Fluctuation and scattering

Masatsugu Sei Suzuki
Department of Physics, SUNY at Binghamton
(Date: November 17, 2018)

Here we discuss the fluctuations. We also show how the fluctuation can be measured by using the x-ray diffraction and neutron scattering.

1. Average number:

$$Z_G = \sum_{N=0} z^N Z_{CN}(\beta)$$

$$\frac{\partial Z_G}{\partial z} = \sum_{N=0} N z^{N-1} Z_{CN}(\beta)$$

or

$$z\frac{1}{Z_G}\frac{\partial Z_G}{\partial z} = z\frac{\partial \ln Z_G}{\partial z} = \frac{1}{Z_G}\sum_{N=0} N z^N Z_{NC}(\beta) = \langle N \rangle$$

Note that

$$z\frac{\partial}{\partial z} = z\frac{\partial \mu}{\partial z}\frac{\partial}{\partial \mu} = z\frac{1}{\frac{\partial z}{\partial \mu}}\frac{\partial}{\partial \mu} = \frac{z}{\beta z}\frac{\partial}{\partial \mu} = k_B T\frac{\partial}{\partial \mu}$$

where $z = e^{\beta\mu}$, $\qquad \frac{\partial z}{\partial \mu} = \beta e^{\beta\mu} = \beta z$

Thus we have

$$\boxed{\langle N \rangle_G = z\frac{\partial \ln Z_G}{\partial z} = k_B T\left(\frac{\partial}{\partial \mu}\ln Z_G\right)_{T,V}}$$

or

$$\boxed{\langle N \rangle_G = \frac{z}{Z_G}\frac{\partial Z_G}{\partial z} = z\frac{\partial \ln Z_G}{\partial z}}$$

2. Variance in the number

$$z\frac{\partial Z_G}{\partial z} = \sum_{N=0} N z^N Z_{CN}(\beta)$$

$$z\frac{\partial}{\partial z} z\frac{\partial Z_G}{\partial z} = \sum_{N=0} N^2 z^N Z_{CN}(\beta) = Z_G\left\langle N^2 \right\rangle$$

$$\left\langle N^2 \right\rangle_G = \frac{z}{Z_G}\frac{\partial}{\partial z} z\frac{\partial Z_G}{\partial z} = \frac{(k_B T)^2}{Z_G}\frac{\partial^2 Z_G}{\partial \mu^2}$$

Then we have

$$\begin{aligned}
\left(\Delta N\right)^2 &= \left\langle N^2 \right\rangle_G - \left\langle N \right\rangle_G{}^2 \\
&= \frac{(k_B T)^2}{Z_G}\frac{\partial^2 Z_G}{\partial \mu^2} - \left(k_B T\right)^2 \left(\frac{1}{Z_G}\frac{\partial Z_G}{\partial \mu}\right)^2 \\
&= (k_B T)^2 [\frac{1}{Z_G}\frac{\partial^2 Z_G}{\partial \mu^2} - \frac{1}{Z_G{}^2}\left(\frac{\partial Z_G}{\partial \mu}\right)^2] \\
&= (k_B T)^2 \frac{\partial}{\partial \mu}(\frac{1}{Z_G}\frac{\partial Z_G}{\partial \mu}) \\
&= (k_B T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2}
\end{aligned}$$

Note that

$$\frac{\partial \left\langle N \right\rangle_G}{\partial \mu} = k_B T \frac{\partial^2 \ln Z_G}{\partial \mu^2} = \frac{1}{k_B T}\left(\Delta N\right)^2$$

or

$$\boxed{\left(\Delta N\right)^2 = k_B T \frac{\partial \left\langle N \right\rangle_G}{\partial \mu}}$$

or

$$(\Delta N)^2 = z\frac{\partial \langle N \rangle_G}{\partial z}$$

where $z = e^{\beta\mu}$, $\beta\mu = \ln z$

$$z\frac{\partial}{\partial z} = z\frac{\partial \mu}{\partial z}\frac{\partial}{\partial \mu} = z\frac{1}{\beta z}\frac{\partial}{\partial \mu} = \frac{1}{\beta}\frac{\partial}{\partial \mu} = k_B T\frac{\partial}{\partial \mu}$$

