Classical Reduced Probability Densities

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1 General formulation

- For pairwise-additive potentials, all N-body interactions are represented in terms of interactions of two particles: Averages therefore involve averages over positions (and momenta) of two particles at most.
- Recall we introduced the probability density for the positions as:

$$n(\mathbf{r}^{(N)}) = \int d\mathbf{p}^{(N)} f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = \frac{e^{-\beta U(\mathbf{r}^{(N)})}}{\int d\mathbf{r}^{(N)} e^{-\beta U(\mathbf{r}^{(N)})}} = \frac{e^{-\beta U(\mathbf{r}^{(N)})}}{Z_N}$$

  - $n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$ is the *joint* probability density of finding particle 1 in the vicinity of $\mathbf{r}_1$, particle 2 in the vicinity of of $\mathbf{r}_2$ and so on.
- Integrating over the coordinate positions of particles 2 to N gives:

$$\begin{aligned} n^{(1/N)}(\mathbf{r}_1) &\equiv \int d\mathbf{r}_2 \cdots d\mathbf{r}_N \, n(\mathbf{r}^{(N)}) \\ &= \text{Probability that particle 1 is in vicinity of } \mathbf{r}_1. \end{aligned}$$

- What is this (singlet) probability density for a system without an external potential? Assume

$$\begin{aligned} U(\mathbf{r}^{(N)}) &= \sum_{i<j} U(|\mathbf{r}_i - \mathbf{r}_j|) = \sum_{i=2}^{N} \sum_{j=i+1} U(|\mathbf{r}_i - \mathbf{r}_1 + \mathbf{r}_1 - \mathbf{r}_j|) \\ &= \sum_{i=2}^{N} \sum_{j=i+1} U(|\boldsymbol{\rho}_i - \boldsymbol{\rho}_j|) = \sum_{i=2}^{N} \sum_{j=i+1} U(|\boldsymbol{\rho}_{ij}|) \end{aligned}$$

- Introducing a change of variables from $\{\mathbf{r}_2, \ldots, \mathbf{r}_N\}$ to $\{\boldsymbol{\rho}_2, \ldots, \boldsymbol{\rho}_N\}$, we get

$$\begin{aligned} \int_V d\mathbf{r}_2 \cdots d\mathbf{r}_N \, e^{-\beta U(\mathbf{r}^{(N)})} &= \int_V d\boldsymbol{\rho}_2 \cdots d\boldsymbol{\rho}_N \, e^{-\beta U(\boldsymbol{\rho}_2, \ldots, \boldsymbol{\rho}_N)} = C \quad \text{(a constant)} \\ Z_N &= \int_V d\mathbf{r}_1 \cdots d\mathbf{r}_N \, e^{-\beta U(\mathbf{r}^{(N)})} = \int_V d\mathbf{r}_1 C = CV \\ n^{(1/N)}(\mathbf{r}_1) &= \frac{C}{CV} = \frac{1}{V} \end{aligned}$$

- The probability of finding particle 1 at position $\mathbf{r}_1$ is $1/V$. Thus all points in the volume are equally likely.
- In the absence of an external potential, we are equally likely to find a given particle anywhere in the volume: on average, the system is uniform in particle (or mass) density.

- What is probability $\rho^{(1/N)}(\mathbf{r}_1)$ of finding *any* particle at a position $\mathbf{r}_1$? Note that the choice of reference particle was arbitrary, so

$$\rho^{(1/N)}(\mathbf{r}_1) = \sum_{i=1} n^{(1/N)}(\mathbf{r}_1) = N n^{(1/N)}(\mathbf{r}_1) = \frac{N}{V} = \text{bulk particle density.}$$

- Can we define a *dynamical variable* corresponding to the particle density? In other words, can we define a function $N(\mathbf{x}^{(N)}, \mathbf{r})$ such that $\langle N(\mathbf{x}^{(N)}, \mathbf{r})\rangle = \rho^{(1/N)}(\mathbf{r})$?
  - Need a function that tells us when there is a particle located in the interval $[\mathbf{r}, \mathbf{r} + d\mathbf{r}]$.

- Try the function

$$N(\mathbf{x}^{(N)}, \mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j)$$

  - Note that since all particles are contained in volume, $\int_V d\mathbf{r} N(\mathbf{x}^{(N)}, \mathbf{r}) = N$.

