Physics 504: Statistical Mechanics
Department of Physics, UIUC
Spring Semester 2013
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Problem Set No. 3: Diffusion, Random Walks and Quantum Mechanics at Finite Temperature
Due Date: March 4, 2013, 9:00 am

1 The Boltzmann Transport Equation

In this problem you will consider the relation between the Boltzamnn Transport Equation and Conservation Laws. Let $f(\vec{r}, \vec{p}, t)$ be the one-particle distribution function for gas of molecules of mass m. Let us denote by $\{\vec{p}_1, \vec{p}_2\} \to \{\vec{p}_1', \vec{p}_2'\}$ an arbitrary two-particle collision taking place at $\vec{r}$. Let $X(\vec{r}, \vec{p}) \equiv X$ be a physical property of the molecules that is conserved by the collision, *i. e.* $X_1 + X_2 = X_1' + X_2'$.

1. Let us denote the collision term of the Boltzmann Transport equation by $\left[\frac{\partial f}{\partial t}\right]_{\text{coll}}$, and assume that it obeys the Boltzmann approximation. Show that
$$\int d^3p \; X(\vec{r}, \vec{p}) \left[\frac{\partial f}{\partial t}\right]_{\text{coll}} = 0$$
for all conserved quantities $X(\vec{r}, \vec{p})$.

2. Use this result and the Boltzmann Transport Equation to prove the following Conservation Theorem
$$\frac{\partial}{\partial t}\langle nX\rangle + \frac{\partial}{\partial \vec{r}} \cdot \langle n\vec{v}X\rangle - n\langle \vec{v} \cdot \frac{\partial X}{\partial \vec{x}}\rangle - \frac{n}{m}\langle \vec{F} \cdot \frac{\partial X}{\partial \vec{v}}\rangle - \frac{n}{m}\langle X \; \frac{\partial}{\partial \vec{v}} \cdot \vec{F}\rangle = 0$$
Here $\vec{F}$ are the external forces and $\vec{v} = \frac{\vec{p}}{m}$ the velocity, and we have use the notation
$$\langle A\rangle = \frac{1}{n}\int d^3p \; A \; f(\vec{r}, \vec{p}, t), \qquad n = \int d^3p \; f(\vec{r}, \vec{p}, t)$$

3. Use the Conservation Theorem to derive a conservation law for (a) mass, (b) momentum and (c) energy, for $X = m$, $\vec{X} = m\vec{v}$ and $X = \frac{1}{2}m(\vec{v} - \vec{u}(\vec{r}, t))^2$ respectively, where $\vec{u}(\vec{r}, t) \equiv \langle \vec{v}\rangle$. Write each conservation law in the form of a continuity equation in terms of the mass density $\rho(\vec{r}, t) \equiv m\int d^3p f(\vec{r}, \vec{p}, t)$, the average velocity $\vec{u}(\vec{r}, t)$, the temperature $kT = \theta(\vec{r}, t) \equiv$

$\frac{1}{3}m\langle(\vec{v}-\vec{u})^2\rangle$, the heat flux $\vec{q} \equiv \frac{1}{2}m\rho\langle(\vec{v}-\vec{u})\ (\vec{v}-\vec{u})^2\rangle$, the pressure tensor $P_{ij} \equiv \rho\langle(v_i-u_i)(v_j-u_j)\rangle$ and the velocity strain tensor $\Lambda_{ij} \equiv= m\frac{1}{2}\left(\frac{\partial u_i}{\partial x_j}+\frac{\partial u_j}{\partial x_i}\right)$.

4. Find the explicit form of the conservation laws you just derived for the case in which $f(\vec{r},\vec{p},t)$ is a Maxwell-Boltzmann distribution with temperature $kT=\theta$ and average velocity $\vec{u}(\vec{r},t)$ which are both slowly varying functions of $\vec{r}$ and t. Show that the conservation laws you just derived coincide with the laws of hydrodynamics for a non-viscous flow.

2 Random Walks and Diffusion

Consider the problem of the random walker in d dimensions on a (hyper)cubic lattice with lattice spacing a.

1. Show that the rules for the moves of a random walker on a lattice can be obtained by integrating a Langevin equation over a time step τ.

2. Derive the equation of motion satisfied by the probability $P(\vec{r},\vec{0},N)$ of finding the random walker at site $\vec{r}$ in exactly N time steps of time lapse τ, having begun its journey at the origin $\vec{0}$.

3. Give a detailed and careful derivation of the continuum version of this equation. Explain how do you extract the probability distribution in the continuum limit, $\mathcal{P}(\vec{x},\vec{0},t)$. Find an explicit expression for the diffusion constant in terms of the natural parameters of the random walk.

4. Find an expression for the $t$otal probability of finding the random walker at $\vec{r}$ after at most a time t. How is it related to the probability $P(\vec{r},\vec{0},N)$? Justify your answer.

5. Find an $e$xplicit result for the probability to return to the origin in at most a time t in the continuum limit in d dimensions. What happens to your result if $d=2$?

3 Langevin Equation in a Force Field

Consider a particle of coordinate $\vec{x}$ in three dimensions interacting with a gas which will be regarded as a continuum. The effects of the interactions between the particle and the molecules of the gas is represented by a random force $\vec{\eta}(\vec{x},t)$. These random forces are correlated time according to the law $\langle\eta_i(t)\eta_j(t')\rangle = \Gamma\delta_{ij}\delta(t-t')$ $(i,j=1,2,3)$. The friction coefficient is γ. The particle is also subject to the effects of a conservative force $\vec{F}=-\vec{\bigtriangledown}U$, with $U=U_0\exp(-\vec{r}^2/2\xi^2)$, with $U_0>0$ and $\xi>0$.

1. Derive the Fokker-Planck equation for the probability $P(\vec{x},t)$ to find the particle at $\vec{x}$ at time if it departed from the origin at $t=0$.

2. Find the equilibrium distribution $P_0(\vec{x}) = \lim_{t\to\infty} P(\vec{x}, t)$. Show that it has a Gibbs form. What combination of parameters plays the role of kT?

3. Find an expression for $P(\vec{x}, t)$ in terms of a path integral. What plays the role of the "classical action" in this case? What boundary conditions does your path integral obey?

4. Consider the case in which U_0 is small. Find a dimensionless combination of U_0, γ and Γ to make your answer more concrete. Use first order perturbation theory to compute the difference between the true probability distribution $P(\vec{x}, t)$ at time t and the free walker distribution for the same time t.

5. Use the result you just derived to compute the total probability of return to the origin. Discuss the physical meaning of the dependence of your result upon U_0.

4 Path Integral and the Density Matrix

Consider a particle of mass m and position vector $\vec{x}$ in thre dimensions, moving in a conservative force field $\vec{F} = -\vec{\bigtriangledown} U(\vec{x})$. The particle is in thermal equilibrium with a heat bath at temperature T. The partition function for this particle is

$$Z = \text{tr}\; e^{-\beta H}$$

where H is the quantum mechanical Hamiltonian.

1. Derive the path integral representation for the partition function Z. Make sure you establish what boundary conditions you need to use and why.

2. Assume that the potential $U(\vec{x}) = U(|\vec{x}|)$ is isotropic and that it has a global minimum at $\vec{x} = 0$ where it takes the value $U(0) < 0$, and that it remains negative for some finite distance a. Use the semiclassical methods described in class to compute an approximate expression for this partition function valid in the regime $kT \ll |U_0|$.

3. Find the free energy of this system. Compare it with the free energy of a three-dimensional harmonic oscillator at temperature T.