Documentation for e-module
Virial expansion

Christian Freier

27th November 2007

Technische Universität Berlin
Institut für Theoretische Physik

Abstract

This documentation is a manual for a Mathematica Demonstration Notebook which visualizes the viral expansion of the real gas law. The expansion implements term to the sixth order and it is possible to change the temperature in the phase diagram. This applet has been created within the OWL Project *e-Module for Visualisations of Theoretical Physics.* [1]

---

[1] Translated to English by Philipp Loske 19.03.2014

Contents

About us

Institute for Theoretical Physics
Hardenbergstr. 36, Sekr. EW7-1
10623 Berlin

Project: *Offensive Wissen durch Lernen*
(*Knowledge through Learning*)
e-Module for Visualisations of Theoretical Physics
Head of project: Prof. Dr. Eckehard Schöll, PhD
Contact: owl@itp.physik.tu-berlin.de

1 Introduction

To calculate the thermal equation of state for a real gas it is often necessary to use a power series in the density. This expansion is called viral expansion. With the first two terms of the power series with an approximation of the viral equation of state, it is possible to derive the Van der Waals equation for real gases. This Notebook uses viral coefficients of water to the sixth order from a paper published in 2007. Those viral coefficients have been calculated numerically. For this Mathematica Notebook the numbers are used for the TIP4P water model. For further information about different water models have a look at reference 5 for example.
Nowadays higher viral coefficients are mostly used in the following areas:

- Prognosis and test of intermolecular potentials. It is possible to examine the viral coefficients from those potentials and to compare them to experimental outcomes.
- To determine material parameters for empiric equation of state
- To describe the behaviour of PVT of substances in the super critical phase and their critical properties
- Prognosis of the Joule Thomsen coefficients

2 Manual for the Demonstration Notebook

2.1 How to download and install the Mathematica Player

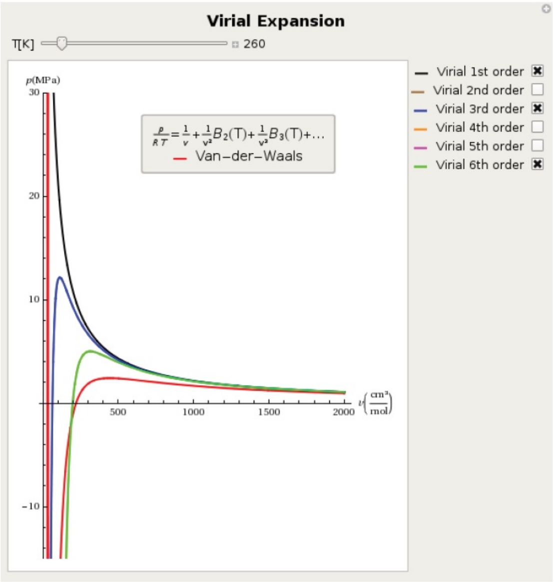
To use the *Demonstration Notebook*, it is necessary to install the free Mathematica Player. It can be downloaded from

- Mathematica Player (`http://www.wolfram.com/products/player/`)

After installing and starting the Mathematica Player, it is possible to open the file *Demonstration Notebook therm_statistics_plot_deutsch.nbp.*

2.2 Control elements

Handling the *Demonstration Notebook* is simple and self-evident. When opening the Mathematica Player, the main interface opens below the heading. Under the interface is a short description with information about the physical content of the Notebook in German.
In the upper part of the interface is a slider $T[K]$ to change the temperature for the equation of states. On the right side of the plot panel are six check boxes for the initial six therms of the viral expansion. The activated boxes are plotted in the plot panel.



T[K] 260

- Virial 1st order ☒
- Virial 2nd order ☐
- Virial 3rd order ☒
- Virial 4th order ☐
- Virial 5th order ☐
- Virial 6th order ☒

Figure 1: Main interface of the Notebook.

