van der Waals Isotherms near $T_c$

$v d W$ "loops" are not physical. Why?

Patch up with Maxwell construction

van der Waals Isotherms, $T/T_c$
van der Waals Isotherms near $T_c$

Look at one of the van der Waals isotherms at a temperature of 0.9 $T_c$

• A $\rightarrow$ D compress the gas at constant $T$,
• F $\rightarrow$ G compress the liquid phase (steep and not very compressible)
• D $\rightarrow$ F vapor condensing (gas and liquid coexist)
These are stable states

F $\rightarrow$ C supercooled liquid
D $\rightarrow$ B superheated gas
These are metastable states

C $\rightarrow$ B a non-physical artifact of vdW (patched up with Maxwell construction)

Metastable example:
Use a very clean glass. Add water and heat for a while with a microwave oven (superheat) Add a drop of sand or perhaps touch with a spoon.
van der Waals EoS

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

* Condensation

* Supercritical Fluid

Fluid with \( T > T_c \), \( P > P_c \)

We can use vdw EoS to approximate features. E.g.,

\[
P_c = \frac{a}{27b^2}
\]

\[
V_c = 3bn
\]

\[
T_c = \frac{8a}{27bR}
\]
Critical Constants of Real Gases

<table>
<thead>
<tr>
<th></th>
<th>$p_c$/atm</th>
<th>$V_c$/cm$^3$ mol$^{-1}$</th>
<th>$T_c$/K</th>
<th>$Z_c$</th>
<th>$T_B$/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>48.0</td>
<td>75.3</td>
<td>150.7</td>
<td>0.292</td>
<td>411.5</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>72.9</td>
<td>94.0</td>
<td>304.2</td>
<td>0.274</td>
<td>714.8</td>
</tr>
<tr>
<td>He</td>
<td>2.26</td>
<td>57.8</td>
<td>5.2</td>
<td>0.305</td>
<td>22.64</td>
</tr>
<tr>
<td>O$_2$</td>
<td>50.14</td>
<td>78.0</td>
<td>154.8</td>
<td>0.308</td>
<td>405.9</td>
</tr>
</tbody>
</table>

Notice that $Z_c$ is essentially 0.3 for all gases, while the other critical properties can be very different from each other. There is a lesson to learn here.

We might think about looking at $T$ and $P$ in terms of reduced parameters: $P_r = P/P_c$ and $V_r = V/V_c$.
Critical Constants of Real Gases

\[ T_r = \frac{T}{T_c} \]
Next Steps . . .

We have not invoked any molecular properties. It is as though the various gases were just different, structureless fluids. We will now change that!
Kinetic Theory of Gases

- Everything up to this point has been empirical
  - There is clearly a great deal of truth in the equations
  - However, there is no physical picture
- To gain insight, one must develop and validate models
- We look at a molecular (kinetic theory of gases) model to begin that process.
- We begin that process today
HCl and NH₃ gases at the same temperature and pressure are introduced at opposite ends of a glass tube. A ring of solid NH₄Cl forms where the two gases meet inside the tube.

\[ \text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl} \]

Where will the ring form?

A. At the center  
B. Closer to the HCl end  
C. Closer to the NH₃ end
Three Postulates of Kinetic Theory of Gases

1. Gas composed of hard spherical particles that are small relative to the mean distances between them.

2. Particles are in constant motion and have kinetic energy.

3. Neither attractive nor repulsive forces exist between the particles except on contact (collision).
ConcepTest #2

Which of the following gases deviates most from the postulates of kinetic molecular theory? (i.e., deviates most from ideal gas behavior)

A. He  
B. H₂  
C. N₂  
D. NH₃  
E. CH₄
Kinetic-Molecular Theory

Consistent with Ideal Gas Law, Dalton’s Law, Graham’s Law and many other observations
Consider a molecule colliding elastically with a wall.

- Velocity, $v_x$
- X-coordinate
- Velocity, $-v_x$
Relationship between Force and Change of Momentum

Momentum, \( p = mv \)

\[ F = ma = m \frac{dv}{dt} = d(mv)dt = dp/dt \]

What is change of velocity on each collision?

\[ \Delta v = v_{\text{final}} - v_{\text{initial}} = v_x - (-v_x) = 2v_x \]

What is change of momentum on each collision?

\[ \Delta p = 2v_x m \]
Collision rate for one molecule with a wall

Number of collisions in time $\Delta t = \frac{v_x \Delta t}{2x}$

Number of collisions per unit time $= \frac{v_x}{2x}$
Force (momentum change) per Unit Time for One Particle

\[ F = ma = \frac{dp}{dt} = (\text{Change of Momentum per Collision}) \times (\text{Number of Collisions per Unit Time}) \]

\[ \frac{dp}{dt} = F_x = (2v_x m) \left( \frac{v_x}{2x} \right) = \frac{mv_x^2}{x} \]

This is the force exerted on the wall by one particle.
Pressure is Force per Unit Area

\[ P_x = \frac{F_w}{A} = \frac{F_x}{yz} \]

\[ F_x = (2v_x m) \left( \frac{v_x}{2x} \right) = \frac{mv_x^2}{x} \]

\[ P_x = \frac{mv_x^2}{xyz} \]

\[ P_x = \frac{mv_x^2}{V} \]
What changes are required when $N$ molecules and a distribution of velocities are considered?

Multiply by $N$

Replace $v_x^2$ with $\langle v_x^2 \rangle$

$P_x = P_y = P_z = P$ implies

$v_x^2 = v_y^2 = v_z^2 = \frac{\langle v^2 \rangle}{3}$

and

$P_x = m\langle v_x^2 \rangle / V \rightarrow P = Nm\langle v^2 \rangle / 3V$
Fundamental Equation from Simple Kinetic Theory of Gases

\[ PV = Nm \langle v^2 \rangle / 3 \]

Parallels the ideal gas law:

\[ PV = nRT \]

\[ nRT = \frac{Nm \langle v^2 \rangle}{3} \]

\[ \langle v^2 \rangle = \frac{3nRT}{Nm} = \frac{3RT}{M} \]

\[ \sqrt{\langle v^2 \rangle} = v_{rms} = \sqrt{\frac{3RT}{M}} \]

with \( M \) (molar mass) = \( mN / n \)
ConcepTest #3

At a given temperature, which of the following gases has the smallest $v_{rms}$?

A. He
B. $H_2$
C. $N_2$
D. $NH_3$
E. $CH_4$
At a given temperature, which of the following gases has the smallest $v_{rms}$?

A. He
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E. $CH_4$
Connection between Kinetic Energy & Temperature

Average Kinetic Energy per Molecule

\[ \langle \mathcal{E} \rangle = \frac{1}{2} m \langle v^2 \rangle \]

Substitute this expression into the pressure equation to obtain the relationship between kinetic energy and T:

\[ E_k = \frac{3}{2} RT \quad \text{(per mole)} \]
Flask A contains 8 g H₂, and Flask B contains 8 g He. The flasks have the same volume and temperature. Compare the gas density (g/cm³), the kinetic energy per mole, and the total kinetic energy of the gases in the two flasks.

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<td>A&gt;B</td>
<td>A=B</td>
</tr>
<tr>
<td>C.</td>
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