3. Number density

We define the density n as

$$n = \frac{\langle N \rangle_G}{V}, \qquad \langle N \rangle_G = nV$$

$$\frac{\partial n}{\partial \mu} = \frac{1}{V}\frac{\partial \langle N \rangle_G}{\partial \mu} = \frac{1}{k_B TV}(\Delta N)^2$$

So the variance of number is given by

$$V\frac{\partial n}{\partial \mu} = \frac{1}{k_B T}(\Delta N)^2, \quad \text{or} \quad \frac{\partial n}{\partial \mu} = \frac{1}{k_B TV}(\Delta N)^2$$

or

$$(\Delta N)^2 = k_B T\frac{\partial n}{\partial \mu}V$$

or

$$\Delta N = \sqrt{k_B T\frac{\partial n}{\partial \mu}V}$$

Thus we have

$$\frac{\Delta N}{\langle N \rangle} = \frac{\sqrt{k_B T\frac{\partial n}{\partial \mu}V}}{nV} = \frac{\sqrt{k_B T\frac{\partial n}{\partial \mu}}}{n}\frac{1}{\sqrt{V}}$$

4. Grand potential

$$\Phi_G = -PV = -k_B T \ln Z_G = F - G$$

$$d\Phi_G = -SdT - PdV - \langle N \rangle_G \, d\mu$$

$$\langle N \rangle_G = -\left(\frac{\partial \Phi_G}{\partial \mu} \right)_{T,V} = k_B T \left(\frac{\partial \ln Z_G}{\partial \mu} \right)_{T,V}$$

$$\langle N \rangle_G = \left(\frac{\partial PV}{\partial \mu} \right)_{T,V} = V \left(\frac{\partial P}{\partial \mu} \right)_{T,V}$$

The number density n is

$$n = \frac{\langle N \rangle_G}{V} = \left(\frac{\partial P}{\partial \mu} \right)_{T,V}$$

5. Isothermal compressibility

The isothermal compressibility is defined by

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,\langle N \rangle}$$

$$\left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \left(\frac{\partial \langle N \rangle}{\partial \mu} \right)_{\alpha}$$

with

$$\alpha = T, V$$

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_\alpha = \frac{\partial(\langle N\rangle,\alpha)}{\partial(\mu,\alpha)}$$

$$= \frac{\partial(\langle N\rangle,\alpha)}{\partial(P,\alpha)}\frac{\partial(P,\alpha)}{\partial(\mu,\alpha)}$$

$$= \left(\frac{\partial\langle N\rangle}{\partial P}\right)_\alpha \left(\frac{\partial P}{\partial\mu}\right)_\alpha$$

$$= \left(\frac{\partial\langle N\rangle}{\partial P}\right)_{T,V} \left(\frac{\partial P}{\partial\mu}\right)_{T,V}$$

Using the relation, $\left(\frac{\partial P}{\partial\mu}\right)_{T,V} = \frac{\langle N\rangle}{V} = n$, we have

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{\langle N\rangle}{V}\left(\frac{\partial\langle N\rangle}{\partial P}\right)_{T,V} = \langle N\rangle\left(\frac{\partial}{\partial P}\frac{\langle N\rangle}{V}\right)_{T,V}$$

We note that

$$n = \frac{\langle N\rangle}{V} = f(P,T)$$

is a function of *P* and *T*. In fact, for ideal gas, we have

$$\frac{\langle N\rangle}{V} = \frac{P}{k_B T}$$

Thus it does not matter whether $\frac{\langle N\rangle}{V}$ is differentiated at constant $\langle N\rangle$ or constant *V*.

or

$$\left(\frac{\partial}{\partial P}\frac{\langle N\rangle}{V}\right)_{T,\langle N\rangle} = \left(\frac{\partial}{\partial P}\frac{\langle N\rangle}{V}\right)_{T,V}$$

