Two-body density operator $\hat{\rho}_2\left(\underline{x}_1,\underline{x}_2\right)$:

$$\hat{\rho}_2\left(\underline{x}_1,\underline{x}_2\right)\psi\left(\underline{R}\right)=\left(\sum_{i=1}^{N}\sum_{\substack{j=1\\j\neq i}}^{N}\delta\left(\underline{x}_1-\underline{r}_i\right)\delta\left(\underline{x}_2-\underline{r}_j\right)\psi\left(\underline{R}\right)\right)$$

$$=\sum_{i\neq j=1}^{N}\delta\left(\underline{x}_1-\underline{r}_i\right)\delta\left(\underline{x}_1-\underline{r}_j\right)\psi\left(\underline{R}\right)\ (37)$$

Two-body density

$$\left\langle\hat{\rho}_2\left(\underline{x}_1,\underline{x}_2\right)\right\rangle=Tr\left\{\hat{\rho}_2\left(\underline{x}_1,\underline{x}_2\right)\hat{W}\right\}=\rho_2\left(\underline{x}_1,\underline{x}_2\right)\ (38)$$

From equation (24);

$$\hat{\rho}_2\left(\underline{x}_1,\underline{x}_2\right)=\int_{V^N}\left[\hat{\rho}_2\left(\underline{x}_1,\underline{x}_2\right)W\left(\underline{R},\underline{R}'\right)\right]\left(\underline{R}'=\underline{R}\right)d\underline{R}$$

$$=\int_{V^N}\left[\sum_{i\neq j=1}^{N}\delta\left(\underline{x}_1-\underline{r}_i\right)\delta\left(\underline{x}_2-\underline{r}_j\right)W\left(\underline{R},\underline{R}'\right)\right]\left(\underline{R}'=\underline{R}\right)d\underline{R}$$

$$=\sum_{i\neq j=1}^{N}\int_{V^N}\delta\left(\underline{x}_1-\underline{r}_i\right)\delta\left(\underline{x}_2-\underline{r}_j\right)\underbrace{W\left(\underline{R},\underline{R}\right)}_{=P\left(\underline{R}\right)}d\underline{R}$$

$$=\sum_{i\neq j=1}^{N}\int_{V^N}\delta\left(\underline{x}_1-\underline{r}_i\right)\delta\left(\underline{x}_2-\underline{r}_j\right)P\left(\underline{r}_1,\underline{r}_2,...,\underline{r}_i,...,\underline{r}_j,...,\underline{r}_N\right)d\underline{r}_1,d\underline{r}_2,...,d\underline{r}_i,...,d\underline{r}_j,...,d\underline{r}_N$$

$$=\sum_{i\neq j=1}^{N}\int_{V^N}\delta\left(\underline{x}_1-\underline{r}_i\right)\delta\left(\underline{x}_2-\underline{r}_j\right)P\left(\underline{r}_i,\underline{r}_2,...,\underline{r}_1,...,\underline{r}_j,...,\underline{r}_N\right)d\underline{r}_i,d\underline{r}_2,...,d\underline{r}_1,...,d\underline{r}_j,...,d\underline{r}_N$$

$$=\sum_{i\neq j=1}^{N}\int_{V^{N-2}}P\left(\underline{x}_1,\underline{x}_2,...,\underline{r}_1,...,\underline{r}_2,...,\underline{r}_N\right)d\underline{r}_3,...,d\underline{r}_1,...,d\underline{r}_2,...,d\underline{r}_N$$

$$=\sum_{i\neq j=1}^{N}\int_{V^{N-2}}P\left(\underline{x}_1,\underline{x}_2,\underline{r}_3,...,\underline{r}_N\right)d\underline{r}_3,...,d\underline{r}_N$$

In this last step, we are relabelling the integration variables $\underline{r}_1=\underline{r}_i$, $\underline{r}_2=\underline{r}_j$.
We get the same result for all $i\neq j$. It equals the number of ordered pairs $\underbrace{\left(i,j\right)}_{i\neq j}=N\left(N-1\right)$.

$$\rho_2\left(\underline{x}_1,\underline{x}_2\right)=N\left(N-1\right)\int_{V^{N-2}}P\left(\underline{x}_1,\underline{x}_2,\underline{r}_3,...,\underline{r}_N\right)d\underline{r}_3...d\underline{r_N}$$

$$=N\left(N-1\right)\int_{V^{N-2}}W\left(\underline{x}_1,\underline{x}_2,\underline{r}_3,...,\underline{r}_N,\underline{x}_1,\underline{x}_2,\underline{r}_3,...,\underline{r}_N\right)d\underline{r}_3...d\underline{r_N}$$

$$=\left\langle\sum_{i\neq j=1}^{N}\delta\left(\underline{x}_1-\underline{r}_i\right)\delta\left(\underline{x}_2-\underline{r}_j\right)\right\rangle\ (39)$$

$$\int_V\rho\left(\underline{x}\right)d\underline{x}=N\ (35)$$

The above can be extended for the two-body density $\rho_2\left(\underline{x}_1,\underline{x}_2\right)$;

$$\int_{V^2}\rho_2\left(\underline{x}_1,\underline{x}_2\right)d\underline{x}_i d\underline{x}_j=N\left(N-1\right)\ (40)$$

because we have $N\left(N-1\right)$ distinct ordered pairs $\left(i,j\right)$ with $1\leq i\neq j\leq N$.

