S6.A. Reduced Probability Densities and the BBGKY Hierarchy

One- and two- body phase functions of an N-body system take the respective forms

$$O^N_{(1)}(\boldsymbol{X}^N) = \sum_{i=1}^{N} O(\boldsymbol{X}_i) \tag{6.61}$$

$$O^N_{(2)}(\boldsymbol{X}^N) = \sum_{i<j}^{N(N-1)/2} O(\boldsymbol{X}_i, \boldsymbol{X}_j) \tag{6.62}$$

where $O(\boldsymbol{X}_i, \boldsymbol{X}_j) = O(\boldsymbol{X}_j, \boldsymbol{X}_i)$ since the bodies are identical.

Familiar examples are the kinetic and pair-wise potential energies

$$K = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} \qquad\qquad U = \sum_{i<j}^{N(N-1)/2} V(|\boldsymbol{q}_i - \boldsymbol{q}_j|)$$

To find the expectation value of an s-body phase function, we need only the s-body reduced probability density

$$\begin{aligned} \rho_s(\boldsymbol{X}^s, t) &= \rho_s(\boldsymbol{X}^s, t) = \rho_s(\boldsymbol{X}_1, \ldots, \boldsymbol{X}_s, t) \\ &\equiv \int d\boldsymbol{X}_{s+1} \ldots \int d\boldsymbol{X}_N\, \rho(\boldsymbol{X}^N, t) \end{aligned} \tag{6.64}$$

Note, since ρ is symmetric with any permutations of its $\boldsymbol{X}^N$ arguments, the integrals in (6.64) can be over any set of $(N-s)$ $\boldsymbol{X}_j$'s.

For example,

$$\begin{aligned} \langle O_{(1)}(t) \rangle &= \int d\boldsymbol{X}_1 \ldots \int d\boldsymbol{X}_N\, \rho(\boldsymbol{X}^N, t)\, O^N_{(1)}(\boldsymbol{X}^N) \\ &= \sum_{i=1}^{N} \int d\boldsymbol{X}_1 \ldots \int d\boldsymbol{X}_N\, \rho(\boldsymbol{X}^N, t)\, O(\boldsymbol{X}_i) \\ &= \sum_{i=1}^{N} \int d\boldsymbol{X}_i\, \rho_1(\boldsymbol{X}_i, t)\, O(\boldsymbol{X}_i) \\ &= N \int d\boldsymbol{X}_1\, \rho_1(\boldsymbol{X}_1, t)\, O(\boldsymbol{X}_1) \end{aligned} \tag{6.65}$$

$$\begin{aligned} \langle O_{(2)}(t) \rangle &= \int d\boldsymbol{X}_1 \ldots \int d\boldsymbol{X}_N\, \rho(\boldsymbol{X}^N, t)\, O^N_{(2)}(\boldsymbol{X}^N) \\ &= \sum_{i<j}^{N(N-1)/2} \int d\boldsymbol{X}_1 \ldots \int d\boldsymbol{X}_N\, \rho(\boldsymbol{X}^N, t)\, O(\boldsymbol{X}_i, \boldsymbol{X}_j) \\ &= \frac{1}{2} N(N-1) \int d\boldsymbol{X}_1 \int d\boldsymbol{X}_2\, \rho_2(\boldsymbol{X}_1, \boldsymbol{X}_2, t)\, O(\boldsymbol{X}_1, \boldsymbol{X}_2) \end{aligned} \tag{6.66}$$

Instead of ρ_s, it is sometimes more convenient to deal with the quantity

$$\begin{aligned} F_s(\boldsymbol{X}^s, t) &= F_s(\boldsymbol{X}_1, \ldots, \boldsymbol{X}_s, t) \\ &\equiv V^s \rho_s(\boldsymbol{X}^s, t) \\ &= V^s \int d\boldsymbol{X}_{s+1} \ldots \int d\boldsymbol{X}_N\, \rho(\boldsymbol{X}^N, t) \end{aligned} \tag{6.67}$$

with

$$F_N(\boldsymbol{X}^N, t) = V^N \rho_s(\boldsymbol{X}^N, t) \tag{6.68}$$

Consider now the Hamiltonian

$$H^N(\boldsymbol{X}^N) = \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j}^{N(N-1)/2} \phi_{ij} \tag{6.69}$$

$$= \sum_{i=1}^{N} \frac{\boldsymbol{p}_i^2}{2\,m} + \frac{1}{2} \sum_{i,j\,(i\neq j)}^{N} \phi_{ij}$$

where

$$\phi_{ij} = \phi(\,|\,\boldsymbol{q}_i - \boldsymbol{q}_j\,|\,) = \phi_{ji}$$

is a 2-body spherically symmetric (or central) interaction potential.

