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:**

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

or

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

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

Note that

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

where \( z = e^{\beta \mu} \), \( \frac{\partial z}{\partial \mu} = \beta e^{\beta \mu} = \beta z \)

Thus we have

\[
\langle N \rangle_G = z \frac{\partial}{\partial z} \ln Z_G = k_B T \left( \frac{\partial}{\partial \mu} \ln Z_G \right)_{T,F}
\]

or

\[
\langle N \rangle_G = \frac{z}{Z_G} \frac{\partial Z_G}{\partial z} = z \frac{\partial}{\partial z} \ln Z_G
\]
2. **Variance in the number**

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

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

\[
\langle N^2 \rangle_G = z \frac{\partial}{\partial z} \frac{\partial Z_G}{\partial z} = \frac{(k_b T)^2}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2}
\]

Then we have

\[
(\Delta N)^2 = \langle N^2 \rangle_G - \langle N \rangle_G^2
\]

\[
= \left(\frac{k_b T}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} \right)^2 - \left(\frac{1}{Z_G} \frac{\partial Z_G}{\partial \mu} \right)^2
\]

\[
= (k_b T)^2 \frac{1}{Z_G} \frac{\partial^2 Z_G}{\partial \mu^2} \left( \frac{\partial Z_G}{\partial \mu} \right)^2
\]

\[
= (k_b T)^2 \frac{\partial^2 \ln Z_G}{\partial \mu^2}
\]

Note that

\[
\frac{\partial \langle N \rangle_G}{\partial \mu} = k_b T \frac{\partial^2 \ln Z_G}{\partial \mu^2} = \frac{1}{k_b T} (\Delta N)^2
\]

or

\[
(\Delta N)^2 = k_b T \frac{\partial \langle N \rangle_G}{\partial \mu}
\]

or
\[(\Delta N)^2 = z \frac{\partial \langle N \rangle_G}{\partial z}\]

where \[z = e^{\beta \mu}, \quad \beta \mu = \ln z\]

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

3. **Number density**

We define the density \(n\) as

\[n = \frac{\langle N \rangle_G}{V}, \quad \langle N \rangle_G = nV\]

\[\frac{\partial n}{\partial \mu} = \frac{1}{V} \frac{\partial \langle N \rangle_G}{\partial \mu} = \frac{1}{k_B T V} (\Delta N)^2\]

So the variance of number is given by

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

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

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

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

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

with

\[ \alpha = T, V \]
\[
\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_a = \frac{\partial \langle N \rangle, \alpha}{\partial (\mu, \alpha)} = \frac{\partial (\langle N \rangle, \alpha)}{\partial (P, \alpha)} \frac{\partial (P, \alpha)}{\partial (\mu, \alpha)} = \left( \frac{\partial \langle N \rangle}{\partial P} \right)_a \left( \frac{\partial P}{\partial \mu} \right)_a = \left( \frac{\partial \langle N \rangle}{\partial P} \right)_{T,Y} \left( \frac{\partial P}{\partial \mu} \right)_{T,Y}
\]

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

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

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

\[
\left( \frac{\partial \langle N \rangle}{\partial P} \right)_{T,\langle N \rangle} = \left( \frac{\partial \langle N \rangle}{\partial P} \right)_{T,Y}
\]

Then we have
\[
\left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{T,V} = \langle N \rangle \left( \frac{\partial \langle N \rangle}{\partial P} \frac{\partial}{\partial V} \right)_{T,V} \\
= \langle N \rangle \left( \frac{\partial \langle N \rangle}{\partial P} \frac{1}{V} \right)_{T,\langle N \rangle} \\
= -\langle N \rangle^2 \frac{1}{V^2} \left( \frac{\partial V}{\partial P} \right)_{T,\langle N \rangle}
\]

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

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

Thus we get

\[
(\Delta N)^2 = k_b T \frac{\partial \langle N \rangle}{\partial \mu} \\
= \langle N \rangle \left( \frac{\partial \langle N \rangle}{\partial \mu} \right) \frac{k_b T}{V} \kappa_T \\
= \langle N \rangle nk_b T \kappa_T
\]

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

\[
n(n) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)
\]
\[ N = \int n(r)dr \]

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

\[ \langle N \rangle = \int \langle n(r) \rangle dr . \]

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

\[ \langle n(r) \rangle = n \]

Then we get

\[ \langle N \rangle = nV \quad \text{or} \quad n = \frac{\langle N \rangle}{V} \]

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

\[ \langle N^2 \rangle = \iint \langle n(r)n(r') \rangle drdr' \]

\[ \langle n(r)n(r') \rangle = \left( \sum_i \delta(r - r_i)\delta(r' - r_i) \right) + \left( \sum_{i,j} \delta(r - r_i)\delta(r' - r_j) \right) \]

The first term

\[ I_1 = \iint \left( \sum_i \delta(r - r_i)\delta(r' - r_i) \right) drdr' \]

In this term the integrand is not zero only for \( r = r_i \) and \( r' = r_i \), or \( r = r' \)

\[ \sum_i \delta(r - r_i)\delta(r' - r_i) = \sum_i \delta(r - r_i)\delta(r - r') \]

