Problem Set 6 – Statistical Physics B

Problem 1: Gymnastics with functional derivatives

(a) Consider the functional $F[u] = \int_{-\infty}^{\infty} dx\, a(x)u(x)$, for a given function a. Determine $\dfrac{\delta F[u]}{\delta u(x)}$.

(b) Let $t_1 > 0$, on which the functional $G[u; t_1]$ depends parametrically. In particular, we set $G[u; t_1] = \int_0^{\infty} dt\, K(t_1, t)u(t)$. Compute $\dfrac{\delta G[u; t_1]}{\delta u(t)}$.

(c) Take the functional $H[u; x'] = u(x')$. Compute $\dfrac{\delta H[u]}{\delta u(x)}$.

(d) Determine $\dfrac{\delta I[u]}{\delta u(x)}$ for the functional $I[u] = \int_{-\infty}^{\infty} dx\, \ln[1 + u(x)]$.

(e) Let $K : \mathbb{R}^3 \to \mathbb{R}$ be a completely symmetric function. Determine $\dfrac{\delta J[u]}{\delta u(x_1, x_2)}$ for the functional

$$J[u] = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \int_{-\infty}^{\infty} dx_3\, K(x_1, x_2, x_3)u(x_1, x_2)u(x_2, x_3)u(x_3, x_1).$$

(f) Take the functional $S[u] = \int_0^{\infty} dt\, f(u(t), \dot{u}(t))$, where $\dot{u}(t) = du/dt$. Determine $\dfrac{\delta S[u]}{\delta u(t)} = 0$. Where have you seen this equation before in physics?

Problem 2: An ideal gas in an external potential

(a) Write down the grand potential Ω for N identical particles interacting via a pairwise additive potential $v(r)$ in an external field $V_{\text{ext}}(\mathbf{r})$. Viewing Ω as a functional of the intrinsic chemical potential $u(\mathbf{r})$ or $v(\mathbf{r}, \mathbf{r}')$, show by explicit functional differentiation that $\delta\Omega/\delta u(\mathbf{r}) = -\rho(\mathbf{r})$ and $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = 2\delta\Omega/\delta v(\mathbf{r}, \mathbf{r}')$.

(b) Prove that

$$\langle \delta\hat{\rho}(\mathbf{r}_1)....\delta\hat{\rho}(\mathbf{r}_n)\rangle = -\frac{\delta^n \beta\Omega[u]}{\delta\beta u(\mathbf{r}_1)...\delta\beta u(\mathbf{r}_n)}, \quad n \geq 2. \tag{1}$$

(c) Consider an ideal gas, $v = 0$. Derive from $\Omega[u]$ an expression for $\rho(\mathbf{r})$ in an external potential.

(d) Write using DFT a formal expression for constancy of the chemical potential. From it, determine $\mathcal{F}[\rho]$ for an ideal gas. Show that it is of the local form.

(e) Show that $\langle \beta^{-1} \ln f_N\rangle = -TS$, with T temperature, S entropy, and f_N the grand-canonical probability distribution. Argue that $\mathcal{F}[\rho]$ is indeed the intrinsic Helmholtz free energy. Does this interpretation depend on the type of interaction potential?

(f) Compute $\langle \delta\hat{\rho}(\mathbf{r}_1)....\delta\hat{\rho}(\mathbf{r}_n)\rangle$ and $c^{(n)}(\mathbf{r}_1, ..., \mathbf{r}_n)$ for an ideal gas in an external field.

Problem 3: Sedimentation in the local density approximation

In the local density approximation we set $\mathcal{F}[\rho] = \int d\mathbf{r}\, f(\rho(\mathbf{r}))$, with $f(\rho)$ the Helmholtz free energy density of a homogeneous bulk system.

(a) Show that the equilibrium density profiles satisfy the Euler-Lagrange equation $f'(\rho(\mathbf{r})) + V_{\text{ext}}(\mathbf{r}) = \mu$, with prime denoting differentiation to the argument. Give a physical interpretation for $f'(\rho)$.

(b) Rewrite your answer from (a) as $\nabla p(\rho(\mathbf{r})) = -\rho(\mathbf{r})\nabla V_{\text{ext}}(\mathbf{r})$. Prove that this is equivalent to the condition for hydrostatic equilibrium.

(c) Calculate within the local-density approximation $c(\mathbf{r}, \mathbf{r}')$ and $h(\mathbf{r}, \mathbf{r}')$ and show that both are proportial to $\delta(\mathbf{r} - \mathbf{r}')$ reflecting the local nature of the approximation.

(d) Take $V_{\text{ext}}(\mathbf{r}) = mgz$, with m the mass, g the gravitational acceleration and z the altitude. This describes the situation where particles sediment in an extenal gravititational field. Under what conditions do you expect that the local-density approximation describes this situation accurately?

(e) Prove that

$$\frac{d\ln[\rho(z)\mathcal{V}]}{dz} = -\frac{\bar{\kappa}_T(\rho(z))}{\ell_g}, \quad \bar{\kappa}_T(\rho) = \left[\beta\rho\left(\frac{\partial\mu}{\partial\rho}\right)\right]^{-1}, \tag{2}$$

for some constant $\mathcal{V}$ with dimensions of volume. Give an expression for ℓ_g. What is the physical interpretation of $\bar{\kappa}_T$?

(f) Compute the density profile for an ideal gas. How is the integration constant determined?

(g) Suppose we have measured the density profile of some system. Argue that from this information we can obtain the equation of state for the system.

(h) Let us describe the situation where colloidal spheres are sedimenting in some simple fluid with density profile $\rho(z)$. How do the above considerations change? Hint: Because the colloidal particles are much larger than the particles in the “solvent", you can assume the solvent to be a structureless medium with given mass density ρ_{s}. Derive an expression for the external potential on a single particle using the equation for hydrostatics.