Then we have

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \langle N\rangle\left(\frac{\partial}{\partial P}\frac{\langle N\rangle}{V}\right)_{T,V}$$

$$= \langle N\rangle\left(\frac{\partial}{\partial P}\frac{\langle N\rangle}{V}\right)_{T,\langle N\rangle}$$

$$= -\langle N\rangle^2\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_{T,\langle N\rangle}$$

Using the definition of κ_T; $\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\langle N\rangle}$, we have

$$\left(\frac{\partial\langle N\rangle}{\partial\mu}\right)_{T,V} = \frac{\langle N\rangle^2}{V}\kappa_T$$

Thus we get

$$(\Delta N)^2 = k_B T\frac{\partial\langle N\rangle}{\partial\mu}$$

$$= \langle N\rangle[\frac{\langle N\rangle}{V}k_B T]\kappa_T$$

$$= \langle N\rangle n k_B T\kappa_T$$

Since the compressibility of an ideal gas is

$$\kappa_T{}^0 = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,\langle N\rangle} = \frac{1}{nk_B T}$$

Thus we have

$$\frac{\kappa_T}{\kappa_T{}^0} = \frac{(\Delta N)^2}{\langle N\rangle}$$

6. Density fluctuation

The number density is defined by

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

$$N = \int n(\boldsymbol{r}) d\boldsymbol{r}$$

In a volume V, the average number of atoms is given by

$$\langle N \rangle = \int \langle n(\boldsymbol{r}) \rangle d\boldsymbol{r} \, .$$

If the system is homogeneous in space, $\langle n(\boldsymbol{r}) \rangle$ does not depend on the position:

$$\langle n(\boldsymbol{r}) \rangle = n$$

Then we get

$$\langle N \rangle = nV \qquad \text{or} \qquad n = \frac{\langle N \rangle}{V}$$

Now let us consider the fluctuation of the number of atoms in volume V,

$$\langle N^2 \rangle = \iint \langle n(\boldsymbol{r}) n(\boldsymbol{r}') \rangle d\boldsymbol{r} d\boldsymbol{r}'$$

$$\langle n(\boldsymbol{r}) n(\boldsymbol{r}') \rangle = \left\langle \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \delta(\boldsymbol{r}' - \boldsymbol{r}_i) \right\rangle + \left\langle \sum_i \sum_{j \neq i} \delta(\boldsymbol{r} - \boldsymbol{r}_i) \delta(\boldsymbol{r}' - \boldsymbol{r}_j) \right\rangle$$

The first term $\qquad I_1 = \iint \left\langle \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \delta(\boldsymbol{r}' - \boldsymbol{r}_i) \right\rangle d\boldsymbol{r} d\boldsymbol{r}'$

In this term the integrand is not zero only for $\boldsymbol{r} = \boldsymbol{r}_i$ and $\boldsymbol{r}' = \boldsymbol{r}_i$, or $\qquad \boldsymbol{r} = \boldsymbol{r}'$

$$\sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \delta(\boldsymbol{r}' - \boldsymbol{r}_i) = \sum_i \delta(\boldsymbol{r} - \boldsymbol{r}_i) \delta(\boldsymbol{r} - \boldsymbol{r}')$$

Then we have

$$
\begin{aligned}
I_1 &= \iint \left\langle \sum_i \delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}-\boldsymbol{r}') \right\rangle d\boldsymbol{r}d\boldsymbol{r}' \\
&= \int \left\langle \sum_i \delta(\boldsymbol{r}-\boldsymbol{r}_i) \right\rangle d\boldsymbol{r} \\
&= \int \langle n(\boldsymbol{r})\rangle d\boldsymbol{r} \\
&= nV \\
&= \langle N\rangle
\end{aligned}
$$