Then we have
\[ I_1 = \iint \left( \sum_i \delta(r - r_i) \delta(r - r') \right) dr dr' \]
\[ = \int \left( \sum_i \delta(r - r_i) \right) dr \]
\[ = \int \langle n(r) \rangle dr \]
\[ = nV \]
\[ = \langle N \rangle \]

The second term:
\[ I_2 = \iint \left( \sum_i \delta(r - r_i) \delta(r' - r_j) \right) dr dr' \]
\[ \langle n(r)n(r') \rangle = n^2 = \left( \frac{\langle N \rangle}{V} \right)^2 \quad \text{for } |r - r'| \to \infty \]
\[ \left( \sum_i \sum_{j \neq i} \delta(r - r_i) \delta(r' - r_j) \right) = \left( \frac{\langle N \rangle}{V} \right)^2 g(s) = n^2 g(s) \]

with
\[ s = |r - r'| \]

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
\[ \langle N^2 \rangle = \langle N \rangle + \iint \left( \frac{\langle N \rangle}{V} \right)^2 g(s) dr dr' \]
\[ = \langle N \rangle + \left( \frac{\langle N \rangle}{V} \right)^2 \iint dr dr' + \left( \frac{\langle N \rangle}{V} \right)^2 \iiint [g(s) - 1] dr ds \]
\[ = \langle N \rangle + \langle N \rangle^2 + V \left( \frac{\langle N \rangle}{V} \right)^2 \int [g(s) - 1] ds \]
Thus we have

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

\[
\frac{(\Delta N)^2}{\langle N \rangle} = \frac{\langle N \rangle^2 - \langle N \rangle^2}{\langle N \rangle}
\]

\[
= 1 + \frac{\langle N \rangle}{V} \int [g(r) - 1] dr
\]

\[
= 1 + n \int [g(r) - 1] dr
\]

((Note))

\[
\int \int \langle n(r) n(r') \rangle dr dr' = V \int \langle n(r) n(0) \rangle dr
\]

\[
= V [n + \int n^2 g(r) dr]
\]

or

\[
\int \langle n(r) n(0) \rangle dr = n + \int n^2 g(r) dr
\]

or

\[
\langle n(r) n(0) \rangle = n \delta(r) + n^2 g(r)
\]

A divergent compressibility near \( T_c \) corresponds mathematically to an increase in the range of the pair correlation function \( G(r - r') \). Sufficiently close to \( T_c \), the correlation length becomes as long as the wavelength of light and the density inhomogeneities scatter light strongly, leading to the optical opalescence.

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

\[
\frac{I(Q)}{I_0(Q)} = \frac{1}{\langle N \rangle} \left\langle \sum_{i,j} \exp[iQ \cdot (r_i - r_j)] \right\rangle \\
= \frac{1}{\langle N \rangle} \left[ \int dr dr' \sum_{i,j} \delta(r - r_i)\delta(r' - r_j) \exp[iQ \cdot (r_i - r_j)] \right] \\
= \frac{1}{\langle N \rangle} \left[ \int dr dr' \exp[iQ \cdot (r - r')] \sum_{i,j} \delta(r - r_i)\delta(r' - r_j) \right] \\
= \frac{1}{\langle N \rangle} \left[ \int dr dr' \exp[iQ \cdot (r - r')] \langle n(r)n(r') \rangle \right]
\]

Here we note that

\[
\langle N^2 \rangle = \int dr dr' \langle n(r)n(r') \rangle \\
= V \int dr \langle n(r)n(0) \rangle \\
= \langle N \rangle + \frac{\langle N \rangle^2}{V} \int dr \rho(r)
\]

or

\[
\langle n(r)n(0) \rangle = n \delta(r) + n^2 g(r)
\]

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

\[
\frac{I(Q)}{I_0(Q)} = \frac{1}{\langle N \rangle} \left[ \int dr dr' \exp[iQ \cdot (r - r')] \langle n(r-r')n(0) \rangle \right] \\
= \frac{V}{\langle N \rangle} \int dr \exp(iQ \cdot r) \langle n(r)n(0) \rangle \\
= \frac{1}{n^2} \int dr \exp(iQ \cdot r) [n \delta(r) + n^2 g(r)] \\
= 1 + n \int dr \exp(iQ \cdot r) g(r)
\]

where \( n \) is the number density,
\[ n = \frac{N}{V} \]

It is customary to omit the first term,

\[ \frac{I(Q)}{I_0(Q)} = S(Q) = n \int dr \exp(iQ \cdot r) g(r) \]

\( S(Q) \); Structure factor which is the Fourier transform of correlation function.

\( g(r) \); Correlation function.

