Problem set 3: Computational Molecular Physics and Methods of Molecular Simulations

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1. Isobaric-isothermal ensemble (15 points)

- Derive the isobaric-isothermal distribution function for a system with constant particle number N, constant pressure p and constant temperature T, coupled to a bath of constant volume and energy. Use the following relations

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} =: \frac{1}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_{T,\mu} =: \frac{p}{T} \tag{1}$$

- Derive an expression for the mean (expectation) value of the volume.

2. Grand-canonical ensemble (15 points)

- Derive the grand canonical distribution function for a system with constant volume V, heat exchange and particle exchange, coupled to a bath of constant energy, and particle number. Use the following relations

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} =: \frac{1}{T} \text{ and } \left(\frac{\partial S}{\partial N}\right)_{U,V} =: -\frac{\mu}{T} \tag{2}$$

- Derive an expression for the grand potential (Landau free energy)

$$\Phi = U - TS - \mu N \tag{3}$$

3. Markov-chains (15 points)

- Generate a Markov chain of length $N = 10, 100, 1000$ from the following transition matrices

$$P_1 = \begin{pmatrix} 1/2 & 2/5 & 1/10 \\ 8/25 & 2/5 & 7/25 \\ 2/19 & 7/19 & 10/19 \end{pmatrix}, P_2 = \begin{pmatrix} 1/2 & 1/4 & 1/4 \\ 1/3 & 0 & 2/3 \\ 0 & 5/9 & 4/9 \end{pmatrix} \tag{4}$$

- Do the transition matrices obey detailed balance, i. e.

$$p_i P_{i\to j} = p_j P_{j\to i} \tag{5}$$