1. Consider an ensemble of one-particle systems, each evolving in one spatial dimension according to an equation of motion of the form
\[ \dot{x} = -\alpha x, \]
where \( x(t) \) is the position of the particle at time \( t \) and \( \alpha \) is a constant. Since the compressibility of this system is nonzero, the ensemble distribution function \( f(x, t) \) satisfies a Liouville equation of the form
\[ \frac{\partial f}{\partial t} - \alpha x \frac{\partial f}{\partial x} = \alpha f. \]
Suppose that at \( t = 0 \), the ensemble distribution has a Gaussian form
\[ f(x, 0) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-x^2/(2\sigma^2)}. \]

a. Find a solution of the Liouville equation that also satisfies this initial distribution.

**Hint:** Show that the substitution \( f(x, t) = e^{\alpha t} \tilde{f}(x, t) \) yields an equation for a conserved distribution \( \tilde{f}(x, t) \). Next, try multiplying the \( x^2 \) in the initial distribution by an arbitrary function \( g(t) \) that must satisfy \( g(0) = 1 \). Use the Liouville equation to derive an equation that \( g(t) \) must satisfy and then solve this equation.

b. Describe the evolution of the ensemble distribution qualitatively and explain why it should evolve this way.

c. Show that your solution is properly normalized in the sense that
\[ \int_{-\infty}^{\infty} dx f(x, t) = 1. \]

2. An alternative definition of entropy was proposed by Gibbs, who expressed the entropy in terms of the phase space distribution function \( f(x, t) \) as
\[ S(t) = -k \int dx f(x, t) \ln f(x, t). \]
Here, \( f(x, t) \) satisfies the Liouville equation. The notation \( S(t) \) expresses the fact that an entropy defined this way is an explicit function of time.

a. Show that for an arbitrary distribution function, the entropy is actually constant, i.e., that \( dS/dt = 0 \), \( S(t) = S(0) \), so that \( S(t) \) cannot increase in time for any ensemble. Is this in violation of the second law of thermodynamics?

**Hint:** Be careful how the derivative \( d/dt \) is applied to the integral!

b. The distribution \( f(x, t) \) is known as a “fine-grained” distribution function. Because \( f(x, t) \) is fully defined at every phase space point, it contains all of the detailed microstructure of the phase space, which cannot be resolved in reality. Consider, therefore, introducing a “coarse-grained” phase space distribution \( \bar{f}(x, t) \) defined via the following operation: Divide phase space into the smallest cells over which \( \bar{f}(x, t) \) can be defined. Each cell \( C \) is then subdivided into small subcells such that each subcell of volume \( \Delta x \) centered
on the point $x$ has an associated probability $f(x,t)\Delta x$ at time $t$. Assume that at $t = 0$, $f(x,0) = \bar{f}(x,0)$.

In order to define $\bar{f}(x,t)$ for $t > 0$, at each point in time, we transfer probability from subcells of $C$ where $f > \bar{f}$ to cells where $f < \bar{f}$. Then, we use $\bar{f}(x,t)$ to define a coarse-grained entropy

$$ \bar{S}(t) = -k \int dx \, \bar{f}(x,t) \ln \bar{f}(x,t) $$

where the integral should be interpreted as a sum over all cells $C$ into which the phase space has been divided. For this particular coarse-graining operation, show that $\bar{S}(t) \geq \bar{S}(0)$ where equality is only true in equilibrium.

**Hint:** Show that the change in $\bar{S}$ on transferring probability from one small subcell to another is either positive or zero. This is sufficient to show that the total coarse-grained entropy can either increase in time or remain constant.

3. Suppose the interactions in an $N$-particle system are described by a pair potential of the form

$$ U(r_1,\ldots,r_N) = \sum_{i=1}^{N} \sum_{j>i}^{N} u(|r_i - r_j|) $$

In the low density limit, we can assume that each particle interacts with at most one other particle.

a. Show that the canonical partition function in this limit can be expressed as

$$ Q(N,V,T) = \frac{(N-1)!!V^{N/2}}{N!\lambda^N} \left[ 4\pi \int_0^\infty dr \, r^2 e^{-\beta u(r)} \right]^{N/2} $$

b. Show that the radial distribution function $g(r)$ is proportional to $\exp[-\beta u(r)]$ in this limit.

c. Show that the second virial coefficient in the low density limit becomes

$$ B_2(T) = -2\pi \int_0^\infty dr \, r^2 f(r) $$

where $f(r) = e^{-\beta u(r)} - 1$.

4. The radial distribution function $g(r)$ can be measured in neutron and X-ray scattering experiments. In such experiments, the observed intensity of scattered neutrons or X-rays at a given angle is proportional to the structure factor $S(k)$ given by

$$ S(k) = \frac{1}{N} \left| \sum_{j=1}^{N} e^{ikr_j} \right|^2 $$

where $k$ is the vector difference between the wave vectors of the incident and scattered neutrons or X-rays and $N$ is the number of particles in the system. (Note that the term $j = k$ is not excluded from this sum!) Assuming a pair potential, show that $S(k)$ depends only on the magnitude $k = |k|$ and is given in terms of $g(r)$ by

$$ S(k) = 1 + \frac{4\pi\rho}{k} \int_0^\infty dr r g(r) \sin(kr) $$

where $\rho$ is the number density $\rho = N/V$.