Chemistry 40642/60642 Spring 2016
Professor J. Daniel Gezelter Due Friday 4/1/2016

Problem Set 3

In class, we stated that the self-correlation function $F_s(r, t)$ for an ideal gas is

$$F_s(r, t) = c(t)e^{-\beta m r^2/2t^2} \tag{1}$$

where $c(t)$ is the normalization constant. In this problem set, you will derive this result, making use of Fourier transforms.

For any function $f(\vec{r})$, where $\vec{r}$ is a position in three dimensional space, we can define the Fourier transform,

$$\hat{f}(\vec{k}) = \int d\vec{r} e^{-i\vec{k}\cdot\vec{r}} f(\vec{r}), \tag{2}$$

where $\vec{k}$ is a wave vector.

There is a Fourier representation of Dirac's delta function,

$$\delta(\vec{r}) = \int d\vec{k} \frac{1}{(2\pi)^3} e^{\pm i\vec{k}\cdot\vec{r}}, \tag{3}$$

so we can show an inverse transform back to real space,

$$f(\vec{r}) = \int d\vec{k} \frac{1}{(2\pi)^3} e^{i\vec{k}\cdot\vec{r}} \hat{f}(\vec{k}). \tag{4}$$

Now, on to the problems:

1. Start from the definition of the self-correlation function that we talked about in class (not the ideal result) and show that the Fourier transform of $F_s(r, t)$ is

$$\hat{F}_s(\vec{k}, t) = \langle e^{i\vec{k}\cdot\vec{r}_1(0)} e^{-i\vec{k}\cdot\vec{r}_1(t)} \rangle \tag{5}$$

2. For an isotropic fluid, $F_s(\vec{r}, t)$ is dependent only on the length $r = |\vec{r}|$. Show that this fact implies

$$\hat{F}_s(\vec{k}, t) = \hat{F}_s(k, t), \text{ with } k = |\vec{k}| \tag{6}$$

and that

$$F_s(r, t) = \frac{1}{(2\pi)^2} \frac{1}{r} \int_{-\infty}^{\infty} dk k \sin(kr) \hat{F}_s(k, t). \tag{7}$$

3. For the ideal gas, $\vec{r}_1(t) = \vec{r}_1(0) + \vec{v}_1 t$. As a result,

$$\hat{F}_s(k, t) = \langle e^{-i\vec{k}\cdot\vec{v}_1 t} \rangle \tag{8}$$

Use this formula together with the fact that the velocity distributions of a classical equilibrated system are Gaussian to show that

$$\hat{F}_s(k, t) = e^{-k^2 t^2 \langle v_1^2 \rangle / 6}. \tag{9}$$

4. Perform the inverse Fourier transform of the formula derived in Part 3 to determine $F_s(r,t)$ for the ideal gas.

5. Consider a fluid of interacting particles, and assume that for such a system, $\vec{r}_1(t) - \vec{r}_1(0)$ is a Gaussian random variable. With that assumption, show that

$$\hat{F}_s(k,t) = \exp\left[-k^2 R^2(t)/6\right]. \tag{10}$$

where

$$R^2(t) = \langle|\vec{r}_1(t) - \vec{r}_1(0)|^2\rangle \tag{11}$$