Real gases

Compressibility

- The compressibility of a gas is defined by

$$Z = \frac{pV_m}{RT}$$

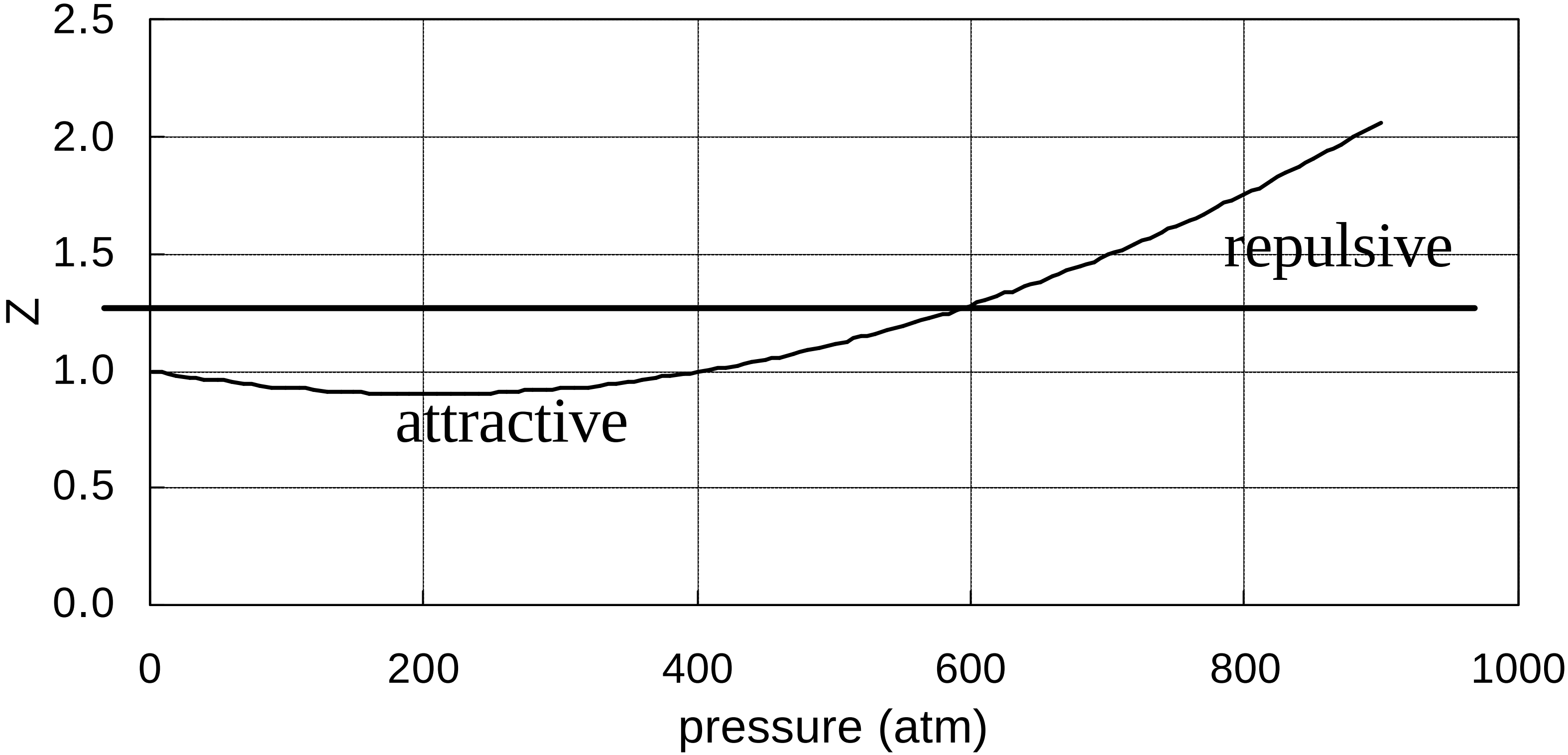
$V_m = V/n$ = molar volume

- If the gas behaves ideally, then Z=1 at all pressures and temperatures.
- For real gases, however, Z varies with pressure, and deviates from its ideal value

