

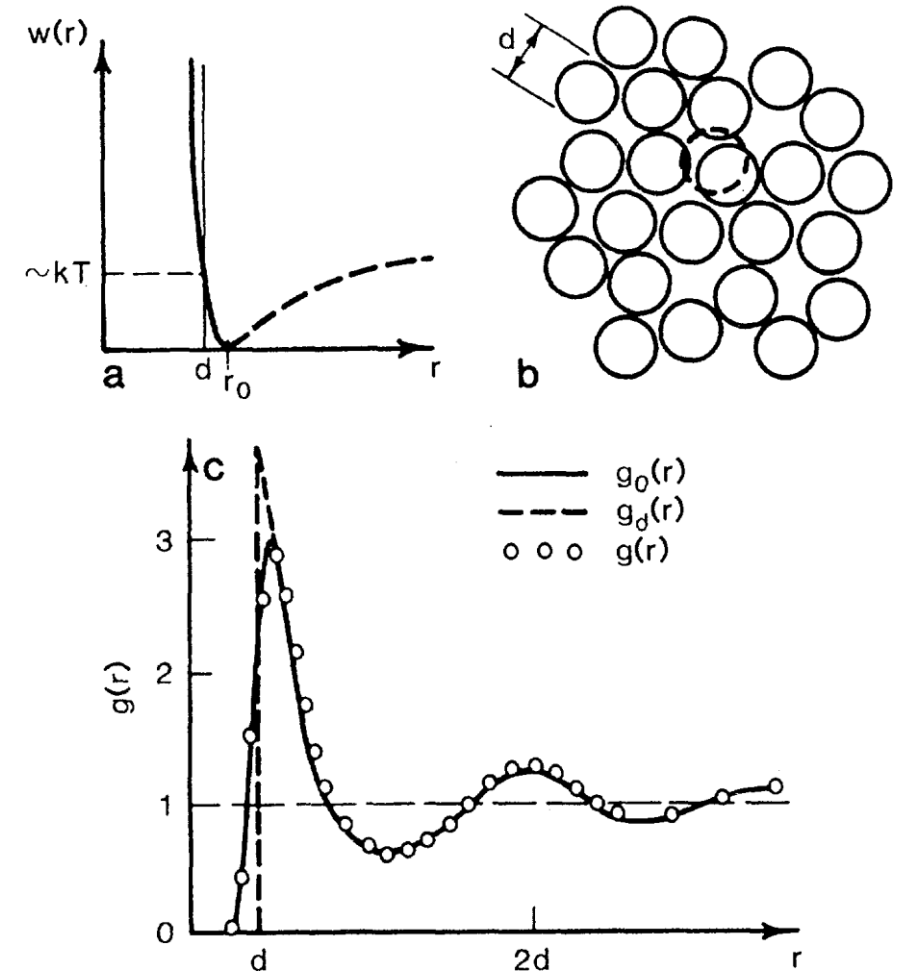


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## The Ornstein–Zernike function

# Recapitulation: Density operators

- One particle  $n(r) = \langle \sum_i \delta(r - r_i) \rangle$
- Two particle  $n(r, r') = \langle \sum_{i \neq j} \delta(r - r_i) \delta(r' - r_j) \rangle$ ,  
the correlation of a particle with other particles.
- Pair correlation function  $g(r, r') = \frac{n(r, r')}{n(r)n(r')}$
- A typical  $W$  is the Lennard-Jones (LJ) potential:
- $w(r) = w_0 \left[ \left( \frac{r}{\sigma} \right)^{12} - \left( \frac{r}{\sigma} \right)^6 \right]$



# Pair correlation function can be measured experimentally

- Pair correlation function  $g(r, r') = \frac{n(r, r')}{n(r)n(r')}$
- In scattering experiments, one can measure
- $S(k) = \sum \exp(ik \cdot r_{jl}) / N$
- $S(k) = \int \frac{dr dr'}{N} \langle n(r)n(r') \rangle e^{i k(r-r')} = 1 + n \int (g - 1) e^{i k(r-r')}$
- The compressibility  $n kT \chi = \frac{kT}{\partial p / \partial n} = 1 + n \int d^3 r (g - 1)$  can be related to the zero  $q$  limit of  $S(q)$ !



