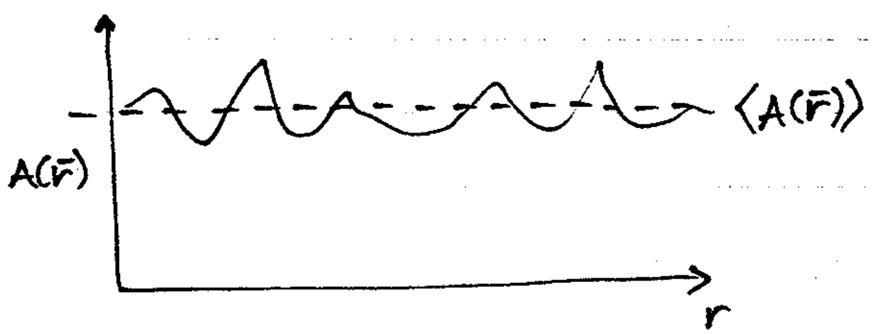
SPACE CORRELATION FUNCTIONS

Let $A(\bar{r})$ be a spatially varying property

$$\langle A(\bar{r})\rangle = \frac{1}{V}\int A(\bar{r})\,d\bar{r} \qquad \text{classical ensemble average}$$

$\langle A(\bar{r})\rangle$ is independent of $\bar{r}$, but $A(\bar{r})$ varies:



DEFINE:

$$C_{AA}(\bar{r},\bar{r}') = \langle A(\bar{r})A(\bar{r}')\rangle \qquad \text{for fixed time, } t \quad \langle A(\bar{r},t)\,A(\bar{r}',t)\rangle$$

also $\quad \delta A(\bar{r}) = A(\bar{r}) - \langle A(\bar{r})\rangle$

$$C_{\delta A\delta A}(\bar{r},\bar{r}') = \langle \delta A(\bar{r})\,\delta A(\bar{r}')\rangle$$

PROPERTIES of Space Correlation Functions

1. $C_{AA}(\bar{r},\bar{r}) = \langle A^2(\bar{r})\rangle \geq 0$

   $C_{\delta A\delta A}(\bar{r},\bar{r}) = \langle \delta A^2(\bar{r})\rangle \geq 0$

2. $C_{AA}(\bar{r},\bar{r}') = C_{AA}(\bar{r}-\bar{r}')$ for a homogeneous system.

   for A scalar and isotropic

   $$C_{AA}(\bar{r},\bar{r}') = C_{AA}(|\bar{r}-\bar{r}'|)$$

3. If $\bar{r}-\bar{r}'$ is large, then variations in position become uncorrelated.

   $$\lim_{\bar{r}-\bar{r}'\to\infty} C_{AA}(\bar{r},\bar{r}') = \langle A(\bar{r})\rangle\langle A(\bar{r}')\rangle = \langle A^2\rangle$$

   $$\lim_{\bar{r}-\bar{r}'\to\infty} C_{\delta A\delta A}(\bar{r},\bar{r}') = 0 \quad \text{since} \quad \langle \delta A(\bar{r})\rangle = 0$$

4. For classical mechanics

   $$C_{AA}(\bar{r},\bar{r}') = C_{AA}(\bar{r}',\bar{r})$$

   $$C_{AA}(\bar{r}) = C_{AA}(-\bar{r})$$

EXAMPLE: Atomic Liquid $\quad A(\bar{r}) \equiv n(\bar{r})$ number density

$$n(\bar{r}) = \sum_i \delta(\bar{r}-\bar{r}_i)$$

$\bar{r}_i$ is the position of the i^{th} atom.

Spatial ensemble average

$$\frac{1}{V}\int d\bar{r} \sum_{i=1}^{N} \delta(\bar{r}-\bar{r}_i) = \frac{N}{V} = \rho$$

average number density

$$C_{nn}(\bar{r},\bar{r}') = \langle n(\bar{r})\, n(\bar{r}')\rangle$$

$$= \sum_{i,j=1}^{N} \langle \delta(\bar{r}-\bar{r}_i)\, \delta(\bar{r}'-\bar{r}_j)\rangle$$

$$= N \langle \delta(\bar{r}-\bar{r}_i)\,\delta(\bar{r}-\bar{r}_i)\rangle \qquad i=j$$

$$+ N(N-1)\langle \delta(\bar{r}-\bar{r}_i)\,\delta(\bar{r}-\bar{r}_j)\rangle \qquad i\neq j$$

Two terms:

1) $i=j$ $\quad N\langle \delta(\bar{r}-\bar{r}_i)\,\delta(\bar{r}-r_i)\rangle$

$$= N\int d\bar{r}_i\, \delta(\bar{r}-\bar{r}_i)\,\delta(\bar{r}'-\bar{r}_i) = N\int d\bar{r}_i\, \delta(\bar{r}-\bar{r}')\,\delta(\bar{r}-\bar{r}_i)$$

$$= \frac{N}{V}\,\delta(\bar{r}-\bar{r}') = \rho\,\delta(\bar{r}-\bar{r}')$$

2) $i \neq j$ $\quad N(N-1)\langle \delta(\bar{r}-\bar{r}_i)\,\delta(\bar{r}'-\bar{r}_j)\rangle$

$$= N(N-1)\int d\bar{r}_i \int d\bar{r}_j\; \delta(\bar{r}-\bar{r}_i)\,\delta(\bar{r}'-\bar{r}_j)$$

all pairwise correlations with $(i \neq j)$

$$\equiv \frac{N^2}{V^2}\, g(\bar{r},\bar{r}') = \rho^2 g(\bar{r},\bar{r}')$$

$g(\bar{r},\bar{r}')$ is the radial pair distribution function, which describes spatial correlation between molecules.

$$\therefore\; C_{nn}(\bar{r},\bar{r}') = \rho\,\delta(\bar{r}-\bar{r}') + \rho^2 g(\bar{r},\bar{r}')$$

<u>Properties</u> of $g(\bar{r},\bar{r}') = g(|\bar{r}-\bar{r}'|)$

1. as $|\bar{r}-\bar{r}'| \to \infty$ $\quad C_{NN}(\bar{r},\bar{r}') \to \frac{N^2}{V^2}$ $\quad g(\bar{r},\bar{r}') \to 1$

2. as $|r-r'| \to 0$ $\quad g \to 0$ (repulsive forces)