After starting the applet the plot panel shows the Van der Waals equation in red and the ideal gas law in black, which correlate with the first term of the viral expansion. In addition to that the panel shows the third order of the equation in blue and the sixth order in green. The temperature is far below the critical temperature $T_C = 647,3K$ of water, so the Van der Waals equation has a distinct maximum and minimum.

3 Theory

This chapter wants to give a brief introduction to the basics of the viral expansion and the results of the initial viral coefficients.

3.1 Viral expansion of the ideal gas law

The viral expansion is a power series of the thermal equation of state in the density $\frac{1}{v}$, with the volume v. For molar state variables the equation is:

$$\frac{p}{RT} = \frac{1}{v} + \frac{1}{v^2}B_2(T) + \frac{1}{v^3}B_3(T) + \frac{1}{v^4}B_4(T) + \frac{1}{v^5}B_5(T) + \frac{1}{v^6}B_6(T) + \ldots \qquad (1)$$

With the temperature T, the universal gas constant R and pressure p. $B_i(T)$ is the i-th viral coefficient and is directly related to the interaction with i molecule in the gas. Accordingly the initial term in equation (1) is contributed by the ideal gas and

describes gas particles without interaction with other molecules. Therms of higher order describe the interaction with other molecules which take place in non ideal gases. $B_2(T)$ represents the interaction of two gas particles, $B_3(T)$ of three particles and so on.
To find the viral expansion, the equation to start with are the relations for pressure p and medial number of particles $\overline{N}$

$$\frac{pV}{kT} = \ln(\Xi) \tag{2}$$

$$\overline{N} = \frac{1}{\beta}\left(\frac{d\ln(\Xi)}{d\mu}\right)_{\beta,V} \tag{3}$$

Ξ is the grand canonical partition function, μ the chemical potential and $\beta = \frac{1}{kT}$.
The viral expansion results, if equations (2) and (3) are expanded in one parameter, f.e. the fugacity $\xi = e^{\beta\mu}$. After the expansion the parameter is eliminated in between the two equations. The result is a power series in the density $\frac{1}{v}$ or pressure p as an independent parameter. In the following part of this chapter we will have a closer look at a power series in the pressure with the density as an independent parameter.
A more complex derivation of the viral coefficients is explained in reference (3). Reference (2) concentrates specifically on the second viral coefficient. In the following the results up to the fourth term of the viral expansion for a gas without internal degrees of freedom are presented briefly.
For a more abbreviated form the Mayer functions are defined as:

$$f_{ij} = e^{-\beta u(r_{ij})} - 1$$

$u(r_{ij}$ is the interaction potential between particle i and j. The second viral coefficient results to:

$$B_2(T) = -\frac{1}{N_A}\int_V d\vec{r}_{12} f_{12} = -\frac{1}{N_A} \tag{4}$$

To get to the third viral coefficient it is necessary to use the potential $U_3 = U(\vec{r}_{12}, \vec{r}_{23}, \vec{r}_{13})$ in between three interactive particles. Generally this potential can be spit into an additive and a non additive part:

$$U_3 = u(\vec{r}_{12}) + u(\vec{r}_{23}) + u(\vec{r}_{13}) + \Delta u(\vec{r}_{12}, \vec{r}_{23}, \vec{r}_{13}) =: u_{12} + u_{23} + u_{13} + \Delta u_3$$

The additive and non additive component both contribute to $B_3(T)$:

$$
\begin{aligned}
B_3(T) &= B_{3add}(T) + \Delta B_3(T) && (5)\\
B_{3add}(T) &= -\frac{N_A^2}{3V}\int_V d\vec{r}_{12} d\vec{r}_{23} d\vec{r}_{13} f_{12} f_{23} f_{13} = -\frac{N_A^2}{3V} && (6)\\
\Delta B_3(T) &= -\frac{N_A^2}{3V}\int_V d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 \left[e^{-\frac{\Delta u_3}{kT}} - 1\right] e^{-\frac{u_{12}+u_{23}+u_{31}}{kT}} && (7)
\end{aligned}
$$