- Now

$$\begin{aligned}
\langle N(\mathbf{r})\rangle &= \int d\mathbf{r}^{(N)} d\mathbf{p}^{(N)} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \\
&= \frac{\int d\mathbf{r}^{(N)} \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j) e^{-\beta U(\mathbf{r}^{(N)})}}{\int d\mathbf{r}^{(N)} e^{-\beta U(\mathbf{r}^{(N)})}} \\
&= \int d\mathbf{r}^{(N)} \frac{N\delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\mathbf{r}^{(N)})}}{\int d\mathbf{r}^{(N)} e^{-\beta U(\mathbf{r}^{(N)})}} \\
&= N\langle \delta(\mathbf{r} - \mathbf{r}_1)\rangle \\
&= \frac{N \int d\mathbf{r}_1 d\boldsymbol{\rho}_2 \cdots d\boldsymbol{\rho}_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\boldsymbol{\rho}_2, \ldots, \boldsymbol{\rho}_N)}}{\int d\mathbf{r}_1 d\boldsymbol{\rho}_2 \cdots d\boldsymbol{\rho}_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\boldsymbol{\rho}_2, \ldots, \boldsymbol{\rho}_N)}} \\
&= \frac{N \int d\boldsymbol{\rho}_2 \cdots d\boldsymbol{\rho}_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\boldsymbol{\rho}_2, \ldots, \boldsymbol{\rho}_N)}}{\int d\mathbf{r}_1 d\boldsymbol{\rho}_2 \cdots d\boldsymbol{\rho}_N\, \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\boldsymbol{\rho}_2, \ldots, \boldsymbol{\rho}_N)}} \\
&= \frac{NC}{CV} = \frac{N}{V} = \rho^{(1/N)}(\mathbf{r}).
\end{aligned}$$

- These concepts are generalized in a straightforward fashion:

$$\begin{aligned}
\rho^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) &= N(N-1)\cdots(N-q+1) n^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) \\
&= \frac{N!}{(N-q)!} n^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) \\
n^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) &= \frac{\int d\mathbf{r}_{q+1} \cdots d\mathbf{r}_N\, e^{-\beta U(\mathbf{r}^{(N)})}}{Z_N}
\end{aligned}$$

- By definition, the *reduced density* can be interpreted to mean:

$$\rho^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) \;\; = \;\; \text{joint prob. that any particle is near } \mathbf{r}_1\text{, another near } \mathbf{r}_2 \text{ ....}$$

- **Properties of reduced probability density**

  1. From the definition of $\rho^{(q)}$ and the fact that $\int d\mathbf{r}_1\cdots d\mathbf{r}_q\, n^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = 1$,

$$\int d\mathbf{r}_1\cdots d\mathbf{r}_q\,\rho^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = \frac{N!}{(N-q)!}.$$

  2. Since by definition $\int d\mathbf{r}_q\, n^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = n^{(q-1/N)}(\mathbf{r}_q,\ldots,\mathbf{r}_{q-1})$, we have

$$\int d\mathbf{r}_q\,\rho^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = \frac{1}{N-q}\rho^{(q-1/N)}(\mathbf{r}_q,\ldots,\mathbf{r}_{q-1})$$

- Example: $\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = \langle N(\mathbf{x}^{(N)},\mathbf{r}_1)N(\mathbf{x}^{(N)},\mathbf{r}_2)\rangle = N(N-1)n^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)$.
- We define yet another reduced density (loosely called a distribution function) via the relation

$$\rho^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) = \rho^{(1/N)}(\mathbf{r}_1)\rho^{(1/N)}(\mathbf{r}_2)\cdots\rho^{(q/N)}(\mathbf{r}_q)g^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q)$$

  – In the absence of an external potential $\rho^{(1/N)}(\mathbf{r}_1) = N/V = \rho$, and $\rho^{(q/N)} = \rho^q g^{(q/N)}$.
- From this definition, we see that

$$\begin{aligned} g^{(q/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_q) &= \left(\frac{V}{N}\right)^q \frac{N!}{(N-q)!}\frac{\int d\mathbf{r}_{q+1}\cdots d\mathbf{r}_N\, e^{-\beta U}}{Z_N} \\ &= V^q\left(1+O\left(\frac{1}{N}\right)\right)\frac{\int d\mathbf{r}_{q+1}\cdots d\mathbf{r}_N\, e^{-\beta U}}{Z_N} \end{aligned}$$

- Consider $g^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)$. Since

$$\begin{aligned} U(\mathbf{r}^{(N)}) &= U(|\mathbf{r}_1-\mathbf{r}_2|) + \sum_{i=3}^{N}\left[U(|\mathbf{r}_i-\mathbf{r}_1|) + U(\mathbf{r}_i-\mathbf{r}_2) + \sum j = i+1^N U(|\mathbf{r}_j-\mathbf{r}_i|)\right] \\ &= U(\rho_2) + \sum_{i=3}^{N} U(|\boldsymbol{\rho}_i-\boldsymbol{\rho}_2|) + \sum_{i=3}\left[U(\rho_i) + \sum_{j=i+1}^{N} U(|\boldsymbol{\rho}_j-\boldsymbol{\rho}_i|)\right], \end{aligned}$$