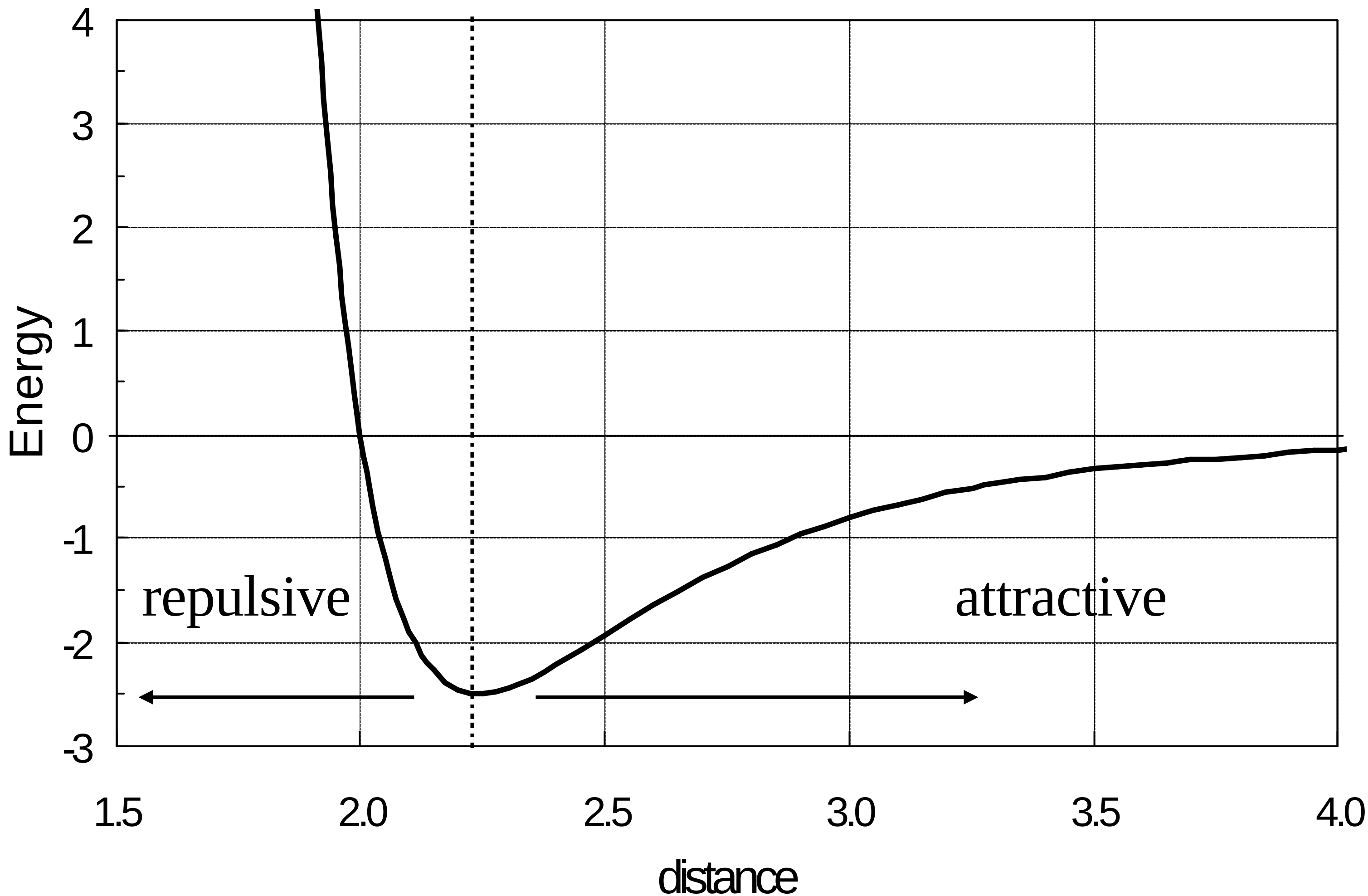
Argon Compressibility

273 K

$$Z = pV_m/RT$$

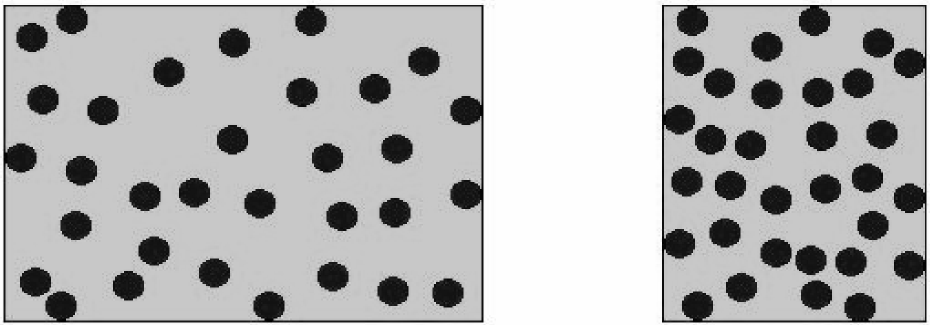


Intermolecular Forces

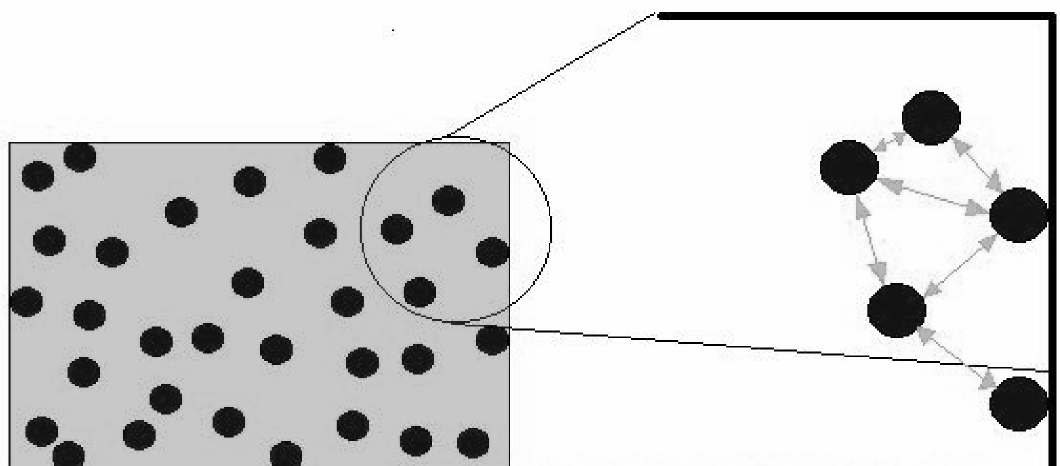


$V_{eff} = V_{meas} - nb$

Light blue represents the V_{eff}



At low pressure, the effective volume of the container and the measured volume are almost the same because $V_{meas} - nb \simeq V_{meas}$. At high pressures, the volume of the molecules themselves becomes a significant fraction of the measured volume so the effective volume is less than the measured volume.



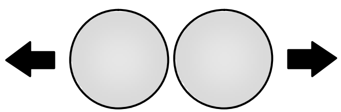
Intermolecular forces serve to lessen the velocity of impact of a particle striking the surface, thus lowering the observed pressure.

van der Waals Equation

$$\boxed{p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}}$$

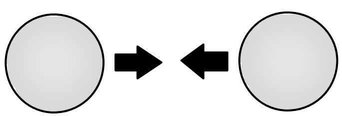
van der Waals Equation

$$\left(p + a / V_m^2\right)\left(V_m - b\right) = nRT$$



$$V_{m,eff} = V_m - b$$

repulsion



$$p_{eff} = p + a / V_m^2$$

attraction

van der Waals Equation of State:

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

Redlich-Kwong Equation of State:

$$\left[[P + \frac{n^2 a}{T^{1/2} V (V + nb)}\right](V - nb) = nRT$$

Virial Equation of State:

$$P = \frac{nRT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2} + \ldots\right)$$

van der Waals constants

	a (dm^6 atm mole^{-1})	b (dm mole^{-1})
He	0.034	0.0237
Ar	1.345	0.0322
N_2	1.390	0.0391
O_2	1.360	0.0318
CO_2	3.592	0.0427

Successive Approximation

$$V_m = \frac{RT}{p + \frac{a}{V_m^2}} + b$$

- "Solve" the *van der Waals equation* for V.
- Use an intial estimate to evaluate the right hand side.
- Use this *calculated* value of V as a better estimate.
- Repeat till converged.