**Reversion Relations**

$$\int_V \rho_2(\underline{x}_1,\underline{x}_2)\,d\underline{x}_2 = (N-1)\rho(\underline{x}_1) \quad (41)$$

where $N$ is the total number of particles.

$$\int_V \rho_2(\underline{x}_1,\underline{x}_2)\,d\underline{x}_1 = (N-1)\rho(\underline{x}_2) \quad (42)$$

**Exchange Symmetry of Two-Body Density**

$$\rho_2(\underline{x}_1,\underline{x}_2) = \rho_2(\underline{x}_2,\underline{x}_1) \quad (43)$$

$\rho_2(\underline{x}_1,\underline{x}_2)$ is the probability density for a particle to be at $\underline{x}_1$ and another at $\underline{x}_2$.

$\rho_2(\underline{x}_1,\underline{x}_2)d\underline{x}_1 d\underline{x}_2$ is the probability for a particle to be in volume element $d\underline{x}_1 = dx_1dy_1dz_1$ centered at $\underline{x}_1$ and another particle to be in volume element $d\underline{x}_2 = dx_2dy_2dz_2$ centered on $\underline{x}_2$.

**Translational Invariance**

For a liquid, translational invariance yields $\rho(\underline{x}+\underline{a}) = \rho(\underline{x})$ for <u>any</u> 3D translation $\underline{a}$.

→ $\rho(\underline{x}) = \rho_0 = const.$

$$\rho_2(\underline{x}_1+\underline{a},\underline{x}_2+\underline{a}) = \rho_2(\underline{x}_1,\underline{x}_2)$$

for any 3D translation $\underline{a}$.

Take $\underline{a} = -\underline{x}_2$;

$$\rho_2(\underline{x}_1,\underline{x}_2) = \rho_2(\underline{x}_1-\underline{x}_2,0) = \rho_2(\underline{x}_1-\underline{x}_2)$$

For a liquid, $\rho_2(\underline{x}_1,\underline{x}_2)$ is a function of the relative coordinates $\underline{r} = \underline{x}_1-\underline{x}_2$ only.

$$\rho_2(\underline{x}_1,\underline{x}_2) = \rho_2(\underline{x}_1-\underline{x}_2) = \rho_2(\underline{r}) \quad (44)$$

where $\underline{r} = \underline{x}_1-\underline{x}_2$.

**Potential Energy for a Liquid**

From equation (25);

$$E_{pot} = \int_{V^N} V(\underline{R})W(\underline{R},\underline{R})d\underline{R}$$
$$= \frac{1}{2}\sum_{i\neq j=1}^{N}\int_{V^N} v(\underline{r}_{ij})W(\underline{R},\underline{R})d\underline{R}$$

where $v(\underline{r}_{ij}) = v(|\underline{r}_i-\underline{r}_j|)$.

$$E_{pot} = \frac{1}{2}\int_{V^2} v(|\underline{x}_1-\underline{x}_2|)\underbrace{\left[\int_{V^N}\left\{\sum_{i\neq j=1}^{N}\delta(\underline{x}_1-\underline{r}_i)\delta(\underline{x}_2-\underline{r}_j)\right\}W(\underline{R},\underline{R})d\underline{R}\right]}_{\substack{=\left\langle \sum_{i\neq j=1}^{N}\delta(\underline{x}_1-\underline{r}_i)\delta(\underline{x}_2-\underline{r}_j)\right\rangle \\ =\langle\rho_2(\underline{r}_1,\underline{r}_2)\rangle \\ =\rho_2(\underline{x}_1,\underline{x}_2)}} d\underline{x}_1 d\underline{x}_2$$

$$= \frac{1}{2}\int_{V^2}\rho_2(\underline{x}_1,\underline{x}_2)v(|\underline{x}_1-\underline{x}_2|)d\underline{x}_1 d\underline{x}_2 \quad (45)$$

For a liquid,

$$E_{pot} = \frac{1}{2}\int_{V^2}\rho_2(\underline{x}_1-\underline{x}_2)v(|\underline{x}_1-\underline{x}_2|)d\underline{x}_1 d\underline{x}_2$$

$$\rho_2(\underline{x}_1,\underline{x}_2)=\rho_2(\underline{x}_1-\underline{x}_2)=\rho_2(|\underline{r}|)=\rho_2(|\underline{x}_1-\underline{x}_2|)$$

Rotational invariance of a uniform liquid – no directional dependence.

$$\rho_0=\frac{N}{V}=\rho(\underline{x})=const.$$

where $\rho_0$ is the bulk particle number density.