  we see that U is independent of $\mathbf{r}_1$ but depends on $\rho_2 = \mathbf{r}_2 - \mathbf{r}_1$. Thus integration of $\exp\{-\beta U\}$ over $\boldsymbol{\rho}_3,\ldots,\boldsymbol{\rho}_N$ yields a function of $\boldsymbol{\rho}_2$:

$$g^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = \frac{V^2\int d\boldsymbol{\rho}_3\cdots d\boldsymbol{\rho}_N\, e^{-\beta U}}{\int d\mathbf{r}_1 d\boldsymbol{\rho}_2\cdots d\boldsymbol{\rho}_N e^{-\beta U}} = g^{(2)}(r_{12}),$$

  with $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$ for a spherically-symmetric potential $U(\mathbf{r}_{12}) = U(r_{12})$.
- For a system with a spherically-symmetric potential,

$$\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2) = \rho^2 g^{(2/N)}(r_{12}).$$

- Can be interpreted as probability of observing a second particle a distance r_{12} away from first particle in the volume.

- Note that since $\int d\mathbf{r}_1 d\mathbf{r}_2\, \rho^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) = N(N-1)$,

$$N(N-1) \;=\; \rho^2 \int d\mathbf{r}_1 d\mathbf{r}_2\, g^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) = \rho^2 \int d\mathbf{r}_1 d\mathbf{r}_{12}\; g^{(2/N)}(r_{12}) = N\rho \int d\mathbf{r}_{12}\; g^{(2/N)}(r_{12}),$$

so $\rho \int d\mathbf{r}_{12}\; g^{(2/N)}(r_{12}) = N - 1 = \int_0^\infty dr\; 4\pi r^2 \rho g^{(2/N)}(r)$.

- Often, superscript on *radial distribution function* $g^{(2/N)}(r) = g(r)$ is dropped.
- $\rho g(r) d\mathbf{r}$ is the probability of observing a particle in volume $d\mathbf{r}$ around a particle located at origin.
- $g(r)$ can be measured directly through light or x-ray scattering experiments.

1.1 Relationship of radial distribution function to thermodynamic parameters

- Averages of dynamical variables that depend on pairwise interactions can be expressed as averages over reduced distribution functions.
- The average energy in the canonical ensemble is given by:

$$E \;=\; \langle H(\mathbf{x}^{(N)}) \rangle = \int d\mathbf{x}^{(N)}\, H(\mathbf{x}^{(N)}) f(\mathbf{x}^{(N)}) = \int d\mathbf{x}^{(N)} \left[\frac{\mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}}{2m} + \sum_{i<j} U(r_{ij}) \right].$$

- For this Hamiltonian, the coordinates and momenta are separable, and hence the canonical probability density can be written:

$$f(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \;=\; \Pi(\mathbf{p}^{(N)}) n(\mathbf{r}^{(N)}) \qquad \Pi(\mathbf{p}^{(N)}) = \frac{e^{-\beta \mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}/2m}}{\int d\mathbf{p}^{(N)} e^{-\beta \mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}/2m}}$$

  - The density $\Pi(\mathbf{p}^{(N)})$ is known as the *Maxwell distribution.*

- The average of the kinetic energy part gives the ideal gas contribution $3/2\, NkT$, so

$$\begin{aligned}
E \;&=\; \frac{3}{2}NkT + \sum_{i<j} \int d\mathbf{r}^{(N)}\, U(r_{ij}) n(\mathbf{r}^{(N)}) = \frac{3}{2}NkT + \frac{N(N-1)}{2} \int d\mathbf{r}^{(N)}\, U(r_{12}) n(\mathbf{r}^{(N)}) \\
&=\; \frac{3}{2}NkT + \frac{N(N-1)}{2} \int d\mathbf{r}_1 d\mathbf{r}_2\, U(r_{12}) n^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \\
&=\; \frac{3}{2}NkT + \frac{N(N-1)}{2} \int d\mathbf{r}_1 d\mathbf{r}_2\, U(r_{12}) n^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \\
&=\; \frac{3}{2}NkT + \frac{1}{2} \int d\mathbf{r}_1 d\mathbf{r}_2\, U(r_{12}) \rho^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \qquad \text{since } N(N-1)n^{(2/N)} = \rho^{(2/N)} \\
&=\; \frac{3}{2}NkT + \frac{V}{2} \int d\mathbf{r}_{12}\, U(r_{12}) \rho^{(2/N)}(r_{12}) \\
&=\; N\left(\frac{3}{2}kT + \frac{1}{2\rho} \int d\mathbf{r}_{12}\, U(r_{12}) \rho^{(2/N)}(r_{12}) \right) \\
&=\; N\left(\frac{3}{2}kT + \frac{1}{2}\rho \int d\mathbf{r}_{12}\, U(r_{12}) g(r_{12}) \right) \qquad \text{since } \rho^{(2/N)} = \rho^2 g
\end{aligned}$$

so

$$\boxed{E = N\left(\tfrac{3}{2}kT + 2\pi\rho\int_0^\infty dr_{12}\; r_{12}^2 U(r_{12}) g(r_{12})\right)}$$

