Problem 1. **(Points: 10+10+10+10=40)**

A classical system of N particles is described by specifying a set of generalized coordinates $\{q_i\}$ and generalized momenta $\{p_i\}$, where $i = 1, ..N$. The dynamics of q_i and p_i is governed by Hamilton's equations

$$\dot{q}_i = \frac{\partial H}{\partial p_i}; \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}; \quad \dot{A} \equiv \frac{dA}{dt}$$

where H is the Hamiltonian of the system, $H = H(\{q_i\}, \{p_i\})$. A collection of $\mathcal{N}$ copies of a system with the same Hamiltonian H, but in $\mathcal{N}$ different states, is called an *ensemble*. Furthermore, we define a *phase-space* as a space spanned by $(q, p) = (\{q_i\}, \{p_i\})$. From $\mathcal{N}$ initial states at $t = 0$, the ensemble evolves in phase-space according to Hamilton's equations.

a Show that points in (q, p), where each point describes one of the $\mathcal{N}$ systems in phase space, do not cross or disappear.

b For a very large number $\mathcal{N}$, we may consider a density $\rho = \rho(t, \{q_i, p_i\}$ of points in phase-space as a continuous function of its variables. Use the result of **a** to show that there is a continuity equation for ρ given by

$$\frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0,$$

where $\vec{\nabla}$ is a gradient in phase-space (q, p) and $\vec{v} \equiv (\dot{q}, \dot{p})$ is a velocity in phase-space.

c Use Hamilton's equations to show that the continuity equation for ρ may be written on the form

$$\frac{\partial \rho}{\partial t} + \{\rho, H\} = 0$$

where

$$\{A, B\} \equiv \sum_i \left(\frac{\partial A}{\partial q_i}\frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i}\frac{\partial B}{\partial q_i} \right).$$

d For a stationary state, we have $\partial \rho / \partial t = 0$. Show that in this case, we may set

$$\rho(\{q_i, p_i\}) = \rho(H(\{q_i, p_i\})).$$

Give a physical interpretation of ρ. Explain how this equation facilitates a computation of macroscopically measurable quantities from a microscopic description of a system given by H.

Problem 2. **(Points: 10+10+10=30)**

A system of classical interacting spins on a 3D simple cubic lattice $\{\mathbf{S_i}\}$ in a uniform externally controlled magnetic field along the x-axis, $\mathbf{B} = B\hat{x}$, is defined by the Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \mathbf{B} \cdot \sum_i \mathbf{S}_i$$

Here, $\langle i, j, \rangle$ denotes a sum over all lattice sites i and their nearest neighbors j, while the spin-variables take on the values $\mathbf{S}_i = (S_{xi}, S_{yi}) = S[\cos(\phi_i), \sin(\phi_i)]$, with $\phi_i \in [0, 2\pi\rangle$. Here, ϕ_i is the angle of the spin $\mathbf{S}_i$ with respect to the x-axis. The number of lattice sites is N. $J > 0$ is the strength of the spin-spin coupling in the system. In a so-called mean-field approximation, we set $\mathbf{S}_i = \mathbf{m} + \delta\mathbf{S}_i$ and disregard terms that are quadratic in $\delta\mathbf{S}_i$.

a Show that in the mean-field approximation, the Hamiltonian may be written on the form

$$H = JNz\mathbf{m}^2 - \mathbf{B}_{\text{eff}} \cdot \sum_i \mathbf{S}_i$$

and provide an expression for $\mathbf{B}_{\text{eff}}$. Here, $\langle \delta\mathbf{S}_i \rangle = 0$.

b Show that the Gibbs energy is given by,

$$\begin{aligned} G &= JNz\mathbf{m}^2 - \frac{N}{\beta} \ln\left(I_0(x)\right) \\ I_0(x) &\equiv \frac{1}{2\pi} \int_0^{2\pi} d\phi \; e^{ix\phi} \end{aligned}$$

and give an expression for x. Here, $\beta = 1/k_B T$, k_B is Boltzmanns constant, T is the temperature. Compute G in the limit $T \to 0$.

c This treatment of the system predicts that it undergoes a phase-transition at $B = 0$ from a high-temperature state with no magnetic ordering (a paramagnetic state), to a low-temperature state with magnetic ordering (a ferromagnetic state). The transition occurs at a critical temperature T_c. Find T_c.

