Exam 2

Soft Condensed Matter

June 29th, 2010

This is an open book exam. You can use the book (R. J. Hunter, Foundations of Colloid Science) and the handouts provided by the lecturers. The actual exam questions are on p.2 and p.3, while p.1 contains some background information that you may find useful.

In this exam we will consider classical one-component systems of N identical particles with hamiltonian $H(\mathbf{r}_1, \cdot, \mathbf{r}_N; \mathbf{p}_1, \cdot, \mathbf{p}_N)$, where $\mathbf{r}_i$ and $\mathbf{p}_i$ denote the position and linear momentum of particle $i \in \{1, 2, \cdots, N\}$. The volume of the system is V, the temperature T, the pressure p, the chemical potential μ, the entropy S, the canonical partition function Z, and the internal energy E. Some well-known relations include

$$\begin{aligned} dE &= TdS - pdV + \mu dN; \\ Z &= \frac{1}{N!h^{3N}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N \exp(-\beta H) \end{aligned}$$

where h is the Planck constant and $\beta = 1/k_B T$ with $k_B = 1.38 \times 10^{-23}$J/K the Boltzmann constant.

For the case of pairwise interactions between the particles, described a pair potential $u(r)$ at particle-particle distance r, the following results are also known

$$\begin{aligned} B_2(T) &= -\frac{1}{2} \int d\mathbf{r} \Big(\exp(-\beta u(r)) - 1 \Big) \\ \beta p &= N/V - \frac{1}{6 k_B T V} \int_V d\mathbf{r}_1 d\mathbf{r}_2 r_{12} u'(r_{12}) \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \end{aligned} \tag{1}$$

where $u'(r) = du(r)/dr$ and where the two-body density is defined by

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{Q(N,V,T)} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N \exp[-\beta \sum_{i<j}^{N} u(r_{ij})], \tag{2}$$

and the configurational integral by

$$Q(N,V,T) = \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp[-\beta \sum_{i<j}^{N} u(r_{ij})]. \tag{3}$$

In fluids the radial distribution function $g(r) = 1 + h(r)$ with $h(r)$ the total correlation function, which is related to the direct correlation function $c(r)$ by the Ornstein-Zernike relation

$$h(r) = c(r) + \rho \int d\mathbf{r}' c(|\mathbf{r}'|) h(|\mathbf{r} - \mathbf{r}'|), \tag{4}$$

where $\rho = N/V$ is the density. The structure factor $S(k)$ satisfies, for wavevector $\mathbf{k} \neq 0$,

$$S(k) = 1 + \rho \int d\mathbf{r} \Big(g(r) - 1 \Big) \exp(i\mathbf{k} \cdot \mathbf{r}), \tag{5}$$

where $k = |\mathbf{k}|$.

For hard spheres with diameter σ, the non-ideal part of the Helmholtz free energy F is accurately described by

$$\frac{F - F_{id}}{N k_B T} = \frac{4\eta - 3\eta^2}{(1-\eta)^2}, \tag{6}$$

where $\eta = (\pi/6)\rho\sigma^3$.

1. All items concern a one-component classical fluid of identical particles.

   (a) Calculate the second virial coefficient of hard spheres with particle diameter σ.

   (b) Give a (simple) estimate of the hard-sphere packing fraction η at which the hard-sphere pressure is 1 percent larger than that of an ideal gas at the same density and temperature. Motivate your answer.

   (c) Sketch the radial distribution function of a hard-sphere system (diameter σ) as a function of the interparticle separation r, for packing fractions (i) $\eta = 10^{-4}$ and (ii) $\eta = 0.49$. Carefully consider the scales on the horizontal and vertical axes of the graph.

   (d) Show that the internal energy $E = \langle H \rangle$ of a fluid of N particles with pair potential $u(r)$ at temperature T and density ρ can be written as

$$E = \frac{3Nk_BT}{2} + \frac{N\rho}{2} \int d\mathbf{r} g(r) u(r), \tag{7}$$

   with $g(r)$ the radial distribution function. Calculate E for a hard-sphere system.

   (e) Show that the structure factor $S(k)$ can be written as $S(k) = 1/\big(1 - \rho\hat{c}(k)\big)$, with $\hat{c}(k) = \int d\mathbf{r} c(r) \exp(i\mathbf{k}\cdot\mathbf{r})$ the Fourier transform of $c(r)$.

2. The equation of state of a certain classical fluid is well-described by

$$\frac{p}{k_BT} = \rho + (b - \frac{a}{k_BT})\rho^2 + b^2\rho^3 \tag{8}$$

where $\rho = N/V$ is the number density, p the pressure, T the temperature, N the number of particles, V the volume, k_B Boltzmann's constant and $a, b > 0$ phenomenological constants.

   (a) Sketch the equation of state, i.e., p as a function of ρ, (i) for extremely high T and (ii) for extremely low T. Do you expect a gas-liquid coexistence regime at high or low T, or at both or at none? Motivate your answer.

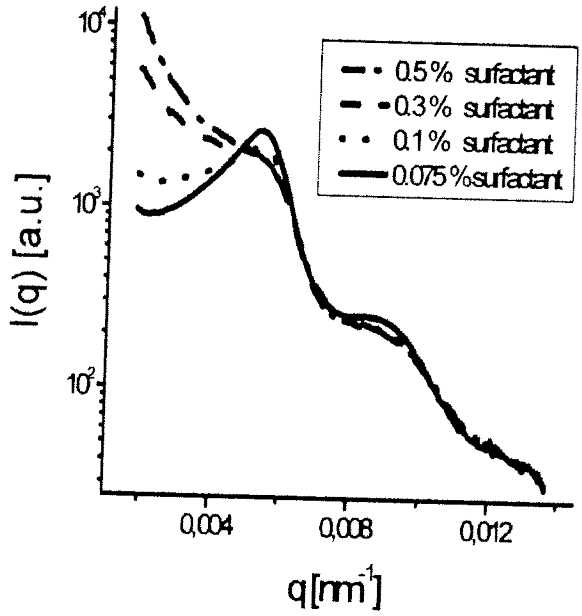
At sufficiently low temperature, the equation of state can be simplified by

$$\frac{p}{k_BT} = \rho - \frac{a}{k_BT}\rho^2 + b^2\rho^3 \tag{9}$$

   (b) Calculate the critical pressure p_c, critical density ρ_c, and critical temperature T_c using (9).

   (c) Calculate the chemical potential $\mu(\rho, T)$ using the approximate equation of state (9).

   (d) What are the conditions for phase coexistence? Describe how gas-liquid equilibrium coexistence can be determined from $\mu(\rho, T)$ and $p(\rho, T)$ for $T < T_c$.



3. The figure shows light scattering data taken on a monodisperse emulsion of silicone oil in a solvent mixture of water and glycerol. The wavelength of the light was 632.8 nm. The emulsion was stabilized with the non-ionic surfactant Triton X-100. Four different concentrations of surfactant were used, keeping everything else the same. The concentrations are given as a weight percentage: 0.1% means 0.1 gram per 100 milliliter of solvent. The lowest concentration is just enough to keep the emulsion stable. Excess surfactant just forms micelles, which are too small to scatter significantly.

   In answering the following questions always explain your answer. If you don't know the answer, but need it in the remainder, you may choose a reasonable value.

   (a) Give a reason why these measurements could not have been done with either water or glycerol as the solvent.

   (b) Estimate the size of the emulsion droplets.

   (c) Estimate the volume fraction of the emulsion.

   (d) Explain why the scattered intensity at small wave vector *decreases* when the surfactant concentration *increases*.