- Recall that the pressure is given by:

$$\begin{aligned} P &= kT\left(\frac{\partial \ln Q_N}{\partial V}\right)_T \qquad \text{but since } Q_N = \left(\frac{2\pi mkT}{h^2}\right)^{3N/2}\frac{1}{N!}Z_N(V,\beta) \\ &= kT\left(\frac{\partial \ln Z_N}{\partial V}\right)_T = \frac{kT}{Z_N}\frac{\partial}{\partial V}\left[\int_V d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})}\right] \end{aligned}$$

  - The partial derivative of $Z_N(V,\beta)$ with respect to V is tricky to evaluate since the volume dependence is in the limits of the integral.
  - Trick: define a coordinate transform $x_i = V^{-1/3} r_i$ for each component of $\mathbf{r}_i$, then $d\mathbf{r}_i = V d\mathbf{x}$, so $d\mathbf{r}^{(N)} = V^N d\mathbf{x}^{(N)}$ with $\mathbf{r}^{(N)} = V^{1/3}\mathbf{x}^{(N)}$. With this transform,

$$Z_N(V,\beta) = V^N \int_{\text{unit sphere}} d\mathbf{x}^{(N)}\, e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})}$$

  - Note that

$$\frac{\partial U(V^{1/3}\mathbf{x}^{(N)})}{\partial V} = \frac{\partial U}{\partial(V^{1/3}\mathbf{x}^{(N)})}\frac{\partial(V^{1/3}\mathbf{x}^{(N)})}{\partial V} = \frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}}\cdot\frac{1}{3V}V^{1/3}\mathbf{x}^{(N)} = \frac{1}{3V}\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}}\cdot\mathbf{r}^{(N)}$$

    so

$$\begin{aligned} \frac{\partial Z_N}{\partial V} &= NV^{N-1}\int_{\text{u.s}} d\mathbf{x}^{(N)}\, e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} + V^N\int d\mathbf{x}^{(N)}\,\frac{\partial}{\partial V}e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} \\ &= \frac{N}{V}V^N\int_{\text{u.s}} d\mathbf{x}^{(N)}\, e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} - V^N\frac{\beta}{3V}\int d\mathbf{x}^{(N)}\left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}}\cdot\mathbf{r}^{(N)}\right)e^{-\beta U(V^{1/3}\mathbf{x}^{(N)})} \\ &= \rho\int_V d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})} - \frac{\beta}{3V}\int d\mathbf{r}^{(N)}\left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}}\cdot\mathbf{r}^{(N)}\right)e^{-\beta U(\mathbf{r}^{(N)})} \\ &= \rho Z_N - \beta\int d\mathbf{r}^{(N)}\,\frac{1}{3V}\left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}}\cdot\mathbf{r}^{(N)}\right)e^{-\beta U(\mathbf{r}^{(N)})} \end{aligned}$$

  - Using this expression in the equation for the pressure gives:

$$\begin{aligned} P &= \frac{kT}{Z_N}\frac{\partial}{\partial V}\left[\int_V d\mathbf{r}^{(N)}\, e^{-\beta U(\mathbf{r}^{(N)})}\right] \\ &= \rho kT - \frac{1}{Z_N}\frac{1}{3V}\int_V d\mathbf{r}^{(N)}\left(\frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}}\cdot\mathbf{r}^{(N)}\right)e^{-\beta U(\mathbf{r}^{(N)})} \end{aligned}$$

  - Now for a pairwise additive potential,

$$\begin{aligned} \frac{\partial U(\mathbf{r}^{(N)})}{\partial \mathbf{r}^{(N)}} \equiv \sum_{k=1}^{N}\frac{\partial U}{\partial \mathbf{r}_k}\cdot\mathbf{r}_k &= \sum_{i<j}\left(\mathbf{r}_i\cdot\frac{\partial U(r_{ij})}{\partial \mathbf{r}\_i} + \mathbf{r}_j\cdot\frac{\partial U(r_{ij})}{\partial \mathbf{r}_j}\right) \\ &= \sum_{i<j}\frac{dU(r_{ij})}{d\mathbf{r}_{ij}}\cdot\mathbf{r}_{ij} \end{aligned}$$