Problem 3. **(Points: 10+10+10=30)**

The virial-expansion for the pressure p of a real gas is given by

$$\beta p = \sum_{l=1}^{\infty} B_l(T)\ \rho^l$$

Here, $B_l(T)$ are virial-coefficients, $\beta = 1/k_B T$, k_B is Boltzmann's constant, and T is the temperature. The canonical partition function for a general classical system is given by

$$Z = \frac{Q_N}{\lambda^{3N} N!}$$

with $\lambda \equiv 1/\sqrt{2\pi m k_B T}$, where m is the mass of the particles in the system. Here, Q_N is the so-called configurational integral, given by

$$Q_N \equiv \int ... \int d^3r_1 ... d^3r_N\ e^{-\beta\Phi(r_1,..,r_N)}$$

where $\Phi(r_1, .., r_N)$ is the interaction potential between the particles in the system.

a Compute $B_1(T)$.

b Show that for $l \geq 2$, we have

$$B_l(T) = \frac{1}{(l-1)!} \frac{\partial^l(\beta p/\rho)}{\partial \rho^l}$$

c An equation of state for a system of particles is given by

$$p = \frac{N k_B T}{V - Nb} - a\left(\frac{N}{V}\right)^2$$

Here, b is a parameter that sets the volume of a hard core repulsion in the system, and a is a parameter that sets the magnitude of a long-range weak attraction between particles. Compute all virial coefficients $B_l(T)$ for this system.

Useful formulae:

Partition function in the canonical ensemble:

$$Z = e^{-\beta F}$$

Partition function in the Gibbs ensemble:

$$Z = e^{-\beta G}$$

Partition function in the grand canonical ensemble:

$$Z_g = e^{\beta pV}$$

Thermodynamic identity

$$TdS = dU + pdV$$

Helmholtz free energy

$$\begin{aligned} F &= U - TS \\ dF &= dU - TdS - SdT \end{aligned}$$

Generalized Equipartition Principle:

Let the Hamiltonian of a system be given by $H = \alpha|q|^\nu + H^{'}$. Here q is a generalized coordinate or momentum which does not appear in $H^{'}$. Let the partition function be given by

$$Z = \int dq \int d\Gamma^{'} e^{-\beta H},$$

such that we have

$$\langle \alpha|q|^\nu \rangle = \frac{1}{Z} \int dq \int d\Gamma^{'} \alpha|q|^\nu \; e^{-\beta H}.$$

Then we have

$$\langle \alpha|q|^\nu \rangle = \frac{k_B T}{\nu}.$$

Zeroth order modified Bessel functions $I_0(x)$

$$I_0 \equiv \frac{1}{2\pi} \int_0^{2\pi} \; d\phi \; e^{x\cos(\phi)}$$

Power series in x:

$$I_0(x) = \sum_{k=0}^{\infty} \frac{x^{2k}}{2^{2m}\,(k!)^2}$$

Small x:

$$I_0(x) = 1 + \frac{x^2}{4} + \frac{x^4}{64} + ...$$

Large x:

$$I_0(x) \approx \frac{1}{\sqrt{2\pi x}} \; e^x$$

Gauss' theorem

Let S be a closed surface encompassing a volume V in some space of arbitrary dimension. Let $\hat{\mathbf{n}}dS$ be a directed surface element of S pointing *out* of the volume V. Then, for any vector $\vec{F}$ in this space, we have

$$\iiint_V (\nabla \cdot \mathbf{F})\, \mathrm{d}V \quad = \quad \oint\!\!\!\!\oint_{S(V)} \mathbf{F} \cdot \hat{\mathbf{n}}\, \mathrm{d}S$$