For atoms and molecules without free valence electrons the non additive part is small compared to the additive term. For atoms with free valence electrons this is not necessarily true. For example, a H-atom attracts another H-atom to become H_2 but a third H-atom will not be attracted.
For the fourth term of the viral expansion the same method is used. The potential results to:

$$
U_4 = u_{12} + u_{23} + u_{34} + u_{14} + u_{13} + u_{24} + \Delta u_4
$$

The fourth term of the viral expansion results to:

$$
\begin{aligned}
B_4(T) &= B_{4add}(T) + \Delta B_4(T) && (8)\\
B_{4add}(T) &= -\frac{N_A^3}{8V}\int_V d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 f_{12} f_{23} f_{34} f_{41} (3 + 6 f_{13} + f_{12} f_{24}) && (9)\\
&= -\frac{N_A^3}{8V} && (10)\\
\Delta B_4(T) &= -\frac{N_A^3}{8V}\int_V d\vec{r}_1 d\vec{r}_2 d\vec{r}_3 d\vec{r}_4 \cdot \\
&\left[\left(e^{\frac{\Delta}{kT}} - 1\right) e^{-\frac{u_{14}+u_{24}+u_{34}}{kT}} - 4\left(e^{\frac{\Delta u_3}{kT}} - 1\right)\left(e^{\frac{\Delta u_{14}}{kT}} - 2\right)\right] e^{-\frac{u_{12}+u_{23}+u_{31}}{kT}} && (11)
\end{aligned}
$$

4 Programme

The Demonstration Note has been written with Mathematica 6. It was created with the Wolfram Demonstration Project. For more information about the Wolfram Demonstration Project visit the website under
(`http://demonstrations.wolfram.com/`).
The source code is saved in the Demonstration Notebook and opening the Input line in the interface makes the source code visible. Therefore double-click on the black vertical line next to the interface. The source code is added at the end of this document, too.

4.1 Programme structure

With Mathematica version 6.0 or higher it is possible to change the source code. Mathematica 6.0 is available in the PC-pool at the physic department of the TU. The Demonstration Notebook's main tool is a “manipulate” command with the possibility to add plots. For further information have a look at the manual of Mathematica.

4.1.1 numerical calculation of viral coefficients

For simple potentials like the hard ball potential or the rectangle potential numerical viral coefficients have been calculated up to the tenth order. For f.e. water these potentials are not very realistic because of the polarity in between the molecules. In the paper (see reference [4]) the viral coefficients have been calculated up to the sixth order for different models (see reference [5]). Those calculation gives a more accurate simulation for the interaction in between water molecules. The viral coefficients have been taken from table 6 from reference [4] for different temperatures. In between those temperatures the viral coefficients have been interpolated.

