Institute of Theoretical Physics
University of Warsaw

Mid-term exam (kolokwium) Topics in Modern Statistical Physics

Wednesday, 6 December 2023, 9:00-12:00

- *Read every question carefully before answering. The exam consists of four problems and a total of 100 points can be earned.*
- *Make sure to answer every question as complete as possible. When you do calculations, make sure to provide sufficient explanation for all steps.*
- *Write clearly and structured, unreadable work cannot be corrected.*
- *Make sure to divide your time on the problems equally, considering the amount of points you can earn for each question. If you think you made somewhere a calculational mistake, point it out in words, and do not spend too much time on correcting e.g. minus signs.*

Problem 1: Statistical mechanics of interacting classical systems (*25 points*)
Consider the classical canonical partition function

$$Z(N,V,T) = \frac{1}{N!h^{3N}} \int d\mathbf{r}^N \int d\mathbf{p}^N \, \exp\left[-\beta H(\mathbf{r}^N, \mathbf{p}^N)\right],$$

with a generic Hamiltonian of the form

$$H(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \Phi(\mathbf{r}^N).$$

(a) (*3 points*) Explain in sufficient detail why the Planck constant h and the factor $N!$ appear in this expression. Write down and explain the definition of the quantum-mechanical canonical partition function and give sufficient reasons whether these factors also occur there.

(b) (*5 points*) The classical density operator is given by $\hat{\rho}(\mathbf{r}) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i)$. We assume that the potential energy is pairwise additive $\Phi(\mathbf{r}^N) = \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|)$. Prove that in this case $\rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle$ equals a constant denoted by $\rho_{\rm b}$. Derive an expression for $\rho_{\rm b}$ in the canonical ensemble and in the grand-canonical ensemble. Comment on how they differ.

(c) (*5 points*) Consider the correlation function,

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \left\langle \sum_{i \neq j} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\mathbf{r}' - \mathbf{r}_j) \right\rangle.$$

We define the radial distribution function as $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho_{\rm b}^2 g(|\mathbf{r} - \mathbf{r}'|)$, which is valid for homogeneous and isotropic systems. Give two physical interpretations of $g(r)$. Motivate these interpretations sufficiently with mathematical equations.

(d) (*5 points*) Sketch $g(r)$ for a typical gas, liquid, and solid and comment on the differences. Make sure to mark important features of $g(r)$ in your sketch.

(e) (*5 points*) Consider a typical phase diagram of a one-component classical system. Can the liquid-solid melting transition line end in a critical point? Motivate your answer.

(f) (*2 points*) Explain what is a polymer. What is meant by the persistence length of a polymer?

Problem 2: The virial route to thermodynamics (*25 points*)

The classical canonical partition function can be simplified by integrating out the momenta

$$Z(N,V,T) = \frac{Q(N,V,T)}{\Lambda^{3N} N!}.$$

When we take a pairwise additive interacting system, the configurational integral is given by

$$Q(N,V,T) = \int d\mathbf{r}^N \exp\left[-\beta \sum_{i<j} v(r_{ij}) \right],$$

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. Furthermore, $\mathbf{r}_i = (x_i, y_i, z_i)$ in Cartesian coordinates for $i = 1, ..., N$.

(a) (*2 points*) Derive an expression for Λ. Give an interpretation of Λ and its usefulness.

(b) (*10 points*) Prove directly from the partition function the virial route to thermodynamics,

$$p = \rho k_{\mathrm{B}} T - \frac{\rho^2}{6} \int d\mathbf{r}\, r g(r) v'(r).$$

You are NOT allowed to use the virial theorem from classical mechanics here. *Hint: First show that $\beta p = (1/Q)(\partial Q/\partial V)_{N,T}$ and then use rescaled coordintates $s_{i\alpha} = r_{i\alpha} V^{-1/3}$ for $\alpha = x, y, z$ and $i = 1, ..., N$. Note that $\mathbf{s}_i$ is dimensionless.*

(c) (*3 points*) How does the expression you derived in (c) change in one and two spatial dimensions? Motivate your answer.

(d) (*5 points*) In the low-density limit, we have that $g(r) = \exp[-\beta v(r)]$. Use the virial route to thermodynamics to show that the pressure takes the form

$$\beta p(\rho, T) = \rho + B_2(T)\rho^2 + ...$$

and derive an explicit formula for $B_2(T)$ in terms of the Mayer function.

(e) (*5 points*) What does the sign of $B_2(T)$ tell you? Motivate your answer. Make a sketch of representative pressure isotherms to highlight the difference between $B_2(T) < 0$ and $B_2(T) > 0$.

Problem 3: The random-phase approximation (*25 points*)

(a) (*3 points*) Consider the direct correlation function $c(r)$ and a density-independent pair potential $v(r)$. What is the asymptotic behaviour of $c(r)$? How do we approximate $c(r)$ within the random-phase approximation (RPA) and for what kind of systems does this make sense?

(b) (*2 points*) Write down an expression for the static structure factor $S(k)$ within the RPA for a general pair potential $v(r)$. Focus on a bulk fluid with overall density ρ. When is the expression for $S(k)$ well defined?

(c) (*5 points*) Consider the Gaussian-core model with pair potential

$$v(r) = \epsilon \exp(-r^2/R^2), \tag{1}$$

which models polymer blobs that are allowed to overlap. Here $\epsilon > 0$ is an energy scale and R is roughly the radius of gyration of a polymer coil. Within the RPA, compute $S(k)$ of a homogeneous and isotropic Gaussian-core fluid.

