I. PROBLEM SESSION 5

A. Problem 5.1

Fundamental theory of diffusion:
The time dependent auto-correlation function $g(\vec{r},t)$ is defined such that

$$g(\vec{r},t)d^3\vec{r} \tag{1}$$

describes the probability that a particle, initially at $r = 0$, moves within a time t from its starting point into a volume element $d^3\vec{r}$ which is $\vec{r}$ away. The auto-correlation function is a probability distribution and therefore normalized. Einstein presented a differential equation by which $g(\vec{r},t)$ can be calculated. The starting point is the equation

$$g(\vec{r},t+\Delta t) = \int g(\vec{r}-\vec{r'},t)g(\vec{r'},\Delta t)d^3\vec{r'}. \tag{2}$$

a)Describe the physics behind this equation.
b) Eq.(2) can be transformed to an differential equation, carry out this transformation and show that it leads to the famous diffusion equation

$$\frac{\partial g(\vec{r},t)}{\partial t} = D_s\nabla^2 g(\vec{r},t). \tag{3}$$

And find an expression for the diffusion constant D_s. Hint: Do a series expansion with respect to time on the left side of Eq. (2) and with respect to position on the right side. Some of the terms you will obtain will vanish due to symmetry.
optional: c) Use your expression for the diffusion constant D_s to show that the mean squared displacement of a particle increases linearly with time. (Make use of the assumption that the random walk consist of uncorrelated steps)

B. Problem 5.2

Description through the particle density: Imagine that a large number of colloids is restricted at the start to a very small volume. A current of colloidal particles would then be observed, whose local density ρ is given by Fick's law.

$$\vec{j} = -D\nabla\rho. \tag{4}$$

Use mass conservation to find a diffusion equation in terms of the particle density. Compare with Eq. (2). Is D and D_s equivalent?

C. Problem 4.3

It is generally observed that a colloid in solution under the influence of a small external force, moves at a constant velocity, which is proportional to the force: $v = c * f$. This also statistically holds for electrons in a metal, moving under influence of a electric field. In spite of the motion caused by the field there is a stationary state ρ_{eq} for the the equilibrium distribution of particles. It is given by Boltzmann statistics as

$$\rho_{eq} = Ce^{\frac{-u_{pot}}{k_b T}} \tag{5}$$

Einstein explained this in terms of a dynamical equilibrium between to competing particle currents. There is a particle current density $\vec{j}_f = \rho\vec{v} = \rho c\vec{f}$, where $\vec{f} = -\nabla u_{pot}$. The second opposing current is driven by the gradients in the particle density, thus Fick's law Eq.(4) applies. From this, derive the Einstein relation:

$$D = k_B T * c \tag{6}$$

Where $c = v/f$ is the mobility of the particles. We have thus shown that the mobility of particles responding to an external force, is related to the diffusion constant that describe only the mean field displacement of a particle in the absence of forces, solely driven by collisions with neighbouring molecules.