– Thus the pressure equation is:

$$\begin{aligned}
\frac{P}{kT} &= \rho - \frac{\beta}{3V}\frac{\int_V d\mathbf{r}^{(N)} \sum_{i<j} \left(\nabla_{\mathbf{r}_{ij}} U(r_{ij}) \cdot \mathbf{r}_{ij}\right) e^{-\beta U}}{Z_N} \\
&= \rho - \frac{\beta}{3V}\frac{N(N-1)}{2}\frac{\int d\mathbf{r}_1 d\mathbf{r}_2 \left(\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12}\right) \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U}}{Z_N} \\
&= \rho - \frac{\beta}{3V}\frac{N(N-1)}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 \ \left(\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12}\right) \frac{1}{V^2} g^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \\
& \qquad \text{since} g^{(2/N)}(\mathbf{r}_1, \mathbf{r}_2) \approx \frac{V^2 \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U}}{Z_N} \\
&\approx \rho - \rho^2 \frac{\beta}{6V}\int d\mathbf{r}_1 d\mathbf{r}_2 \left(\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12}\right) g(r_{12})
\end{aligned}$$

so we conclude that

$$\boxed{\frac{P}{kT} = \rho - \frac{\beta}{6}\rho^2 \int_V d\mathbf{r}_{12} \ \left(\nabla_{\mathbf{r}_{12}} U(r_{12}) \cdot \mathbf{r}_{12}\right) g(r_{12})}$$

- Note that these equations are *exact* in the thermodynamic limit. All that is required is knowledge of $g(r)$.
- As is evident from this result, an estimator for the pressure is:

$$\begin{aligned}
\Pi_p(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) &= \frac{1}{3V}\sum_{i=1}^{N}\left(\frac{p_i^2}{m} - \sum_{j<i}\left(\nabla_{\mathbf{r}_{ij}} U(r_{ij}) \cdot \mathbf{r}_{ij}\right)\right) \\
\langle \Pi_p(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \rangle &= P \qquad \text{since} \left\langle \frac{\mathbf{p}^{(N)} \cdot \mathbf{p}^{(N)}}{m} \right\rangle = 3NkT.
\end{aligned}$$

- Density expansion of $g(r)$ in pressure equation should give same results as virial expansion.

2 BBGKY Hierarchy

- Can we construct and solve differential equations for the reduced distribution functions?
- Consider the reduced distribution function:

$$\begin{aligned}
\rho^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) &\equiv \frac{N!}{(N-q)!}\frac{\int d\mathbf{r}_{q+1} \cdots d\mathbf{r}_N \, e^{-\beta U}}{Z_N} \\
\nabla_{\mathbf{r}_1} \rho^{(q/N)}(\mathbf{r}_1, \ldots, \mathbf{r}_q) &= \frac{N!}{(N-q)!\, Z_N}\int d\mathbf{r}_{q+1} \cdots d\mathbf{r}_N \ (-\beta \nabla_{\mathbf{r}_1} U) \, e^{-\beta U} \qquad \text{but} \\
\nabla_{\boldsymbol{r}_1} U &= \nabla_{\boldsymbol{r}_1}\left(\sum_{i<j} U(r_{ij})\right) = \nabla_{\boldsymbol{r}_1} \sum_{j=2}^{q} U(r_{1j}) + \sum_{j=q+1}^{N} U(r_{1j}) \qquad \text{so} \\
\nabla_{\boldsymbol{r}_1} \rho^{(q/N)} &= -\frac{N!\beta}{(N-q)!\, Z_N}\left[\sum_{j=2}^{q} \nabla_{\boldsymbol{r}_1} U(r_{1j}) \int d\boldsymbol{r}_{q+1} \cdots d\boldsymbol{r}_N e^{-\beta U}\right. \\
& \qquad \left. + \int d\boldsymbol{r}_{q+1} \cdots d\boldsymbol{r}_N \left(\sum_{j=q+1}^{N} \nabla_{\boldsymbol{r}_1} U(r_{1j})\right) e^{-\beta U}\right]
\end{aligned}$$

Now choosing $j = q+1$, the second term on the r.h.s can be written as

$$
\begin{aligned}
-\frac{\beta(N-q)N!}{(N-q)!\,Z_N}&\int d\boldsymbol{r_{q+1}}\cdots d\boldsymbol{r_N}\;\nabla_{\boldsymbol{r}_1}U(r_{1q+1})e^{-\beta U} \\
&= -\frac{\beta N!}{(N-(q+1))!\,Z_N}\int d\boldsymbol{r}_{q+1}\,\nabla_{\boldsymbol{r}_1}U(r_{1q+1})\int d\boldsymbol{r_{q+2}}\cdots d\boldsymbol{r_N}\,e^{-\beta U} \\
&= -\beta\int d\boldsymbol{r}_{q+1}\,\nabla_{\boldsymbol{r}_1}U(r_{1q+1})\rho^{((q+1)/N)}(\mathbf{r}_1,\ldots,\mathbf{r}_{q+1}).
\end{aligned}
$$

so

$$
\boxed{\nabla_{\boldsymbol{r}_1}\rho^{(q/N)}(\mathbf{r}_1,\ldots\mathbf{r}_q) = -\beta\sum_{j=1}^{q}\nabla_{\boldsymbol{r}_1}U(r_{1j})\rho^{(q/N)} - \beta\int d\boldsymbol{r}_{q+1}\nabla_{\boldsymbol{r}_1}U(r_{1q+1})\rho^{(\frac{q+1}{N})}(\mathbf{r}_1,\ldots,\mathbf{r}_{q+1})}
$$

- Differential equation expresses derivatives of $\rho^{(q/N)}$ to *higher order* reduced distribution.

