Worksheet 6
Phase transitions and solubilities

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January 9, 2014
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Important remarks

- You can access the ICP web page to download important materials via the username **icp** and the password **icp**.
- Due date: **Monday, January 20th, 2013, 12:00**
- You can either send a PDF file to Jens Smiatek (smiatek@icp.uni-stuttgart.de) or submit a hand-written copy.
- Please write your name on each page and make sure that the pages are easily readable.
- If you have further questions, contact Jens Smiatek (smiatek@icp.uni-stuttgart.de) or Stefan Kesselheim (Stefan.Kesselheim@icp.uni-stuttgart.de).
- The solutions will be discussed on Thursday, January 23rd, 2013 at 8:00.

1 Short questions - short answers (6 points)

Remember the food science lecture and have a look at the corresponding lecture notes. Please give precise and short answers to the questions.

1. What is the reason for the stability of the oil-water mixture? Describe the corresponding effect and explain the influence of surfactants.
2. What is the reason for the occurrence of the Aperol-caviar? Remember, a polyelectrolyte-aperol mixture and water with salt was used. Describe the physical mechanism.

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3. What is the reason that meat gets soft at higher cooking temperatures? What happens and what is the underlying biophysical effect?

2 Van-der-Waals gas - The principle of corresponding states

Consider the van-der-Waals equation

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \tag{1}$$

where p, R, T, V_m, a and b denote the pressure, the molar gas constant, the temperature, the molar volume and the van der Waals coefficients. A good starting point to read more about van der Waals gases is the textbook

- P. W. Atkins, *Physical Chemistry*, 6th edition, Oxford University Press, Oxford: UK (1998)

where most of the properties of the equation are discussed.

Task 1: Van-der-Waals isotherms (1 point)

Have a look at Fig. 1. What happens physically for temperatures $T \leq T_c$ where T_c is the critical temperature? Is there a physical reason for this effect?

Task 2: The principle of corresponding states (3 points)

For $T \leq T_c$ both a maximum and a minimum can be observed. For $T = T_c$ the extrema coincide. The expressions for the critical pressure, the critical molar volume as well as the critical temperature can be calculated by setting the first and the second derivative of Eqn. 1 to zero Please conduct this calculation and determine the values for the above mentioned state variables. Furthermore, the critical compression factor Z_c is given by

$$Z_c = \frac{p_c V_c}{RT_c} \tag{2}$$

where the values for the critical variables can be inserted. The critical compression factor Z_c is a unique feature for all van-der-Waals gases and can be used as a good test case for the comparison with real gases. Determine the numerical value for the compression factor. Please find or determine the values for Argon, CO_2, Helium, O_2, HCl and NH_3 and compare them to the predicted values. Is the van-der-Waals equation a good approximation? Where do deviations occur and what is the reason for that?

Task 3: Gibbs free energy of a van-der-Waals gas (3 points)

The Gibbs free energy is given by

$$G = F + pV \tag{3}$$

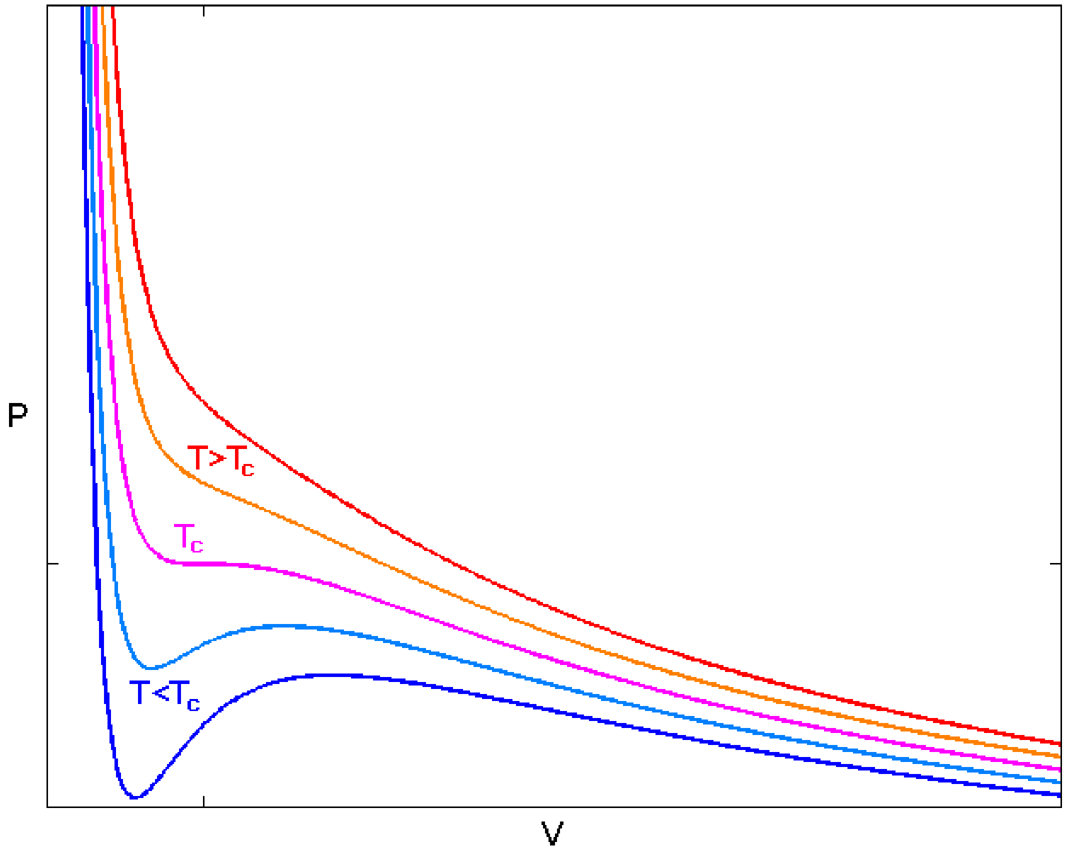

Figure 1: Van-der-Waals equation of states isotherms for different equations of states according to Eqn. 1 for different temperatures. Taken from en.wikipedia.org.

where F denotes the free energy. The Gibbs free energy is dependent on the temperature, the pressure and the particle number in terms of $G(T, p, N)$. Please first calculate the free energy for F(T,V,N) and transform it into G(T,p,N). Numerically calculate the values for G/RT_c vs. p/p_c for $T = T_c$ and $T = 0.95T_c$.
Hint: You may have a look at

- C. Kittel and H. Kroemer, *Thermal Physics*, 2nd edition, W. H. Freeman & Co., New York: USA (1980)

3 Solvent mixtures

Task 1: Expression for solubility (1 point)

Use regular solution theory to derive an approximate expression, valid in the limit of a large, positive value of the interaction parameter ξ, for the limit of solubility of one immiscible liquid in another.

Task 2: Limiting solubilities of hydrocarbons (3 points)

The value of ξ between water and linear hydrocarbons may be taken to be given by the formula $\xi = 3.04 + 1.37 n_C$, where n_C is the number of carbon atoms in the hydrocarbon. Use the formula derived in the last question to compare the limiting solubilities in water of hexane (C_6H_{14}), octane (C_8H_{18}) and decane ($C_{10}H_{22}$).

Task 3: Interfacial tension (3 points)

Estimate the interfacial tension between octane and water (have a look at the lecture notes for the corresponding equation). You may take the interaction parameter between octane and water as $\xi = 14.0$ and the molar volume as $V_m = 2.36 \times 10^{-29}$ m^3.