VAN DER WAALS EQUATION IN REDUCED FORM

Statement

We intend to make use of van der Waals equation of state as a corresponding state model (i.e. with the constants deduced from critical point data and not from a general fitting). One wants:

a) Compute a, b and R as a function of T_{cr}, p_{cr} and v_{cr}.

b) Compute a, b and v_{cr} as a function of T_{cr}, p_{cr} and R. This is best because R thence corresponds to the ideal gas model and because v_{cr} has great experimental uncertainty.

c) Express the compressibility factor as a function of reduced variables.

d) Express the reduced pressure as a function of other reduced variables.

e) Loci of horizontal points of the isotherms in the Z-p diagram, and Boyle temperature.

f) Inversion curve and inversion temperature.

🇪🇸Se va a hacer uso de la ecuación de van der Waals con las constantes determinadas a partir de las condiciones en el punto crítico, en lugar de por ajuste en una zona más amplia. Se pide:

a) Calcular a, b y R en función de T_{cr}, p_{cr} y v_{cr}.

b) Calcular a, b y v_{cr} en función de T_{cr}, p_{cr} y R. Esto es mejor porque así la R corresponde a la de los gases ideales y porque la v_{cr} tiene gran incertidumbre experimental.

c) Expresión del factor de compresibilidad en función de las magnitudes reducidas.

d) Expresar la presión reducida en función de las otras magnitudes reducidas.

e) Puntos en los que las isotermas son horizontales en el diagrama Z-p y temperatura de Boyle, temperatura de Boyle y comparación con la del diagrama generalizado de compresibilidad.

f) Curva de inversión y temperatura de inversión, y comparación con la del diagrama generalizado de compresibilidad.

Solution.

a) Compute a, b and R as a function of T_{cr}, p_{cr} and v_{cr}.

Van der Waals equation of state is (4.33): $\left(p+\dfrac{a}{v^2}\right)(v-b)=RT$, or $p=\dfrac{RT}{v-b}-\dfrac{a}{v^2}$, or, with

$Z\equiv pv/(RT)$, $Z=\dfrac{v}{v-b}-\dfrac{a}{vRT}$, and may be viewed as a p-v-T relation with 3 constants $\{a,b,R\}$.

The aim here is to find out the constants from critical point data $\{T_{cr},p_{cr},v_{cr}\}$ instead of from experimental fitting to other data points. The constrains to be imposed are that, at the critical point, the maxima and minima in the isotherms in the $p(v)$-diagram coincide, i.e. the critical point must be an inflexion point in the isotherms:

$$\left\{ p_{cr}\left(v_{cr},T_{cr}\right)=\frac{RT_{cr}}{v_{cr}-b}-\frac{a}{v_{cr}^2},\ \left.\frac{\partial p_{cr}\left(v_{cr},T_{cr}\right)}{\partial v_{cr}}\right|_{T_{cr}}=0,\ \left.\frac{\partial^2 p_{cr}\left(v_{cr},T_{cr}\right)}{\partial v_{cr}^2}\right|_{T_{cr}}=0 \right\}$$

Solving these 3 equations for the 3 unknowns one gets: $\{ a = 3 p_{cr} v_{cr}^2, b = \dfrac{1}{3} v_{cr}, R = \dfrac{8}{3} \dfrac{p_{cr} v_{cr}}{T_{cr}} \}$.

But that procedure has a handicap: we know that R is not 'another constant' like a and b, but the universal gas constant if v is the molar volume, or the universal gas constant divided by the molar mass of the particular substance if v is the specific volume.

b)   Compute a, b and v_{cr} as a function of T_{cr}, p_{cr} and R. This is best because R thence corresponds to the ideal gas model and because v_{cr} has great experimental uncertainty.

The problem now is to solve the same 3 equations at the critical point, but in terms of the new tern $\{T_{cr}, p_{cr}, R\}$; the result is: $\{ a = \dfrac{27}{64} \dfrac{R^2 T_{cr}^2}{p_{cr}}, b = \dfrac{1}{8} \dfrac{R T_{cr}}{p_{cr}}, v_{cr} = \dfrac{3}{8} \dfrac{R T_{cr}}{p_{cr}} \}$.

c)   Express the compressibility factor as a function of reduced variables.

