Tutorial sheet 10

Discussion topic: BBGKY hierarchy, single-particle kinetic equations

21. Two-particle phase space density in a classical ideal gas

The purpose of this exercise is to show that even in a classical ideal gas of identical particles, (small) correlations between particles arise when their total number N is fixed.

i. Canonical equilibrium

Consider first the case of a classical gas of N non-interacting identical particles, each of which is described by a Hamilton function h, so that the total Hamilton function reads

$$H_N = h(1) + h(2) + \cdots + h(N),$$

where the positions and momenta of the particles have been for brevity denoted by the particle label. At thermodynamic equilibrium, the canonical partition function for this gas is

$$Z_N(\beta, \mathcal{V}) = \frac{\left[Z_1(\beta, \mathcal{V})\right]^N}{N!},$$

with Z_1 the partition function for a single particle—which need not be specified hereafter.

a) Compute first the single-particle phase space density $f^{(1)}(\vec{r}_1, \vec{p}_1)$.

b) Write down the two-particle phase space density $f^{(2)}(\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2)$, and compare it to the product of the single-particle densities for particles 1 and 2. What do you notice?

ii. Grand canonical equilibrium

The number of particles in the gas is now allowed to vary, so that the proper description at thermodynamic equilibrium takes place in the grand canonical ensemble, involving the "chemical" Lagrange multiplier $\alpha = \beta\mu$.

a) Recall the expression of the grand canonical partition function $Z(\beta, \mathcal{V}, \alpha)$ in terms of the canonical partition functions Z_N and α, then in terms of Z_1 and α.

b) Derive the single-particle phase space density $f^{(1)}(\vec{r}_1, \vec{p}_1)$.

Hint: Consider first the contribution to $f^{(1)}$ coming from the case when the gas consists of N particles, then carefully sum over all possible values of N.

c) Compute the two-particle phase space density $f^{(2)}(\vec{r}_1, \vec{p}_1, \vec{r}_2, \vec{p}_2)$ and rewrite it as function of the single-particle densities for particles 1 and 2. Compare with the result in the canonical approach.

22. Reduced density matrices

Consider a system of N identical fermions. Assuming they are in a state which can be described by a normalised wave function $\Psi(t, \vec{r}_1, \ldots, \vec{r}_N)$, one defines the corresponding single-particle density matrix by its elements

$$\rho^{(1)}(\vec{r}, \vec{r}') \equiv N \int \Psi(t, \vec{r}, \vec{r}_2, \ldots, \vec{r}_N) \left[\Psi(t, \vec{r}', \vec{r}_2, \ldots, \vec{r}_N)\right]^* \mathrm{d}^3\vec{r}_2 \cdots \mathrm{d}^3\vec{r}_N,$$

where the spin degrees of freedom have not be written.[1] Similarly, one introduces the two-particle density matrix

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2, \vec{r}'_1, \vec{r}'_2) \equiv \frac{N(N-1)}{2} \int \Psi(t, \vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots, \vec{r}_N) \left[\Psi(t, \vec{r}'_1, \vec{r}'_2, \vec{r}_3, \ldots, \vec{r}_N)\right]^* \mathrm{d}^3\vec{r}_3 \cdots \mathrm{d}^3\vec{r}_N,$$

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[1]Each integration over a position coordinate has to be accompanied by a sum over the possible spin states of the corresponding particle, yet this is irrelevant for the following.

and in an analogous manner, a k-particle density matrix for any $k < N$, up to the N-particle density matrix $\rho^{(N)}(\vec{r}_1, \ldots, \vec{r}_N, \vec{r}_1', \ldots, \vec{r}_N') \equiv \Psi(t, \vec{r}_1, \ldots, \vec{r}_N)\big[\Psi(t, \vec{r}_1', \ldots, \vec{r}_N')\big]^*$.