4.2 Source Code

```
Manipulate[Plot[{vdw[v, T], If[O1, p0[v, T]], If[O2, p1[v, T]],
   If[O3, p2[v, T]], If[O4, p[v, T]], If[O5, p3[v, T]], If[O6, p4[v, T]]},
  {v, 22, 2000}, ImageSize → 400, AxesLabel → {v[cm³/mol], p[MPa]}, AspectRatio → 1.5,
  PlotRange → {-15, 30}, PlotStyle → {{Red, Thick}, {Black, Thick}, {Brown, Thick},
    {Blue, Thick}, {Orange, Thick}, {Magenta, Thick}, {Green, Thick}},
  Prolog →
   Inset[
    Panel[Grid[{{Style["p/(R T) = 1/v + 1/v² B₂(T) + 1/v³ B₃(T) + ...", 14]},
       {Grid[{{Graphics[{Red, Thick, Line[{{0, 0}, {1, 0}}]}, ImageSize → 15,
            AspectRatio → .1], Style["Van-der-Waals", 14]}}]}}]
     ], {1300, 25}]],


 {{T, 260, Style["T[K]", 12]}, 210, 750, Appearance → "Labeled"},
 {{O1, True,
   Grid[{{Graphics[{Black, Thick, Line[{{0, 0}, {1, 0}}]}, ImageSize → 15, AspectRatio → .1],
      Style["Virial 1st order"]}}]}, {True, False}},
 {{O2, False, Grid[{{Graphics[{Brown, Thick, Line[{{0, 0}, {1, 0}}]}, ImageSize → 15,
       AspectRatio → .1], Style["Virial 2nd order"]}}]}, {True, False}},
 {{O3, True, Grid[{{Graphics[{Blue, Thick, Line[{{0, 0}, {1, 0}}]}, ImageSize → 15,
       AspectRatio → .1], Style["Virial 3rd order"]}}]}, {True, False}},
 {{O4, False, Grid[{{Graphics[{Orange, Thick, Line[{{0, 0}, {1, 0}}]}, ImageSize → 15,
       AspectRatio → .1], Style["Virial 4th order"]}}]}, {True, False}},
 {{O5, False, Grid[{{Graphics[{Magenta, Thick, Line[{{0, 0}, {1, 0}}]}, ImageSize → 15,
       AspectRatio → .1], Style["Virial 5th order"]}}]}, {True, False}},
 {{O6, True, Grid[{{Graphics[{Green, Thick, Line[{{0, 0}, {1, 0}}]}, ImageSize → 15,
       AspectRatio → .1], Style["Virial 6th order"]}}]}, {True, False}},
 ControlPlacement → {Top, Right, Right, Right, Right, Right, Right},

 FrameLabel → {"", "", Style["Virial Expansion", {16, Bold}], ""},

 Initialization :→
  (B2list = {{210, -92.76}, {230, -34.11}, {250, -15.14}, {270, -7.738}, {290, -4.438},

     {298, -3.639}, {350, -1.315}, {370, -0.9752}, {390, -0.7483}, {410, -0.592},
     {430, -0.4797}, {450, -0.3961}, {470, -0.3328}, {490, -0.2832},
     {510, -0.2443}, {530, -0.2124}, {550, -0.1865}, {570, -0.1647},
     {590, -0.1467}, {610, -0.1313}, {630, -0.1178}, {650, -0.1065}, {670, -0.0962},
     {690, -0.0877}, {710, -0.0797}, {730, -0.0728}, {750, -0.0668}};
   B2 = Interpolation[B2list, InterpolationOrder → 1];
   B3list = {{210, -1.058 10^6}, {230, -5.97 10^4}, {250, -5.85 10^3},
     {270, -888}, {290, -173}, {298, -93}, {350, -4.06}, {370, -1.52},
     {390, -0.605}, {410, -0.2467}, {430, -0.0981}, {450, -0.0341}, {470, -0.00628},
     {490, 0.00589}, {510, 0.01067}, {530, 0.01211}, {550, 0.01199}, {570, 0.01126},
     {590, 0.01025}, {610, 0.0092}, {630, 0.00819}, {650, 0.00728}, {670, 0.006467},
     {690, 0.005749}, {710, 0.005123}, {730, 0.004573}, {750, 0.004098}};
   B3 = Interpolation[B3list, InterpolationOrder → 1];
   B4list = {{210, -2.64 10^9}, {230, -4.16 10^8}, {250, -1.08 10^7},
     {270, -3.87 10^5}, {290, -2.32 10^4}, {298, -8.25 10^3}, {350, -32}, {390, -0.64},
     {410, -0.015}, {430, 0.0597}, {450, 0.0496}, {470, 0.0308}, {490, 0.0184},
     {510, 0.01096}, {530, 0.00644}, {550, 0.00382}, {570, 0.00226}, {590, 0.001326},
     {610, 0.000786}, {630, 0.000436}, {650, 0.000239}, {670, 0.000112},
     {690, 0.000039}, {710, -0.000039}, {730, -0.000031}, {750, -0.000047}};
   B4 = Interpolation[B4list, InterpolationOrder → 1];
   B5list = {{210, -3.76 10^9}, {250, -4.25 10^8}, {270, -1.54 10^7},
     {290, -1.96 10^5}, {298, 3.5 × 10^4}, {350, 170}, {370, 47}, {390, 3.1}, {410, 1.3},
     {430, 0.16}, {450, 0.051}, {470, 0.009}, {490, 0.00016}, {510, -0.00155},
     {530, -0.00149}, {550, -0.00110}, {570, -0.00073}, {590, -0.000514},
```

```
  {610, -0.000337}, {630, -0.000229}, {650, -0.000154}, {670, -0.000105},
  {690, -0.0000723}, {710, -0.0000499}, {730, -0.0000357}, {750, -0.0000256}};
B5 = Interpolation[B5list, InterpolationOrder → 1];
B6list = {{210, -2 10^5}, {250, -1.48 10^5}, {298, -4 10^5}, {350, 359}, {370, 12},
  {390, -1.33}, {430, -0.8}, {450, -0.264}, {470, -0.082}, {490, -0.00786},
  {510, -0.0021}, {530, -0.000586}, {550, -0.00018}, {570, -0.00004},
  {590, 0.000005}, {610, 0.000024}, {630, 0.000017}, {650, 0.000016}, {670, 0.000011},
  {690, 0.00001}, {710, 0.0000074}, {730, 0.000006}, {750, 0.000003}};
B6 = Interpolation[B6list, InterpolationOrder → 1];
```