The second term: $I_2 = \iint \left\langle \sum_i \delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_i) \right\rangle d\boldsymbol{r}d\boldsymbol{r}'$

$$
\langle n(\boldsymbol{r})n(\boldsymbol{r}')\rangle = n^2 = \left(\frac{\langle N\rangle}{V}\right)^2 \qquad \text{for } |\boldsymbol{r}-\boldsymbol{r}'| \to \infty
$$

$$
\left\langle \sum_i \sum_{j\neq i} \delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_j) \right\rangle = \left(\frac{\langle N\rangle}{V}\right)^2 g(s) = n^2 g(s)
$$

with

$$
s = |\boldsymbol{r}-\boldsymbol{r}'|
$$

When the system is large, the correlation usually vanishes for $s \to \infty$, and we have

$$
g(s) \to 1
$$

$g(s)$ is called the radial distribution function. Then we have

$$
\begin{aligned}
\langle N^2\rangle &= \langle N\rangle + \iint \left(\frac{\langle N\rangle}{V}\right)^2 g(\boldsymbol{s})d\boldsymbol{r}d\boldsymbol{r}' \\
&= \langle N\rangle + \left(\frac{\langle N\rangle}{V}\right)^2 \iint d\boldsymbol{r}d\boldsymbol{r}' + \left(\frac{\langle N\rangle}{V}\right)^2 \iint [g(\boldsymbol{s})-1]d\boldsymbol{r}d\boldsymbol{s} \\
&= \langle N\rangle + \langle N\rangle^2 + V\left(\frac{\langle N\rangle}{V}\right)^2 \int [g(\boldsymbol{s})-1]d\boldsymbol{s}
\end{aligned}
$$

Thus we have

$$(\Delta N)^2 = \langle N \rangle + \frac{\langle N \rangle^2}{V}\int [g(\boldsymbol{s}) - 1] d\boldsymbol{s}$$

$$\begin{aligned}
\frac{(\Delta N)^2}{\langle N \rangle} &= \frac{\langle N \rangle^2 - \langle N \rangle^2}{\langle N \rangle} \\
&= 1 + \frac{\langle N \rangle}{V}\int [g(\boldsymbol{r}) - 1] d\boldsymbol{r} \\
&= 1 + n\int [g(\boldsymbol{r}) - 1] d\boldsymbol{r}
\end{aligned}$$

((**Note**))

$$\begin{aligned}
\iint \langle n(\boldsymbol{r}) n(\boldsymbol{r}') \rangle d\boldsymbol{r} d\boldsymbol{r}' &= V\int \langle n(\boldsymbol{r}) n(0) \rangle d\boldsymbol{r} \\
&= V[n + \int n^2 g(\boldsymbol{r}) d\boldsymbol{r}]
\end{aligned}$$

or

$$\int \langle n(\boldsymbol{r}) n(0) \rangle d\boldsymbol{r} = n + \int n^2 g(\boldsymbol{r}) d\boldsymbol{r}$$

or

$$\langle n(\boldsymbol{r}) n(0) \rangle = n\delta(\boldsymbol{r}) + n^2 g(\boldsymbol{r})$$

A divergent compressibility neat T_c corresponds mathematically to an increase in the range of the pair correlation function $G(\boldsymbol{r} - \boldsymbol{r}')$. Sufficiently close to T_c, the correlation length becomesas long as the wavelength of light and the density inhomogenities scatter light strongly., leading to the optical opalescene.

In summary
The three phenomena which are observed near the critical point,

(i) increase in the density fluctuations
(ii) increase in the compressibility
(iii) increase in the range of the density-density correlation function

are all interrelated phenomena.

7. Scattering Intensity:

The scattering intensity is

$$\begin{aligned}
\frac{I(\boldsymbol{Q})}{I_0(\boldsymbol{Q})} &= \frac{1}{\langle N\rangle}\left\langle \sum_{i,j} \exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)]\right\rangle \\
&= \frac{1}{\langle N\rangle}\iint d\boldsymbol{r}d\boldsymbol{r}'\left\langle \sum_{i,j} \delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_i)\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}_i-\boldsymbol{r}_j)]\right\rangle \\
&= \frac{1}{\langle N\rangle}\iint d\boldsymbol{r}d\boldsymbol{r}'\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')]\left\langle \sum_{i,j} \delta(\boldsymbol{r}-\boldsymbol{r}_i)\delta(\boldsymbol{r}'-\boldsymbol{r}_i)\right\rangle \\
&= \frac{1}{\langle N\rangle}\iint d\boldsymbol{r}d\boldsymbol{r}'\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')]\langle n(\boldsymbol{r})n(\boldsymbol{r}')\rangle
\end{aligned}$$