$$\rho_2(r)=\rho_0{}^2 g(r)$$

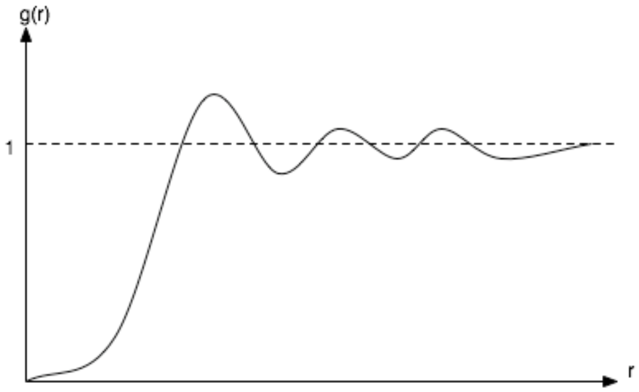
where $g(r)$ is the radial distribution function,

$$g(r)=\frac{\rho_2(r)}{\rho_0{}^2}$$

Let $\varepsilon_{pot}=\frac{E_{pot}}{N}$ be the potential energy per particle. Then,

$$\varepsilon_{pot}=2\pi\rho_0\int_0^\infty g(r)v(r)dr \quad (46)$$

where the $2\pi$ is due to the factor $\frac{1}{2}$ in $E_{pot}$.




$$\xrightarrow[|\underline{x}_1-\underline{x}_2|\to\infty]{\lim}\rho_2(\underline{x}_1,\underline{x}_2)=\rho(\underline{x}_1)\rho(\underline{x}_2)=\rho_0{}^2$$

as particles don't interact over a large distance. The last part of this is true for a liquid.

$$\xrightarrow[r\to\infty]{\lim}\frac{\rho_2(\underline{r})}{\rho_0{}^2}=\xrightarrow[r\to\infty]{\lim}\frac{\rho_0{}^2}{\rho_0{}^2}=1=\xrightarrow[r\to\infty]{\lim}g(r)$$

## 3. Path Integral Representation of the Density Matrix

Coordinate Space Representation of Operators = Coordinate Space Elements of Operators (more generally).

$$\hat{O}_{\underline{R}}\psi(\underline{R})=\tilde{\psi}(\underline{R})=\int_{V^N}\tilde{\psi}(\underline{R}')\delta(\underline{R}'-\underline{R})d\underline{R}'$$

where $\delta(\underline{R}'-\underline{R})$ is a 3N-dimensional delta function.

$$\begin{aligned}\tilde{\psi}(\underline{R}')&=\hat{O}_{\underline{R}'}\psi(\underline{R}')\\&=\int_{V^N}\left[\hat{O}_{\underline{R}'}\psi(\underline{R}')\right]\delta(\underline{R}'-\underline{R})d\underline{R}'\\&=\int_{V^N}\psi(\underline{R}')\left[\hat{O}_{\underline{R}'}\delta(\underline{R}'-\underline{R})\right]d\underline{R}'\end{aligned}$$

$$O(\underline{R},\underline{R}') = \hat{O}_{\underline{R}'}\delta(\underline{R}' - \underline{R})$$

(Apply operator $\hat{O}$ to variable $\underline{R}'$ in the three-dimensional delta function $\delta(\underline{R}' - \underline{R})$)

$$\hat{O}\psi(\underline{R}) = \int_{V^N} O(\underline{R},\underline{R}')\psi(\underline{R}')d\underline{R}' \quad (47)$$

$$O(\underline{R},\underline{R}') = \hat{O}_{\underline{R}'}\delta(\underline{R}' - \underline{R})$$

$O(\underline{R},\underline{R}')$ is the matrix elements of $\hat{O}$ in coordinate space representation of $\hat{O}$.

$$\delta(\underline{R}' - \underline{R}) = \delta(\underline{r}_1' - \underline{r}_1)\delta(\underline{r}_2' - \underline{r}_2)...\delta(\underline{r}_N' - \underline{r}_N)$$
$$= \delta(x_1' - x_1)\delta(y_1' - y_1)\delta(z_1' - z_1)\delta(x_2' - x_2)\delta(y_2' - y_2)\delta(z_2' - z_2)$$
$$...\delta(x_N' - x_N)\delta(y_N' - y_N)\delta(z_N' - z_N)$$

This is the 3N-dimensional Dirac delta function.

$$\int_{V^N} \delta(\underline{R}' - \underline{R})\psi(\underline{R}')d\underline{R}' = \psi(\underline{R})$$
$$= \int_{V^N} \prod_{i=1}^{N} \delta(\underline{r}_i' - \underline{r}_i)\psi(\underline{r}_1', \underline{r}_2', ..., \underline{r}_N')d\underline{r}_1' d\underline{r}_2' ... d\underline{r}_N'$$
$$= \psi(\underline{r}_1, \underline{r}_2, ..., \underline{r}_N) \quad (49)$$

$$\int_{V^N} \delta(\underline{R}' - \underline{R})\psi(\underline{R})d\underline{R} = \psi(\underline{R}')$$

$$\int_{V^N} \delta(\underline{R}' - \underline{R})d\underline{R}' = 1 \quad (50)$$

$$\int_{V^N} \delta(\underline{R}' - \underline{R})d\underline{R} = 1$$