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Advanced Statistical Physics (WS11/12)
Problem sheet 10

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Problem 1: Virial Coefficient

a) Calculate the third virial coefficient a_3, where $P/k_BT \equiv \sum_{l=1} a_l (N/V)^l$. Use the definition of the Mayer function $f = e^{-\omega/(k_BT)} - 1$ and the inversion method of power series.

b) Calculate the second virial coefficient a_2 for a system of hard spheres with diameter d and the interacting potential

$$\omega(\vec{r}) = \begin{cases} \infty & \text{for } |\vec{r}| < d, \\ 0 & \text{otherwise.} \end{cases}$$

How could we calculate the third virial coefficient a_3? Over which geometry respectively volume has to be integrated?

Problem 2: Lennard-Jones Potential

The atom-atom interaction can be approximated by the *Lennard-Jones potential*:

$$w(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \tag{1}$$

where ϵ is the depth of the potential well and σ is the atom diamater.

a) Sketch the potential. Where is the potential zero and where is its minimum?

b) Calculate the second virial coefficient a_2. For $r < \sigma$ use the approximation $\exp(-\beta\, w) \approx 0$ and for $r > \sigma$ approximate up to the first order in $\beta = 1/(k_B\, T)$.

c) Use the virial coefficient to determine a and b in the van-der-Waals equation.

Problem 3: Critical Exponent

a) Rescale the van der Waals-Equation with $\bar{P} = P/P_c$, $\bar{V} = V/V_c$ and $\bar{T} = T/T_c$ to a form without the material constants a and b. (The critical values of the van der Waals-gas are $P_c = a/(27b^2)$, $V_c = 3bN$ and $k_BT_c = 8a/(27b)$.)

b) Show that the result of part a) can be transformed to $2\bar{p}(1 + 7\bar{v}/2 + 4\bar{v}^2 + 3\bar{v}^3/2) = -3\bar{v}^3 + 8\bar{\tau}(1 + 2\bar{v} + \bar{v}^2)$, where $\bar{p} = \bar{P} - 1$, $\bar{v} = \bar{V} - 1$, $\bar{\tau} = \bar{T} - 1$.

c) Use the result of part b) to calculate the critical exponent γ of the isothermal compressibility $\kappa_T(T) \propto |\bar{\tau}|^{-\gamma}$.

Problem 4: Heat Capacities of the van der Waals Gas

Calculate the specific heat capacities C_V and C_P of the van der Waals gas with f degrees of freedom for $V \neq V_C$, where V_C is the critical volume.