Parameter "b" in vdW equation can be viewed as **"excluded" volume** in a gas sample due to the presence of molecules. It is "excluded" in a sense that in the presence of one molecule another molecule cannot move. The effective volume of one molecule is

$$\frac{4}{3}pr^3$$

where ***r*** is the radius of the molecule if we can treat it as a sphere.
The volume in which a pair of molecules cannot move because of each other's presence has radius of molecular diameter **d** = 2***r*.** Thus

Excluded volume per molecule = $\frac{1}{2}(\frac{4}{3}pd^3) = \frac{1}{2}[\frac{4}{3}(2r)^3] = 4(\frac{4}{3}pr^3)$

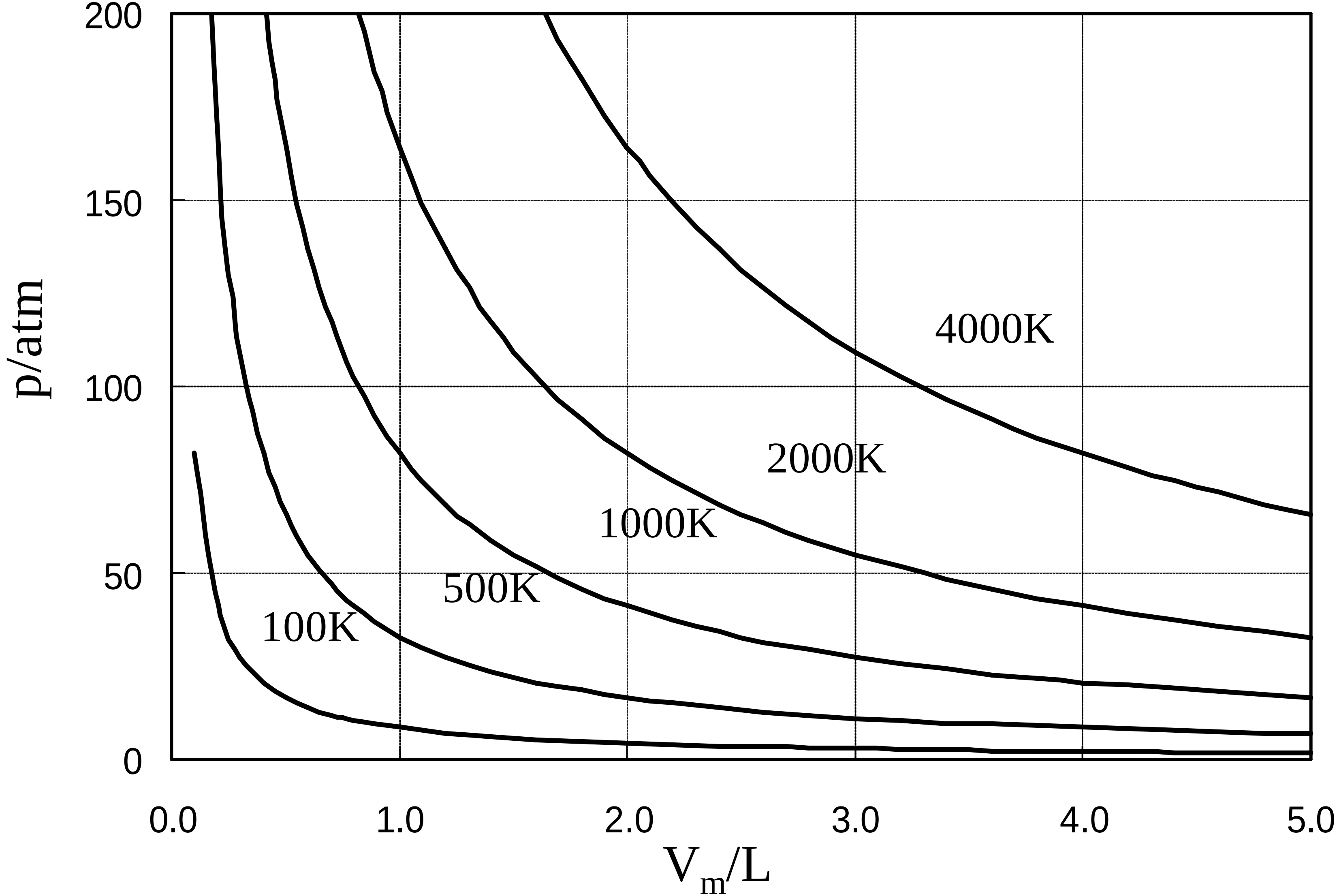
Thus the excluded volume per molecule is 4 times the actual volume of the molecule.

The "b" term is the excluded volume per mole of molecules. Therefore

$$\mathbf{b = 4´ N_A ´ (}\frac{4}{3}pr^3\mathbf{)}$$

and, knowing the value of b, one can estimate the radius of atom or molecule

Ideal Gas Isotherms



van der Waals Isotherms - Ar