Reduced variables are defined as: $T_R \equiv \dfrac{T}{T_{cr}}$, $p_R \equiv \dfrac{p}{p_{cr}}$ and $v_R \equiv \dfrac{v}{v_{cr}}$. Substituting $\{T=T_R T_{cr}, p=p_R p_{cr}, v=v_R v_{cr}\}$ in $Z=v/(v-b)-a/(vRT)$ and the last values for $a(T_{cr},p_{cr},R)$ and $b(T_{cr},p_{cr},R)$, yields $Z = \dfrac{1}{1 - \dfrac{1}{3 v_R}} - \dfrac{9}{8} \dfrac{1}{v_R T_R}$.

Notice that with this fitting of the van der Waals model to the critical point data, the value of the compressibility factor Z at the critical point is $Z=3/8=0.38$, well aside of real experimental data for typical substances: $Z_{cr}(H_2O)=0.23$, $Z_{cr}(NH_3$, alcohols and cetones$)=0.24..0.26$, $Z_{cr}(hydrocarbons)=0.26..0.28$, $Z_{cr}(permanent\ gases)=0.28..0.30$.

d)   Express the reduced pressure as a function of other reduced variables.

Substituting $\{T=T_R T_{cr}, p=p_R p_{cr}, v=v_R v_{cr}\}$ in $Z=pv/(RT)$ and with $Z_{cr}=p_{cr}v_{cr}/(RT_{cr})=3/8$, one may get by elimination: $p_R = \dfrac{Z T_R}{Z_{cr} v_R} = \dfrac{8 T_R}{3 v_R - 1} - \dfrac{3}{v_R^2}$.

It is instructive to plot some isotherms with this model, both in the p_R-v_R and the Z-p_R diagram, as done in Fig. 1, particularly near the critical isotherm (T_R=1).
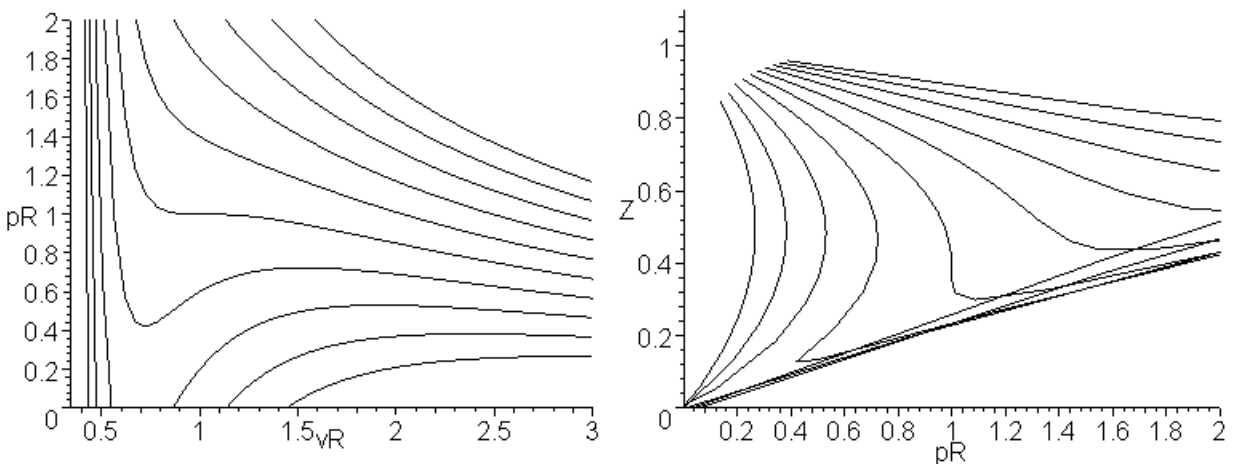

Fig. 1. Reduced van der Waals isotherms.

e) Loci of horizontal points of the isotherms in the Z-p diagram, and Boyle temperature.