Here we note that

$$\begin{aligned}
\langle N^2\rangle &= \iint d\boldsymbol{r}d\boldsymbol{r}'\langle n(\boldsymbol{r})n(\boldsymbol{r}')\rangle \\
&= V\int d\boldsymbol{r}\langle n(\boldsymbol{r})n(0)\rangle \\
&= \langle N\rangle + \frac{\langle N\rangle^2}{V}\int d\boldsymbol{r}g(\boldsymbol{r})
\end{aligned}$$

or

$$\langle n(\boldsymbol{r})n(0)\rangle = n\delta(\boldsymbol{r}) + n^2 g(\boldsymbol{r})$$

The first term: correlation function between the same particles.
The second term: correlation function between the different particles.

$$\begin{aligned}
\frac{I(\boldsymbol{Q})}{I_0(\boldsymbol{Q})} &= \frac{1}{\langle N\rangle}\iint d\boldsymbol{r}d\boldsymbol{r}'\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')]\langle n(\boldsymbol{r}-\boldsymbol{r}')n(0)\rangle \\
&= \frac{V}{\langle N\rangle}\int d\boldsymbol{r}\exp(i\boldsymbol{Q}\cdot\boldsymbol{r})\langle n(\boldsymbol{r})n(0)\rangle \\
&= \frac{1}{n}\int d\boldsymbol{r}\exp(i\boldsymbol{Q}\cdot\boldsymbol{r})[n\delta(\boldsymbol{r}) + n^2 g(\boldsymbol{r})] \\
&= 1 + n\int d\boldsymbol{r}\exp(i\boldsymbol{Q}\cdot\boldsymbol{r})g(\boldsymbol{r})
\end{aligned}$$

where n is the number density,

$$n = \frac{N}{V}$$

It is customary to omit the first term,

$$\frac{I(\boldsymbol{Q})}{I_0(\boldsymbol{Q})} = S(\boldsymbol{Q}) = n\int d\boldsymbol{r}\,\exp(i\boldsymbol{Q}\cdot\boldsymbol{r})g(\boldsymbol{r})$$

$S(\boldsymbol{Q})$;	Structure factor which is the Fourier transform of correlation function.
$g(\boldsymbol{r})$;	Correlation function.

8. x-ray scattering

Suppose that

$$n(\boldsymbol{r}) = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{q}}\exp(i\boldsymbol{q}\cdot\boldsymbol{r})n_{\boldsymbol{q}}$$

$$n(\boldsymbol{r}') = \frac{1}{\sqrt{V}}\sum_{\boldsymbol{q}'}\exp(i\boldsymbol{q}'\cdot\boldsymbol{r}')n_{\boldsymbol{q}'}$$

Thus we get

$$\langle n(\boldsymbol{r})n(\boldsymbol{r}')\rangle = \frac{1}{V}\sum_{\boldsymbol{q},\boldsymbol{q}'}\exp(i\boldsymbol{q}\cdot\boldsymbol{r})\exp(i\boldsymbol{q}'\cdot\boldsymbol{r}')\langle n_{\boldsymbol{q}}n_{\boldsymbol{q}'}\rangle$$

$$\langle n(\boldsymbol{r})n(\boldsymbol{r}')\rangle = \langle n(\boldsymbol{r}-\boldsymbol{r}')n(0)\rangle$$

$$\begin{aligned}\iint d\boldsymbol{r}d\boldsymbol{r}'\langle n(\boldsymbol{r})n(\boldsymbol{r}')\rangle\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')] &= \iint d\boldsymbol{r}d\boldsymbol{r}'\langle n(\boldsymbol{r}-r')n(0))\rangle\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')]\\ &= V\int d\boldsymbol{r}''\langle n(\boldsymbol{r}'')n(0))\rangle\exp(i\boldsymbol{Q}\cdot\boldsymbol{r}'')\\ &= V\int d\boldsymbol{r}\langle n(\boldsymbol{r})n(0))\rangle\exp(i\boldsymbol{Q}\cdot\boldsymbol{r})\\ &= V\int d\boldsymbol{r}g(\boldsymbol{r})\exp(i\boldsymbol{Q}\cdot\boldsymbol{r})\end{aligned}$$