(d) (*2 points*) We define the volume fraction as $\eta = (4/3)\pi R^3\rho$. Does it make sense to take $\eta > 1$ within this model? Do you expect oscillations in $S(k)$ when η is sufficiently high for suitable values of ϵ?

(e) (*5 points*) Recall the compressibility sum rule $\rho k_{\mathrm{B}}T\kappa_T = \lim_{k\to 0} S(k)$. Here κ_{T} is the isothermal compressibility $\kappa_T = -(1/V)(\partial V/\partial p)_{N,T}$. Use this sum rule to find the pressure and Helmholtz free energy of the Gaussian-core model within the RPA .

(f) (*5 points*) Show that the same form of the Helmholtz free energy for a homogeneous and isotropic Gaussian-core system is obtained within classical density functional theory (DFT), with excess functional

$$\mathcal{F}_{\mathrm{ex}}[\rho] = \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\rho(\mathbf{r})\rho(\mathbf{r}')v(|\mathbf{r}-\mathbf{r}'|).$$

What is the Helmholtz free energy for this model when there is a non-vanishing external potential $V_{\mathrm{ext}}(\mathbf{r}) \neq 0$? Express your answer in terms of $\rho(\mathbf{r})$ and $V_{\mathrm{ext}}(\mathbf{r})$.

(g) (*3 points*) Show that the form of $\mathcal{F}_{\mathrm{ex}}[\rho]$ in (f) generates the RPA.

Problem 4: The White-Bear functional for hard-sphere mixtures (*25 points*)
Consider an s-component mixture of hard sphere with radii R_i and corresponding density profiles $\rho_i(\mathbf{r})$ for $i = 1, ..., s$. Within fundamental measure theory (FMT), the excess functional is

$$\beta\mathcal{F}_{\mathrm{ex}}[\{\rho_i\}_{i=1}^s] = \int d\mathbf{r}\,\Phi(\{n_\alpha(\mathbf{r})\}),$$

for a set of weighted densities $\{n_\alpha(\mathbf{r})\}$ given by $n_\alpha(\mathbf{r}) = \sum_{i=1}^s \int d\mathbf{r}'\, w_i^{(\alpha)}(\mathbf{r}-\mathbf{r}')\rho_i(\mathbf{r}')$. Here the weight functions $w_i^{(\alpha)}(\mathbf{r})$ can be either of scalar or vectorial nature. We will specify the weight functions later. For now we do not specify the range of α.

(a) (*5 points*) Discuss in sufficient detail what are the assumptions behind FMT and how one can obtain a set of weight functions. Furthermore, comment on the strenghts of FMT, but also on its weaknesses.

(b) (*10 points*) Prove that the direct correlation functions of order $m \geq 1$ are given within FMT by

$$c^{(m)}_{i_1,\ldots,i_m}(\mathbf{r}_1, ..., \mathbf{r}_m) = -\int d\mathbf{r} \sum_{\alpha_1,\ldots,\alpha_m} \frac{\partial^m \Phi}{\partial n_{\alpha_1}(\mathbf{r})\ldots\partial n_{\alpha_m}(\mathbf{r})} w_{i_1}^{(\alpha_1)}(\mathbf{r}_1-\mathbf{r})\ldots w_{i_m}^{(\alpha_m)}(\mathbf{r}_m-\mathbf{r}).$$

Hint: Compute first $-\delta\beta\mathcal{F}_{\mathrm{ex}}[\{\rho_i\}]/\delta\rho_{i_1}(\mathbf{r}_1)$ *and then use induction.*

In the White-Bear formulation of FMT the set of weight functions are

$$w_i^{(3)}(\mathbf{r}) = \Theta(R_i - r), \quad w_i^{(2)}(\mathbf{r}) = \delta(R_i - r), \quad \boldsymbol{w}_i^{(2)}(\mathbf{r}) = \hat{\mathbf{r}}\delta(R_i - r),$$

$$w_i^{(1)}(\mathbf{r}) = \frac{w_i^{(2)}(r)}{4\pi R_i}, \quad \boldsymbol{w}_i^{(1)}(\mathbf{r}) = \frac{\boldsymbol{w}_i^{(2)}(\mathbf{r})}{4\pi R_i}, \quad w_i^{(0)}(\mathbf{r}) = \frac{w_i^{(2)}(r)}{4\pi R_i^2},$$

for $i = 1, ..., s$. Note that there are four scalar weight functions and two vector weight functions. The weighted densities associated with the vector weights are therefore also of vectorial nature. Furthermore, in this case we have that

$$\Phi(\{n_\alpha\}) = -n_0\ln(1-n_3) + \frac{n_1 n_2 - \mathbf{n}_1\cdot\mathbf{n}_2}{1-n_3} + (n_2^3 - 3n_2\mathbf{n}_2\cdot\mathbf{n}_2)\frac{n_3 + (1-n_3)^2\ln(1-n_3)}{36\pi n_3^2(1-n_3)^2}.$$

(c) (*10 points*) Consider a one-component system of hard spheres ($s = 1$) with density profile $\rho(\mathbf{r}) := \rho_1(\mathbf{r})$. Compute $\mathcal{F}_{\mathrm{ex}}[\rho]$ when $V_{\mathrm{ext}}(\mathbf{r}) = 0$. Considering your final result of this computation, what is the consistency check that is imposed on the White-Bear functional?

⌣̈ END OF EXAM ⌣̈