The Liouville operator is [see (6.26-7)]

$$\hat{L}^N = -i\{\ \ , H^N\}_{\text{qp}}$$

$$= -i \sum_{i=1}^{N} \left(\frac{\partial H^N}{\partial \boldsymbol{p}_i} \cdot \frac{\partial}{\partial \boldsymbol{q}_i} - \frac{\partial H^N}{\partial \boldsymbol{q}_i} \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right)$$

$$= -i \sum_{i=1}^{N} \left(\frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_i} - \sum_{j<k}^{N(N-1)/2} \frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_i} \cdot \frac{\partial}{\partial \boldsymbol{p}_i} \right) \qquad (6.70a)$$

Using

$$\sum_{j<k}^{N(N-1)/2} \frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_i} \cdot \frac{\partial}{\partial \boldsymbol{p}_i}$$

$$= \sum_{i=1}^{N} \sum_{j<k}^{N(N-1)/2} \left(\delta_{ij} \frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_j} + \delta_{ik} \frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_k} \right) \cdot \frac{\partial}{\partial \boldsymbol{p}_i}$$

$$= \sum_{j<k}^{N(N-1)/2} \left(\frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_j} \cdot \frac{\partial}{\partial \boldsymbol{p}_j} + \frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_k} \cdot \frac{\partial}{\partial \boldsymbol{p}_k} \right)$$

$$= \sum_{j<k}^{N(N-1)/2} \hat{\Theta}_{jk}$$

where

$$\hat{\Theta}_{jk} = \frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_j} \cdot \frac{\partial}{\partial \boldsymbol{p}_j} + \frac{\partial \phi_{jk}}{\partial \boldsymbol{q}_k} \cdot \frac{\partial}{\partial \boldsymbol{p}_k} \qquad (6.71)$$

(6.70a) becomes

$$\hat{L}^N = -i \sum_{i=1}^{N} \frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_i} + i \sum_{i<j}^{N(N-1)/2} \hat{\Theta}_{ij} \qquad (6.70)$$

The Liouville equation (6.27) now reads

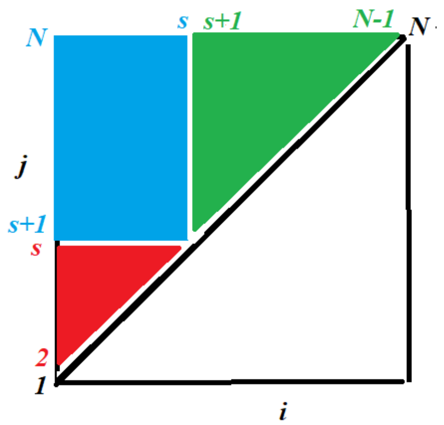
$$\frac{\partial \rho}{\partial t} = -i \hat{L}^N \rho$$

$$= -\sum_{i=1}^{N} \frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial \rho}{\partial \boldsymbol{q}_i} + \sum_{i<j}^{N(N-1)/2} \hat{\Theta}_{ij}\,\rho \qquad (6.71a)$$

$V^s \int d\boldsymbol{X}_{s+1} \ldots \int d\boldsymbol{X}_N$ (6.71 a) gives

$$\frac{\partial F_s}{\partial t} = V^s \int d\boldsymbol{X}_{s+1} \ldots \int d\boldsymbol{X}_N \left(-\sum_{i=1}^{N} \frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial \rho}{\partial \boldsymbol{q}_i} + \sum_{i<j}^{N(N-1)/2} \hat{\Theta}_{ij}\,\rho \right) \qquad (6.71b)$$

The sums can be split into 3 groups, marked as red, blue and green areas in the graph below.



For the red area, $1 \le i < j \le s$, and we have

$$V^s \int d\mathbf{X}_{s+1} \ldots \int d\mathbf{X}_N \left(-\sum_{i=1}^{s} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial \rho}{\partial \mathbf{q}_i} + \sum_{i<j}^{s(s-1)/2} \hat{\Theta}_{ij}\, \rho \right)$$

$$= -\sum_{i=1}^{s} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial F_s}{\partial \mathbf{q}_i} + \sum_{i<j}^{s(s-1)/2} \hat{\Theta}_{ij}\, F_s$$

$$= -i \hat{L}^s F_s$$

The blue area is a rectangle with $i = 1, \ldots, s$; $j = s+1, \ldots, N$.
The green area is a triangle with $s+1 \le i < j \le N$.

(6.71b) thus becomes

$$\frac{\partial F_s}{\partial t} + i \hat{L}^s F_s = V^s \int d\mathbf{X}_{s+1} \ldots \int d\mathbf{X}_N \left[-\sum_{i=s+1}^{N} \frac{\mathbf{p}_i}{m} \cdot \frac{\partial \rho}{\partial \mathbf{q}_i} + \left(\sum_{i=1}^{s} \sum_{j=s+1}^{N} + \sum_{j=s+2}^{N} \sum_{i=s+1}^{j-1} \right) \hat{\Theta}_{ij}\, \rho \right] \qquad (6.72)$$

For a system with finite energy and spatial extent,

$$\rho(\mathbf{X}^N, t) \xrightarrow[|\mathbf{X}_j| \to \infty]{} 0 \qquad \forall\ j, t$$

which we shall assume henceforth.