We also have

$$\iint d\boldsymbol{r}d\boldsymbol{r}'\langle n(\boldsymbol{r})n(\boldsymbol{r}')\rangle \exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')] = \iint d\boldsymbol{r}d\boldsymbol{r}'\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')]$$
$$\times\frac{1}{V}\sum_{\boldsymbol{q},\boldsymbol{q}'}\exp(i\boldsymbol{q}\cdot\boldsymbol{r})\exp(i\boldsymbol{q}'\cdot\boldsymbol{r}')\langle n_{q}n_{q'}\rangle$$

and

$$\iint d\boldsymbol{r}d\boldsymbol{r}'\exp[i\boldsymbol{Q}\cdot(\boldsymbol{r}-\boldsymbol{r}')]\exp(i\boldsymbol{q}\cdot\boldsymbol{r})\exp(i\boldsymbol{q}'\cdot\boldsymbol{r}') = \int d\boldsymbol{r}\exp[i(\boldsymbol{Q}+\boldsymbol{q})\cdot r]$$
$$\times\int d\boldsymbol{r}'\exp[i(-\boldsymbol{Q}+\boldsymbol{q}')\cdot r']$$
$$= V^{2}\delta(\boldsymbol{Q}+\boldsymbol{q})\delta(-\boldsymbol{Q}+\boldsymbol{q}')$$

From these two equations, we get

$$V\int d\boldsymbol{r}n^{2}g(\boldsymbol{r})\exp(i\boldsymbol{Q}\cdot\boldsymbol{r}) = \frac{1}{V}\sum_{\boldsymbol{q},\boldsymbol{q}'}V^{2}\delta(\boldsymbol{Q}+\boldsymbol{q})\delta(-\boldsymbol{Q}+\boldsymbol{q}')\langle n_{q}n_{q'}\rangle$$
$$= V\langle n_{-\boldsymbol{Q}}n_{\boldsymbol{Q}}\rangle$$

or

$$\int d\boldsymbol{r}n^{2}g(\boldsymbol{r})\exp(i\boldsymbol{Q}\cdot\boldsymbol{r}) = \langle n_{-\boldsymbol{Q}}n_{\boldsymbol{Q}}\rangle$$

where

$$n^{2}g(\boldsymbol{r}) = \langle n(\boldsymbol{r})n(0)\rangle$$

Thus the intensity is equal to

$$S(\boldsymbol{Q}) = \frac{1}{n}\int d\boldsymbol{r}\exp(i\boldsymbol{Q}\cdot\boldsymbol{r})n^{2}g(\boldsymbol{r}) = \frac{1}{n}\langle n_{-\boldsymbol{Q}}n_{\boldsymbol{Q}}\rangle = \frac{1}{n}\langle|n_{\boldsymbol{Q}}|^{2}\rangle = \frac{1}{n}\langle|n_{-\boldsymbol{Q}}|^{2}\rangle$$

since $n_{-\boldsymbol{Q}} = n_{\boldsymbol{Q}}{}^{*}$. We note that the Fourier transform of $n(\boldsymbol{r})$ is given by

$$
\begin{aligned}
n_{-Q} &= \frac{1}{\sqrt{V}} \sum_{\boldsymbol{r}} \exp(i\boldsymbol{Q}\cdot\boldsymbol{r}) n(\boldsymbol{r}) \\
&= \frac{1}{\sqrt{V}} \sum_{\boldsymbol{r}} \exp(i\boldsymbol{Q}\cdot\boldsymbol{r}) \sum_{i} \delta(\boldsymbol{r}-\boldsymbol{r}_i) \\
&= \frac{1}{\sqrt{V}} \sum_{i} \exp(i\boldsymbol{Q}\cdot\boldsymbol{r}_i)
\end{aligned}
$$