- Recall that for a uniform system, $\rho^{(q/N)} = \rho^q g^{(q/N)}$, so

$$
\nabla_{\boldsymbol{r}_1}g^{(q/N)}(\mathbf{r}_1,\ldots\mathbf{r}_q) = -\beta\sum_{j=1}^{q}\nabla_{\boldsymbol{r}_1}U(r_{1j})g^{(q/N)} - \beta\rho\int d\boldsymbol{r}_{q+1}\nabla_{\boldsymbol{r}_1}U(r_{1q+1})g^{(\frac{q+1}{N})}(\mathbf{r}_1,\ldots,\mathbf{r}_{q+1})
$$

  and in particular,

$$
\nabla_{\boldsymbol{r}_1}g(r_{12}) = -\beta\left(\nabla_{\boldsymbol{r}_1}U(r_{12})\right)\,g(r_{12}) - \beta\rho\int d\mathbf{r}_3\,\nabla_{\boldsymbol{r}_1}U(r_{13})g^{(3/N)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3).
$$

  - There is a similar equation for $g^{(3/N)}$ that depends on $g^{(4/N)}$. Thus we do not have a closed system of equations.
  - Must make some sort of *closure approximation.*

- **Kirkwood superposition approximation:**

$$
g^{(3/N)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3) \approx g(r_{12})g(r_{13})g(r_{23})
$$

  - Inserting this approximation into equation for the radial distribution function gives:

$$
\nabla_{\boldsymbol{r}_1}g(r_{12}) = -\beta g(r_{12})\left(\nabla_{\boldsymbol{r}_1}U(r_{12})\right) - \beta\rho g(r_{12})\int d\mathbf{r}_3\left(\nabla_{\boldsymbol{r}_1}U(r_{13})\right)g(r_{23})g(r_{13})
$$

    or

$$
\nabla_{\boldsymbol{r}_1}\ln g(r_{12}) = -\beta\nabla_{\boldsymbol{r}_1}U(r_{12}) - \beta\rho\int d\mathbf{r}_3\left(\nabla_{\boldsymbol{r}_1}U(r_{13})\right)g(r_{23})g(r_{13})
$$

  - In the low density limit, the second term is negligible and

$$
\nabla_{\boldsymbol{r}_1}\ln g(r_{12}) = -\beta U(r_{12}) \qquad\Longrightarrow\qquad g(r_{12}) = e^{-\beta U(r_{12})}.
$$

  - Note that the Kirkwood superposition approximation holds exactly in this limit.

- Computer simulations show that the approximation generally works well for gases and some liquids.
- Note that the integro-differential equations are *nonlinear*, and can have complicated behavior.
    * Different closure approximations lead to different predictions. Some work well for some systems but less well for others: called theories of integral equations for liquids and gases.
    * Multiple solutions are possible, and can signify different structure in different phases. For example, the equation for the singlet density $\rho^{(1/N)}(\mathbf{r})$ can be examined for solutions of the form:

    $$\rho^{(1/N)}(\mathbf{r}) = \rho + \sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{r}}\rho(\mathbf{k})$$

    where the emergence of non-zero $\rho(\mathbf{k})$ indicates structure in the singlet density. If the structure is periodic, the density is periodic (i.e. a crystal).

- **The potential of mean force** ω is defined by:

$$\begin{aligned} \rho^{(2/N)}(r_{12}) &= \rho^2 e^{-\beta\omega(r_{12})} \qquad \text{or} \\ g(r_{12}) &= e^{-\beta\omega(r_{12})}. \end{aligned}$$

- From the BBGKY hierarchy and the Kirkwood approximation, we have

$$\nabla_{\boldsymbol{r}_1}\omega(r_{12}) = \nabla_{\boldsymbol{r}_1}U(r_{12}) + \rho\int d\mathbf{r}_3\,\nabla_{\boldsymbol{r}_1}U(r_{13})g(r_{23})g(r_{13}).$$