The integral for i^{th} term in the 1st sum in (6.72) is

$$\int d\mathbf{X}_i \frac{\mathbf{p}_i}{m} \cdot \frac{\partial \rho}{\partial \mathbf{q}_i} = \int d\mathbf{p}_i \oint_{\boldsymbol{\sigma}} d\boldsymbol{\sigma} \cdot \frac{\mathbf{p}_i}{m} \rho \; = 0 \qquad (6.72a)$$

where $\boldsymbol{\sigma}$ is the surface at infinity of the coordinate sub-space $\mathbf{q}_i$.

Hence, the 1st sum in (6.72) vanishes. Likewise the 3rd sum.

(6.72) thus reduces to

$$\frac{\partial F_s}{\partial t} + i \hat{L}^s F_s = V^s \int d\mathbf{X}_{s+1} \ldots \int d\mathbf{X}_N \sum_{i=1}^{s} \sum_{j=s+1}^{N} \hat{\Theta}_{ij}\, \rho \qquad (6.73a)$$

Consider now the relevant integral for the (i, j)-term with $1 \le i \le s$ and $s+1 \le j \le N$,

$$\int d\mathbf{X}_j \hat{\Theta}_{ij}\, \rho = \int d\mathbf{X}_j \left(\frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial \rho}{\partial \mathbf{p}_i} + \frac{\partial \phi_{ij}}{\partial \mathbf{q}_j} \cdot \frac{\partial \rho}{\partial \mathbf{p}_j} \right)$$

$$= \int d\mathbf{X}_j \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial \rho}{\partial \mathbf{p}_i}$$

(6.73a) thus becomes

$$\frac{\partial F_s}{\partial t} + i \hat{L}^s F_s = V^s \sum_{i=1}^{s} \sum_{j=s+1}^{N} \int d\mathbf{X}_j \frac{\partial \phi_{ij}}{\partial \mathbf{q}_i} \cdot \frac{\partial \rho_{s+1}(\mathbf{X}^s, \mathbf{X}_j, t)}{\partial \mathbf{p}_i}$$

$$= V^s (N-s) \sum_{i=1}^{s} \int d\boldsymbol{X}_{s+1} \frac{\partial \phi_{i,s+1}}{\partial \boldsymbol{q}_i} \cdot \frac{\partial \rho_{s+1}(\boldsymbol{X}^{s+1}, t)}{\partial \boldsymbol{p}_i}$$

$$= \frac{N-s}{V} \sum_{i=1}^{s} \int d\boldsymbol{X}_{s+1} \frac{\partial \phi_{i,s+1}}{\partial \boldsymbol{q}_i} \cdot \frac{\partial F_{s+1}(\boldsymbol{X}^{s+1}, t)}{\partial \boldsymbol{p}_i}$$

$$= \frac{N-s}{V} \sum_{i=1}^{s} \int d\boldsymbol{X}_{s+1} \hat{\Theta}_{i,s+1} F_{s+1}(\boldsymbol{X}^{s+1}, t) \qquad (6.73)$$

where we have made use of the fact that, similarly to (6.72a),

$$\int d\boldsymbol{X}_{s+1} \frac{\partial \phi_{i,s+1}}{\partial \boldsymbol{q}_{s+1}} \cdot \frac{\partial F_{s+1}}{\partial \boldsymbol{p}_{s+1}} = 0$$

In the thermodynamic limit ($\lim_{N,V\to\infty} \frac{V}{N} = v$), (6.73) becomes

$$\frac{\partial F_s}{\partial t} + i \hat{L}^s F_s = \frac{1}{v} \sum_{i=1}^{s} \int d\boldsymbol{X}_{s+1} \hat{\Theta}_{i,s+1} F_{s+1}(\boldsymbol{X}^{s+1}, t) \qquad (6.74)$$

(6.74) gives a series of equations for F_s known as the BBGKY hierarchy.

With the help of (6.70), the first 2 equations in the hierarchy are easily found:

$$\frac{\partial F_1}{\partial t} + \frac{\boldsymbol{p}_1}{m} \cdot \frac{\partial F_1}{\partial \boldsymbol{q}_i} = \frac{1}{v} \int d\boldsymbol{X}_2 \hat{\Theta}_{12} F_2(\boldsymbol{X}_1, \boldsymbol{X}_2, t) \qquad (6.75)$$

$$\frac{\partial F_2}{\partial t} + \left(\frac{\boldsymbol{p}_1}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_i} + \frac{\boldsymbol{p}_2}{m} \cdot \frac{\partial}{\partial \boldsymbol{q}_2} - \hat{\Theta}_{12} \right) F_2 \qquad (6.76)$$

$$= \frac{1}{v} \int d\boldsymbol{X}_3 \left(\hat{\Theta}_{13} + \hat{\Theta}_{23} \right) F_3(\boldsymbol{X}_1, \boldsymbol{X}_2, \boldsymbol{X}_3, t)$$

(6.75) is also called the kinetic equation.