$$\mathtt{p0[v\_, T\_] := R\,T\left(\frac{1}{v}\right);}$$

$$\mathtt{p[v\_, T\_] := R\,T\left(\frac{1}{v} + \frac{B2[T]}{v\char`^2} + \frac{B3[T]}{v\char`^3} + \frac{B4[T]}{v\char`^4}\right);}$$

$$\mathtt{p1[v\_, T\_] := R\,T\left(\frac{1}{v} + \frac{B2[T]}{v\char`^2}\right);}$$

$$\mathtt{p2[v\_, T\_] := R\,T\left(\frac{1}{v} + \frac{B2[T]}{v\char`^2} + \frac{B3[T]}{v\char`^3}\right);}$$

$$\mathtt{p3[v\_, T\_] := R\,T\left(\frac{1}{v} + \frac{B2[T]}{v\char`^2} + \frac{B3[T]}{v\char`^3} + \frac{B4[T]}{v\char`^4} + \frac{B5[T]}{v\char`^5}\right);}$$

$$\mathtt{p4[v\_, T\_] := R\,T\left(\frac{1}{v} + \frac{B2[T]}{v\char`^2} + \frac{B3[T]}{v\char`^3} + \frac{B4[T]}{v\char`^4} + \frac{B5[T]}{v\char`^5} + \frac{B6[T]}{v\char`^6}\right);}$$

```
R = 8.314472;
(*Van-der-Waals constants*)
aH2O = 553 600;
bH2O = 30.49;
(*Redlich-Kwong constants*)
cH2O = 21.123;
dH2O = 1.416 × 10^10;
```

$$\mathtt{vdw[v\_, T\_] := \frac{R\,T}{v - bH2O} - \frac{aH2O}{v\char`^2};}$$

$$\mathtt{rk[v\_, T\_] := \frac{R\,T}{v - cH2O} - \frac{dH2O}{v\;(v + cH2O)\,\sqrt{T}};\Big)\Big]}$$

References

[1] Friedrich Schlögl *Probability and Heat - Fundamentals of Thermostatistics*, Vieweg Verlag, 1989

[2] Prof. Dr. Eckehard Schoell *Skript zur Vorlesung Theoretische Physik IV: Thermodynamik und Statistik*

[3] E.A. Mason, T.H. Spurling *The Viral Equation of State*, Pergamon Pr, 1969

[4] Kenneth M. Benjamin, Jayant K. Singh, Andrew J.Schultz, and Divd A.Kofke, *J. Phys. Chem. B 2007, 111, 11463-11473 Higher-Order Viral Coefficients of Water Models*

[5] `http://en.wikipedia.org/wiki/Water_model`

[6] `http://en.wikipedia.org/wiki/Metropolisalgorithmus`