The points wanted must satisfy $\partial Z/\partial p_R|_{T_R}=0$, or:

$$0=\left.\frac{\partial Z}{\partial p_R}\right|_{T_R}=\frac{\left.\dfrac{\partial Z}{\partial v_R}\right|_{T_R}}{\left.\dfrac{\partial p_R}{\partial v_R}\right|_{T_R}} \Rightarrow 0=\left.\frac{\partial Z}{\partial v_R}\right|_{T_R}=\frac{\dfrac{1}{3v_R^2}}{\left(1-\dfrac{1}{3v_R}\right)^2}+\frac{9}{8}\frac{1}{v_R^2 T_R} \Rightarrow T_R=\frac{27}{8}-\frac{9}{4v_R}+\frac{3}{8v_R^2}$$

that tends to $T_R=27/8=3.4$ for $v_R\to\infty$ ($p_R\to0$), a limit known as Boyle's temperature, which is the isotherm horizontally approaching the ideal-gas point, $Z=1$ as $p_R\to0$, i.e. the temperature at which compressibility corrections are negligible up to high-pressure values (i.e. the temperature at which the ideal gas behaviour extends the most at large pressures).

f) Inversion curve and inversion temperature.

The inversion curve separates the regions of positive and negative Joule-Kelvin's coefficient (4.27), i.e. it is the loci of points with $\mu=0$, so that:

$$\mu_{JK}\equiv\left.\frac{\partial T}{\partial p}\right|_h=\frac{-(1-\alpha T)v}{c_p}=0\Rightarrow\alpha=\frac{1}{T}\Rightarrow\frac{1}{v}\left.\frac{\partial v}{\partial T}\right|_p=\frac{1}{T}\Rightarrow\left.\frac{\partial\ln v}{\partial\ln T}\right|_p=1$$

that, with $\ln Z=\ln p+\ln v-\ln R-\ln T$, yields:

$$0=\left.\frac{\partial Z}{\partial T_R}\right|_{p_R}=\left.\frac{\partial Z}{\partial T_R}\right|_{v_R}+\left.\frac{\partial Z}{\partial v_R}\right|_{T_R}\left.\frac{\partial v_R}{\partial T_R}\right|_{p_R}=\left.\frac{\partial Z}{\partial T_R}\right|_{v_R}+\left.\frac{\partial Z}{\partial v_R}\right|_{T_R}\left(-\frac{\left.\dfrac{\partial p_R}{\partial T_R}\right|_{v_R}}{\left.\dfrac{\partial p_R}{\partial v_R}\right|_{T_R}}\right)$$

all terms now explicit with the above-developed functions $Z(T_R,v_R)$ and $p_R(T_R,v_R)$, what finally yields the series:

$$T_{R,inv}=\frac{27}{4}\left(1-\frac{2}{3v_R}-\frac{1}{9v_R^2}\right)$$

The inversion temperature is the particular value when the inversion curve approaches the ideal gas behaviour, i.e. when $v_R\to\infty$ ($p_R\to0$), resulting in $T_{R,inv}=27/4=6.75$. The inversion curve is usually plot in a p-T diagram, what can easily be done here in parametrics with the last expression and $p_R(T_R,v_R)$, as presented in Fig. 2.
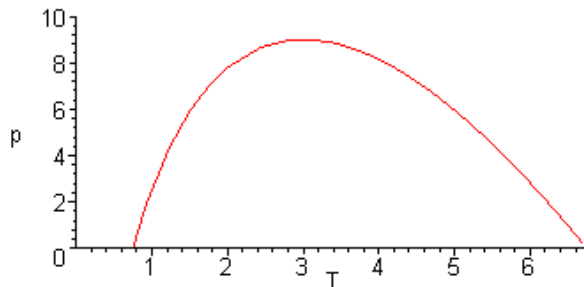

Fig. 2. Inversion curve for van der Waals model fitted to the critical point.

Comments. As said above, this model shows large numerical discrepancies with experimental data, but it is simple enough to allow most thermodynamic functions to be explicitly worked out, being instructive for most accurate models that cannot be so easily grasped.

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