Hand-in sheet 4 – Statistical Physics B

- *Please hand in your solution before Friday 19 December 2025, 12:00. This can be done during the lectures or tutorials or in mailbox 50 (J. Everts) located close to the secretariat of the Institute of Theoretical Physics on the 5th floor.*
- *We only accept hand-written or printed solutions. Digital format, such as pdf, will not be accepted.*
- *Please do not forget to write your name and student number.*
- *Make sure to answer every question as completely as possible. When you do calculations, provide sufficient explanation for all steps. Unless stated otherwise, saying that you used Mathematica (or equivalent) does not count as an explanation!*
- *In total 100 points can be earned.*

Depletion interactions between spherical particles

Consider a binary mixture of two species with N_1 and N_2 particles, respectively. The positional coordinates for species 1 are given by $\mathbf{R}^{N_1} := (\mathbf{R}_1, ..., \mathbf{R}_{N_1})$ and for species 2 by $\mathbf{r}^{N_2} := (\mathbf{r}_1, ..., \mathbf{r}_{N_2})$. The total potential energy can be written as

$$\Phi(\mathbf{R}^{N_1}, \mathbf{r}^{N_2}) = \Phi_{11}(\mathbf{R}^{N_1}) + \Phi_{22}(\mathbf{r}^{N_2}) + \Phi_{12}(\mathbf{R}^{N_1}, \mathbf{r}^{N_2}).$$

(a) (*10 points*) Give two examples of a physical system that conform to the above description.

(b) (*10 points*) Give expressions for the canonical partition function $Z(N_1, N_2, V, T)$ and the semi-grand partition function $\Xi(N_1, \mu_2, V, T)$. Denote the corresponding thermodynamic potentials as $F(N_1, N_2, V, T)$ and $\Omega(N_1, \mu_2, V, T)$, respectively. How are the thermodynamic potentials related? Furthermore, give expressions in terms of the corresponding partition functions.

(c) (*15 points*) Show that we can write for the semi-grand potential

$$\exp[-\beta\Omega(N_1, \mu_2, V, T)] = \frac{1}{N_1!\Lambda^{3N_1}} \int d\mathbf{R}^{N_1} \exp[-\beta\Phi_{\text{eff}}(\mathbf{R}_1^N)].$$

Furthermore, define the induced effective potential Φ_{ind} via $\Phi_{\text{eff}} = \Phi_{11} + \Phi_{\text{ind}}$. What is the difference between Φ_{ind} and Φ_{eff}? Give an expression for both quantities.

(d) (*15 points*) Assume that particles of species 2 do not interact amongst each other ($\Phi_{22} = 0$), but do interact with particles of species 1. Furthermore, assume pairwise additivity,

$$\Phi_{12}(\mathbf{R}^{N_1}, \mathbf{r}^{N_2}) = \sum_{i=1}^{N_1}\sum_{j=1}^{N_2} \phi_{12}(\mathbf{R}_i - \mathbf{r}_j).$$

What kind of physical system can this be? Prove that

$$\Phi_{\text{ind}}(\mathbf{R}^{N_1}; \mu_2, T) = -z_2 k_{\text{B}} T \int d\mathbf{r}\, \exp\left[-\beta \sum_{i=1}^{N_1} \phi_{12}(\mathbf{r} - \mathbf{R}_i)\right] =: -z_2 k_{\text{B}} T V_{\text{f}}(\mathbf{R}^{N_1})$$

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(e) (*10 points*) Suppose $\phi_{12}(r)$ is a hard-sphere potential with hard-core diameter σ_{12}. How can one interpret $V_{\mathrm{f}}(\mathbf{R}^{N_1})$ in this case?

(f) (*20 points*) Consider $N_1 = 2$ and take Φ_{11} to be also a hard-sphere potential with hard-core diameter σ_{11}. Compute $\Phi_{\mathrm{eff}}(\mathbf{R}_1, \mathbf{R}_2)$. Does species 2 generate an attraction or a repulsion between the two spheres? How does the strength of the interaction change when we increase the density of species 2?

(g) (*10 points*) Does the entropy of species 2 increase or decrease when we bring the two spheres closer together? Interpret your answer.

(h) (*10 points*) We replace the two spheres by two hard spherocylinders with arbitrary orientations. Describe in words how you would compute the effective interaction potential as a function of centre-to-centre separation and orientations of the spherocylinders. For which orientations do you expect the largest attraction as a function of separation? Explain your answer.