Note that all these densities are actually, as Ψ itself, time-dependent, although this is usually not explicitly written.

i. Single-particle density matrix

a) Check that $\rho^{(1)}$ is hermitian. What do its diagonal elements $\rho^{(1)}(\vec{r}, \vec{r})$ represent physically? Deduce from this interpretation the value of the trace of $\rho^{(1)}$.

b) Let $\{\phi_k(\vec{r})\}$ denote an orthonormal basis of single-particle wave functions. Show that if Ψ is a (Slater-)determinant of N such single-particle functions ϕ_j (with for simplicity $j = 1, \ldots, N$), then the single-particle density matrix elements simply read

$$\rho^{(1)}(\vec{r}, \vec{r}') = \sum_{j=1}^{N} \phi_j(\vec{r})\big[\phi_j(\vec{r}')\big]^*.$$

Check that in that case $\rho^{(1)}$ obeys the identity $\big(\rho^{(1)}\big)^2 = \rho^{(1)}$. What are then its possible eigenvalues?

ii. Two-particle density matrix

a) Check that $\rho^{(2)}$ is antisymmetric in the variables $\vec{r}_1$ and $\vec{r}_2$ as well as in $\vec{r}_1'$ and $\vec{r}_2'$, and that it is hermitian in the exchange of its unprimed and primed variables. What do the diagonal elements (i.e. with $\vec{r}_1' = \vec{r}_1$, $\vec{r}_2' = \vec{r}_2$) represent physically? What is thus the trace of $\rho^{(2)}$?

b) Compute $\displaystyle\int \rho^{(2)}(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2)\, \mathrm{d}^3\vec{r}_2$.

c) Show that if Ψ is a Slater-determinant as in question **i.b**, then $\rho^{(2)}$ can be expressed in terms of the single-particle density matrix:

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2, \vec{r}_1', \vec{r}_2') = \frac{1}{2}\big[\rho^{(1)}(\vec{r}_1, \vec{r}_1')\rho^{(1)}(\vec{r}_2, \vec{r}_2') - \rho^{(1)}(\vec{r}_1, \vec{r}_2')\rho^{(1)}(\vec{r}_2, \vec{r}_1')\big].$$

iii. Equations of motion

(This question is independent of **i.** and **ii.**) Let $\hat{H}$ denote the Hamilton operator of the system, assumed to involve only the (single-particle) kinetic terms and two-body interactions

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\hat{\triangle}_i + \sum_{i<j} V\big(\hat{\vec{r}}_i - \hat{\vec{r}}_j\big).$$

Starting from the Schrödinger equation for $\Psi(t, \vec{r}_1, \ldots, \vec{r}_N)$, show that the single-particle density matrix is governed by the equation

$$\mathrm{i}\hbar\frac{\partial\rho^{(1)}(\vec{r}, \vec{r}')}{\partial t} = -\frac{\hbar^2}{2m}\big(\triangle - \triangle'\big)\rho^{(1)}(\vec{r}, \vec{r}') + 2\int\big[V(\vec{r}-\vec{r}_2) - V(\vec{r}'-\vec{r}_2)\big]\rho^{(2)}(\vec{r}, \vec{r}_2, \vec{r}', \vec{r}_2)\, \mathrm{d}^3\vec{r}_2,$$

where $\triangle'$ denotes the Laplacian with respect to $\vec{r}'$. Can you tell where this could lead you to, if now were not the proper time no stop the exercise?

23. Collisionless evolution of the single-particle phase space density

Let $f(t, \vec{r}, \vec{p})$ denote the single-particle phase space density of a system of non-interacting particles with mass m evolving in the absence of long-range interactions deriving from a vector potential. Consider the particles which at time t are in an infinitesimal volume element $\mathrm{d}^3\vec{r}\,\mathrm{d}^3\vec{p}$ around the point $(\vec{r}, \vec{p})$.

Where are these particles at the instant $t + \mathrm{d}t$? Show that the volume element $\mathrm{d}^3\vec{r}'\,\mathrm{d}^3\vec{p}'$ they then occupy equals $\mathrm{d}^3\vec{r}\,\mathrm{d}^3\vec{p}$. Derive the partial differential equation governing the evolution of f.