((**Example**))

When

$$g(r) = \frac{1}{r} e^{-\kappa r}$$

with

$$\kappa = \frac{1}{\xi}$$

where ξ is the correlation length. The Fourier transformation of $g(\boldsymbol{r})$ is

$$
\begin{aligned}
I &= \int d^3\boldsymbol{r}\, e^{i\boldsymbol{Q}\cdot\boldsymbol{r}} g(\boldsymbol{r}) \\
&= \int 2\pi r^2 dr \int_0^{\pi} \sin\theta d\theta \frac{e^{-\kappa r}}{r} e^{iQr\cos\theta} \\
&= \int 2\pi r^2 \frac{e^{-\kappa r}}{r} dr \int_0^{\pi} \sin\theta d\theta e^{iQr\cos\theta}
\end{aligned}
$$

Here we calculate

$$J = \int_0^{\pi} \sin\theta d\theta e^{iQr\cos\theta}$$

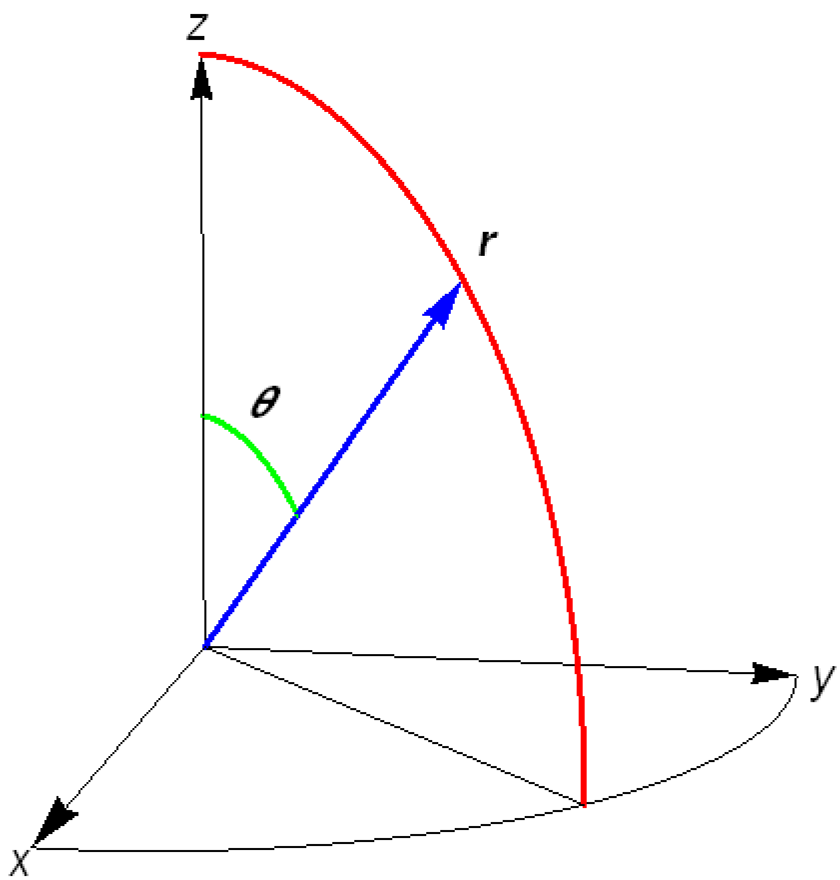
We put $x = \cos\theta$. $dx = -\sin\theta d\theta$

$$J = \int_{-1}^{1} dx e^{iQrx} = [\frac{e^{iQrx}}{iQr}]_{-1}^{1} = \frac{1}{iQr}(e^{iQr} - e^{-iQr}) = \frac{2\sin(Qr)}{Qr}$$

