} - b\right) = RT \qquad (ab/\overline{V}^2 \approx 0)$$

van der Waals Eqn. of State!

Non-Lecture

Square well potential: $u(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon_b & \sigma \le r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$

$$\beta = 4\pi\int_0^\infty dr\, r^2\left[e^{-u(r)/kT} - 1\right]$$

$$= 4\pi\int_0^\sigma dr\, r^2\left(e^{-\infty} - 1\right) + 4\pi\int_\sigma^{\lambda\sigma} dr\, r^2\left(e^{\varepsilon_b/kT} - 1\right) + 4\pi\int_{\lambda\sigma}^\infty dr\, r^2\left(e^{-0} - 1\right)$$

$$= \quad -\frac{4}{3}\pi\sigma^3 \quad + \frac{4}{3}\pi\left[(\lambda\sigma)^3 - \sigma^3\right]\underbrace{\left(e^{\varepsilon_b/kT} - 1\right)}_{\text{expand this}} \quad + \quad 0$$

$$\approx \left(1 + \varepsilon_b/kT - 1\right) \text{ for modest } kT > \varepsilon_b \text{ (weak attraction)}$$

$$\beta = -\frac{4}{3}\pi\sigma^3 + \frac{4}{3}\pi\sigma^3\left(\lambda^3 - 1\right)\varepsilon_b/kT$$

i.e., if T is not too low

$$B_2(T) = -\frac{N_a}{2}\beta(T) = \frac{2}{3}\pi\sigma^3 N_a - \frac{2}{3}\pi\sigma^3 N_a\left(\lambda^3 - 1\right)\varepsilon_b/kT$$

excluded volume + term of opposite sign!

$$p\bar{V} = RT + B_2 \frac{RT}{\bar{V}} \approx RT + B_2 p$$

$$p\left(\bar{V} - B_2\right) = RT$$

$$p\left(\bar{V} - N_a \frac{2\pi\sigma^3}{3}\right) + p \cdot \frac{2}{3}\pi\sigma^3 N_a \left(\lambda^3 - 1\right)\varepsilon_b / kT = RT$$

$$\frac{p}{kT} = \frac{p}{PV/N} = \frac{nN_a}{V} = \frac{N_a}{\bar{V}}$$

$$p\left(\bar{V} - N_a \frac{2\pi\sigma^3}{3}\right) + \frac{2}{3}\pi\sigma^3 N_a^2 \left(\lambda^3 - 1\right)\varepsilon_b / \bar{V} = RT$$

Define $b = N_a \dfrac{2\pi\sigma^3}{3}$, $a = \dfrac{2}{3}\pi\sigma^3 N_a^2 \left(\lambda^3 - 1\right)\varepsilon_b$

$$p\left(\bar{V} - b\right) + a / \bar{V} \approx \left(p + a / \bar{V}^2\right)\left(\bar{V} - b\right) = RT \qquad (ab / \bar{V}^2 \approx 0)$$

van der Waals Eqn. of State!