- What is the physical interpretation of $\nabla_{\boldsymbol{r}_1}\omega(r_{12})$? Consider the mean force on particle 1 when particles 1 and 2 are fixed and all other interactions are averaged:

$$\begin{aligned} \overline{F}_1^{12}(\mathbf{r}_1,\mathbf{r}_2) &= \frac{\int d\boldsymbol{r_3}\cdots d\boldsymbol{r_N}\,\mathbf{F}_1 e^{-\beta U}}{\int d\boldsymbol{r_3}\cdots d\boldsymbol{r_N}\,e^{-\beta U}} = \frac{-\int d\boldsymbol{r_3}\cdots d\boldsymbol{r_N}\,\nabla_{\boldsymbol{r}_1}U e^{-\beta U}}{\int d\boldsymbol{r_3}\cdots d\boldsymbol{r_N}\,e^{-\beta U}} \\ &= \frac{1}{\beta}\frac{\nabla_{\boldsymbol{r}_1}\int d\boldsymbol{r_3}\cdots d\boldsymbol{r_N}\,e^{-\beta U}}{\int d\boldsymbol{r_3}\cdots d\boldsymbol{r_N}\,e^{-\beta U}} = \frac{1}{\beta}\frac{\nabla_{\boldsymbol{r}_1}n^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)}{n^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)} \\ &= \frac{1}{\beta}\frac{\nabla_{\boldsymbol{r}_1}\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)}{\rho^{(2/N)}(\mathbf{r}_1,\mathbf{r}_2)} = \frac{1}{\beta}\nabla_{\boldsymbol{r}_1}\ln\rho^{(2/N)}(r_{12}) = -\nabla_{\boldsymbol{r}_1}\omega(r_{12}) \end{aligned}$$

    * Thus the potential of mean force is the *average effective* two-body potential for the system and gives rise to the mean force acting on a particle when separated from another particle by distance r_{12}.
    * Note that in the low density limit, $\omega(r_{12}) = U(r_{12})$.

3 Measurement of the radial distribution function

- Local changes in polarizability due to density fluctuations lead to non-uniform scattering of light.

– Electrons and nuclei displaced in an electric field induces an oscillating dipole that emits radiation:

$$\mu_i(t) \;=\; \mu(\mathbf{r}_i, t) = \alpha_i E_0 e^{i(\mathbf{k}\cdot\mathbf{r}_i - \omega t)},$$

where μ_i is the induced dipole for particle i located at $\mathbf{r}_i$.

– Can define a total induced dipole for the system as:

$$\begin{aligned}\mu(\mathbf{r}, t) &= \sum_{i=1}^{N} \mu(\mathbf{r}_i, t) \approx \alpha E_0 e^{i(\mathbf{k}\cdot\mathbf{r}_i - \omega_0 t)} \\ &= \alpha E_0 e^{i(\mathbf{k}_0\cdot\mathbf{r} - \omega_0 t)} \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t)) = \alpha E_0(\mathbf{r}, t) N(\mathbf{x}^{(N)}, \mathbf{r}, t)\end{aligned}$$

– Solving Maxwell's equation for the total scattered electric field $E_s(\mathbf{r}, t)$ at position $\mathbf{r}$ far from the sample is complicated, but the solution looks like:

$$E_s(\mathbf{r}, t) \sim \int d\mathbf{r}' \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} d\omega'\, \omega'^2 e^{i(\mathbf{k}\cdot\mathbf{r}' - \omega_0 t)} \exp\left\{ i\omega' \left(t' - t + \frac{r}{c} - \frac{1}{c}\hat{\mathbf{r}}\cdot\mathbf{r}' \right) \right\} N(\mathbf{x}^{(N)}, \mathbf{r}', t')$$

- The measurement process correlates the intensity of the scattered light at different times and time averages:

$$\begin{aligned}I(\mathbf{r}, \omega) &\sim \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \lim_{T\to\infty} \int_{-T}^{T} dt' E_s(\mathbf{r}, t' + \tau) E_s^*(\mathbf{r}, t') \\ &= \int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau} \left\langle E_s(\mathbf{r}, t' + \tau) E_s^*(\mathbf{r}, t') \right\rangle\end{aligned}$$

by the ergodic theorem. Doing lots of math, we get finally

$$I(\mathbf{r}, \omega) \;\sim\; \left(\frac{\alpha}{2\pi c^2 r}\right)^2 S(\mathbf{k}, \Omega)$$

where $\mathbf{k} = \mathbf{k}_0 - (\omega_0/c)\hat{\mathbf{r}}$ and $\Omega = \omega_0 - \omega$ is the frequency shift between the incident and scattered light.

- The *scattering function* $S(\mathbf{k}, \omega)$ is called the *dynamic structure factor* and is given by:

$$\begin{aligned}S(\mathbf{k}, \omega) &\equiv \int_{-\infty}^{-\infty} dt\, e^{i\omega t} \left\langle N(\mathbf{x}^{(N)}, \mathbf{k}, t) N(\mathbf{x}^{(N)}, -\mathbf{k}) \right\rangle \qquad \text{where} \\ N(\mathbf{x}^{(N)}, \mathbf{k}, t) &= \int d\mathbf{r}\, e^{i\mathbf{k}\cdot\mathbf{r}} N(\mathbf{x}, \mathbf{r}, t) = \sum_{i=1}^{N} e^{i\mathbf{k}\cdot r_i(t)}\end{aligned}$$

- This is a *time dependent correlation function.*

- $S(\mathbf{k}, \omega)$ is the Fourier transform in the time domain of $S(\mathbf{k}, t)$, which measures the correlation between the spatial Fourier component of the density at different times.