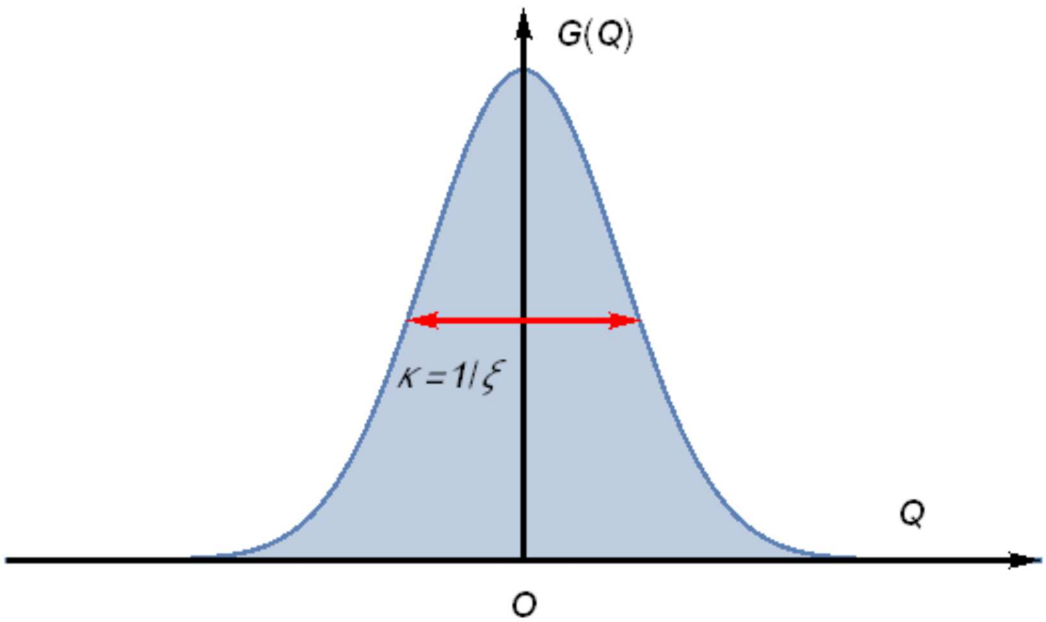
Then we have

$$
\begin{aligned}
I &= \int_0^\infty 2\pi r^2 \frac{e^{-\kappa r}}{r} \frac{2\sin(Qr)}{Qr} dr \\
&= \frac{2\pi}{iQ} \int_0^\infty [e^{(-\kappa+iQ)r} - e^{-(\kappa+iQ)r}] dr \\
&= \frac{2\pi}{iQ} \left(\frac{1}{\kappa - iQ} - \frac{1}{\kappa + iQ}\right) \\
&= \frac{4\pi}{\kappa^2 + Q^2} \\
&= \langle n_{-Q} n_Q \rangle
\end{aligned}
$$

Lorentzian line shape



Fluctuation and correlation



APPENDIX

Isothermal compressibility κ_T

$$
\begin{aligned}
(\Delta N)^2 &= \left\langle (N - \langle N \rangle)^2 \right\rangle \\
&= \frac{\partial \langle N \rangle}{\partial (\beta\mu)} \\
&= k_B T \frac{\partial \langle N \rangle}{\partial \mu}
\end{aligned}
$$

Using the relation

$$\langle N \rangle = k_B T \frac{\partial}{\partial \mu} \ln Z_G$$

we get the expression of number fluctuation as

$$(\Delta N)^2 = k_B{}^2 T^2 \frac{\partial^2}{\partial \mu^2} \ln Z_G \,|_{T,V}$$

((**Note**))

$$\Phi_G = -PV = -k_B T \ln Z_G = F - G$$

$$d\Phi_G = -SdT - PdV - \langle N \rangle d\mu$$

$$\langle N \rangle = -\left(\frac{\partial \Phi_G}{\partial \mu}\right)_{T,V} = \left(\frac{\partial (PV)}{\partial \mu}\right)_{T,V} = V\left(\frac{\partial P}{\partial \mu}\right)_{T,V}$$

or

$$n = \frac{\langle N \rangle}{V} = \left(\frac{\partial P}{\partial \mu}\right)_{T,V}$$