**8. x-ray scattering**

Suppose that

\[ n(r) = \frac{1}{\sqrt{V}} \sum_q \exp(iq \cdot r)n_q \]

\[ n(r') = \frac{1}{\sqrt{V}} \sum_q \exp(iq' \cdot r')n_q' \]

Thus we get

\[ \langle n(r)n(r') \rangle = \frac{1}{V} \sum_{qq'} \exp(iq \cdot r) \exp(iq' \cdot r') \langle n_q n_{q'} \rangle \]

\[ \langle n(r)n(r') \rangle = \langle n(r - r')n(0) \rangle \]

\[ \int \int drdr'\langle n(r)n(r') \rangle \exp[iQ \cdot (r - r')] = \int \int drdr'\langle n(r - r')n(0) \rangle \exp[iQ \cdot (r - r')] \]

\[ = V \int dr''\langle n(r'')n(0) \rangle \exp(iQ \cdot r'') \]

\[ = V \int dr\langle n(r)n(0) \rangle \exp(iQ \cdot r) \]

\[ = V \int drg(r) \exp(iQ \cdot r) \]

We also have
\[ \iint drdr' \langle n(r)n(r') \rangle \exp[i \mathbf{Q} \cdot (r - r')] = \iint drdr' \exp[i \mathbf{Q} \cdot (r - r')] \times \frac{1}{V} \sum_{q,q'} \exp(iq \cdot r) \exp(iq' \cdot r') \langle n_q n_{q'} \rangle \]

and

\[ \iint drdr' \exp[i \mathbf{Q} \cdot (r - r')] \exp(iq \cdot r) \exp(iq' \cdot r') = \int dr \exp[i (\mathbf{Q} + q) \cdot r] \times \int dr' \exp[i (-\mathbf{Q} + q') \cdot r'] = V^2 \delta(\mathbf{Q} + q) \delta(-\mathbf{Q} + q') \]

From these two equations, we get

\[ V \int drn^2 g(r) \exp(i \mathbf{Q} \cdot r) = \frac{1}{V} \sum_{q,q'} V^2 \delta(\mathbf{Q} + q) \delta(-\mathbf{Q} + q') \langle n_q n_{q'} \rangle = V \langle n_0 n_0 \rangle \]

or

\[ \int drn^2 g(r) \exp(i \mathbf{Q} \cdot r) = \langle n_0 n_0 \rangle \]

where

\[ n^2 g(r) = \langle n(r)n(0) \rangle \]

Thus the intensity is equal to

\[ S(\mathbf{Q}) = \frac{1}{n} \int dr \exp(i \mathbf{Q} \cdot r)n^2 g(r) = \frac{1}{n} \langle n_0 n_0 \rangle = \frac{1}{n} \langle n_0^2 \rangle = \frac{1}{n} \langle n_0^2 \rangle \]

since \( n_0 = n_0^* \). We note that the Fourier transform of \( n(r) \) is given by
\[ n_{-q} = \frac{1}{\sqrt{V}} \sum_r \exp(iQ \cdot r)n(r) \]
\[ = \frac{1}{\sqrt{V}} \sum_r \exp(iQ \cdot r)\sum_i \delta(r - r_i) \]
\[ = \frac{1}{\sqrt{V}} \sum_i \exp(iQ \cdot r_i) \]

((Example))

When
\[ g(r) = \frac{1}{r} e^{-\kappa r} \]

with
\[ \kappa = \frac{1}{\xi} \]

where \( \xi \) is the correlation length. The Fourier transformation of \( g(r) \) is

\[ I = \int d^3r \ e^{iQ \cdot r} g(r) \]
\[ = \int 2\pi r^2 dr \sin \theta d\theta \ e^{-\kappa r} \ e^{iQr \cos \theta} \]
\[ = \int 2\pi r^2 \ e^{-\kappa r} \ e^{iQr \cos \theta} \]
\[ J = \int_0^\pi \sin \theta d\theta e^{iQr \cos \theta} \]

Here we calculate

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

We put \( x = \cos \theta \), \( dx = -\sin \theta d\theta \)

\[ J = \int_{-1}^1 dx e^{iQrx} = \left[ \frac{e^{iQrx}}{iQr} \right]_{-1} = \frac{1}{iQr} (e^{iQr} - e^{-iQr}) = \frac{2\sin(Qr)}{Qr} \]
Then we have

\[
I = \int_0^{\infty} 2\pi r^2 e^{-\kappa r} \frac{2\sin(Qr)}{Qr} dr
\]

\[
= \frac{2\pi}{iQ} \int_0^{\infty} \left[ e^{-(\kappa+iQ)r} - e^{-(\kappa+iQ)r} \right] dr
\]

\[
= \frac{2\pi}{iQ} \left( \frac{1}{\kappa - iQ} - \frac{1}{\kappa + iQ} \right)
\]

\[
= \frac{4\pi}{\kappa^2 + Q^2}
\]

\[
= \langle n_{-\Delta} n_Q \rangle
\]

Lorentzian line shape
APPENDIX

Isothermal compressibility $\kappa_T$

$$(\Delta N)^2 = \langle (N - \langle N \rangle)^2 \rangle$$

$$= \frac{\partial \langle N \rangle}{\partial (\beta \mu)}$$

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

Using the relation

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

we get the expression of number fluctuation as
\[ (\Delta N)^2 = k_b^2 T^2 \frac{\partial^2}{\partial \mu^2} \ln Z_G \big|_{T,V} \]

((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

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