– Need an effective theory for evaluating dynamics of system: either computer simulation or a model (will discuss later).

- Measurement process can also focuss on *static* correlations:

$$\begin{aligned} I(\mathbf{r}) &\sim \lim_{T\to\infty}\int_{-T}^{T} dt' E_s(\mathbf{r},t')E_s^*(\mathbf{r},t') \\ &\sim \langle E_s(\mathbf{r},0)E_s^*(\mathbf{r},0)\rangle \sim S(\mathbf{k})\delta(\omega-\omega_0) \end{aligned}$$

  – $S(\mathbf{k})$ is called the *static structure factor* and is given by

$$S(\mathbf{k}) \equiv \left\langle N(\mathbf{x}^{(N)},\mathbf{k})N(\mathbf{x}^{(N)},-\mathbf{k})\right\rangle .$$

  – Note that in this measurement $\omega=\omega_0$ meaning that the scattered light has the same frequency as the incident light (i.e no shift). This is called *Rayleigh scattering*.

- What is the relation between $S(\mathbf{k})$ and $g(r)$?

  – Note that from the definition of $S(\mathbf{k})$,

$$\begin{aligned} S(\mathbf{k}) &= \left\langle \sum_{j=1}^{N}\sum_{l=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_j}e^{-i\mathbf{k}\cdot\mathbf{r}_l}\right\rangle = \left\langle N + N(N-1)e^{i\mathbf{k}\cdot(\mathbf{r}_2-\mathbf{r}_1)}\right\rangle \\ &= \langle N\rangle + \int d\mathbf{r}_1 d\mathbf{r}_2\, e^{i\mathbf{k}\cdot\mathbf{r}_{12}}\rho^{(2/N)}(r_{12}) \\ &= \langle N\rangle + V\rho^2\int d\mathbf{r}_{12}e^{i\mathbf{k}\cdot r_{12}}g(r_{12}) \end{aligned}$$

  – There are two contributions to $S(\mathbf{k})$, that due to scattering off the uniform density and that due to fluctuations. That is, we write:

$$N(\mathbf{x}^{(N)},\mathbf{r}) = \rho + \left(N(\mathbf{x}^{(N)},\mathbf{r}) - \langle N(\mathbf{x}^{(N)},\mathbf{r})\rangle\right) \equiv \rho + \hat{N}(\mathbf{x}^{(N)},\mathbf{r}).$$

  Thus

$$\begin{aligned} N(\mathbf{k}) &= \int d\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}\left(\rho+\hat{N}(\mathbf{r})\right) \\ &= \frac{\langle N\rangle}{V}V\delta(k) + \hat{N}(\mathbf{k}) = \langle N\rangle\delta(k) \end{aligned}$$

  and

$$S(\mathbf{k}) = \langle N\rangle^2\delta(k) + \langle \hat{N}(\mathbf{k})\hat{N}(-\mathbf{k})\rangle.$$

  – From the homework problem, the $\mathbf{k}\neq 0$ (non-forward scattering), is related to the radial distribution function by

$$\begin{aligned} \langle \hat{N}(\mathbf{k})\hat{N}(-\mathbf{k})\rangle &= \int d\mathbf{r}d\mathbf{r}'\, e^{i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}'\cdot\mathbf{r}'}\left(\langle N(\mathbf{r})N(\mathbf{r}')\rangle - \langle N(\mathbf{r})\rangle\langle N(\mathbf{r}')\rangle\right) \\ &= \int d\mathbf{r}d\mathbf{r}'\, e^{i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}'\cdot\mathbf{r}'}\left(\rho\delta(\mathbf{r}-\mathbf{r}') + \rho^2(g(|\mathbf{r}-\mathbf{r}'|)-1)\right) \\ &= \langle N\rangle + \langle N\rangle\rho\int d\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}\left(g(r)-1\right) \\ &= \langle N\rangle\left[1+\rho\int d\mathbf{r}e^{i\mathbf{k}\cdot\mathbf{r}}\left(g(r)-1\right)\right] \end{aligned}$$

- From experimental light-scattering measurements of $S(\mathbf{k})$ over a range of values of $\mathbf{k}$, one can invert the Fourier transform and obtain a functional form for $g(r)$!
- Note that when $k = 0$, $\langle \hat{N}(\mathbf{k})\hat{N}(-\mathbf{k})\rangle = \sigma_N^2$ and is related to the compressibility.
- Since the compressibility diverges as a critical point is approached, the integral

  $$\int d\mathbf{r}\,(g(r) - 1) \to \infty$$

  and the function $g(r) - 1$ becomes *long-ranged*. Thus $S(\mathbf{k})$ becomes very large and there is a lot of light scattering. This is called *critical opalescence*.