## Direct correlation function

### Direct correlation function

Alternative definition

Graphical representation

Experimental  $c(q)$

Experimental  $c(r)$

Physical meaning of OZ function

Correlations in the critical region

Power series for  $c(q)$

Structure factor

Total correlation

Summary

- In 1914, Ornstein and Zernike introduced a function  $c(\vec{r})$  through the definition

$$c(\vec{q}) = 1 - \frac{1}{S(\vec{q})} \quad \text{or} \quad S(\vec{q}) = \frac{1}{1 - c(\vec{q})},$$

where<sup>1</sup>

$$c(\vec{q}) = n \int d^3r \exp(-i\vec{q} \cdot \vec{r}) c(\vec{r}).$$

- Why did they do this?



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$$c(\vec{q}) = n \int d^3r \exp(-i\vec{q} \cdot \vec{r}) c(\vec{r}).$$

- Why did they do this?
- We know that the structure factor of a fluid diverges at small  $q$  near the critical point.
- From the above definition, a divergence of  $S(\vec{q})$  means that

$$c(\vec{q}) \approx 1.$$

- Hence, the quantity  $c(\vec{q})$  is useful for investigating the limit  $q \rightarrow 0$  near the critical point.
- The function  $c(\vec{r})$  is called the **direct correlation function** or the Ornstein–Zernike function.

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<sup>1</sup>An extra factor of  $n$  is included here, to make both  $c(\vec{q})$  and  $c(\vec{r})$  dimensionless.



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- In an alternative approach, we start by defining the **total correlation function**

$$h(\vec{r}) \equiv g(\vec{r}) - 1.$$

- Since  $g(\vec{r}) = 1$  for an ideal gas, the correlations generated by particle interactions are reflected in a nonzero value of  $h$ .



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- Since  $g(\vec{r}) = 1$  for an ideal gas, the correlations generated by particle interactions are reflected in a nonzero value of  $h$ .
- We can then define the direct correlation function  $c(\vec{r})$  through the integral equation

$$h(\vec{r}) = c(\vec{r}) + n \int d^3r' c(\vec{r} - \vec{r}')h(\vec{r}'),$$

which is called the **Ornstein–Zernike equation**.





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- If we now multiply by  $n$  and take a Fourier transform, we obtain

$$S(\vec{q}) - 1 = c(\vec{q}) + c(\vec{q})[S(\vec{q}) - 1],$$

since  $S(\vec{q}) - 1$  is the Fourier transform of  $nh(\vec{r}) = n[g(\vec{r}) - 1]$ .



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- Hence, the Ornstein–Zernike equation is equivalent to the relations

$$S(\vec{q}) = \frac{1}{1 - c(\vec{q})}, \quad c(\vec{q}) = 1 - \frac{1}{S(\vec{q})}.$$



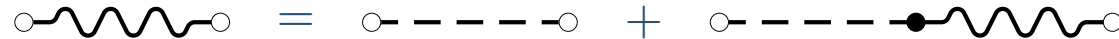
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- We can represent the Ornstein–Zernike equation

$$h(\vec{r}_1 - \vec{r}_2) = c(\vec{r}_1 - \vec{r}_2) + n \int d^3 r_3 c(\vec{r}_1 - \vec{r}_3) h(\vec{r}_3 - \vec{r}_2)$$

by the following graph:



- Here a wavy line represents  $h$ , a dashed line represents  $c$ , and a filled circle represents integration ( $n \int d^3 r$ ).



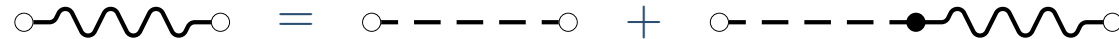
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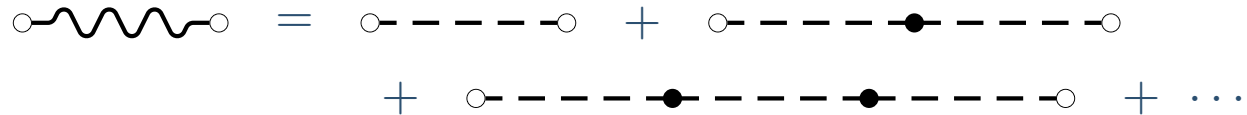
- We can represent the Ornstein–Zernike equation

$$h(\vec{r}_1 - \vec{r}_2) = c(\vec{r}_1 - \vec{r}_2) + n \int d^3 r_3 c(\vec{r}_1 - \vec{r}_3) h(\vec{r}_3 - \vec{r}_2)$$

by the following graph:



- Here a wavy line represents  $h$ , a dashed line represents  $c$ , and a filled circle represents integration ( $n \int d^3 r$ ).
- By iterating, we obtain

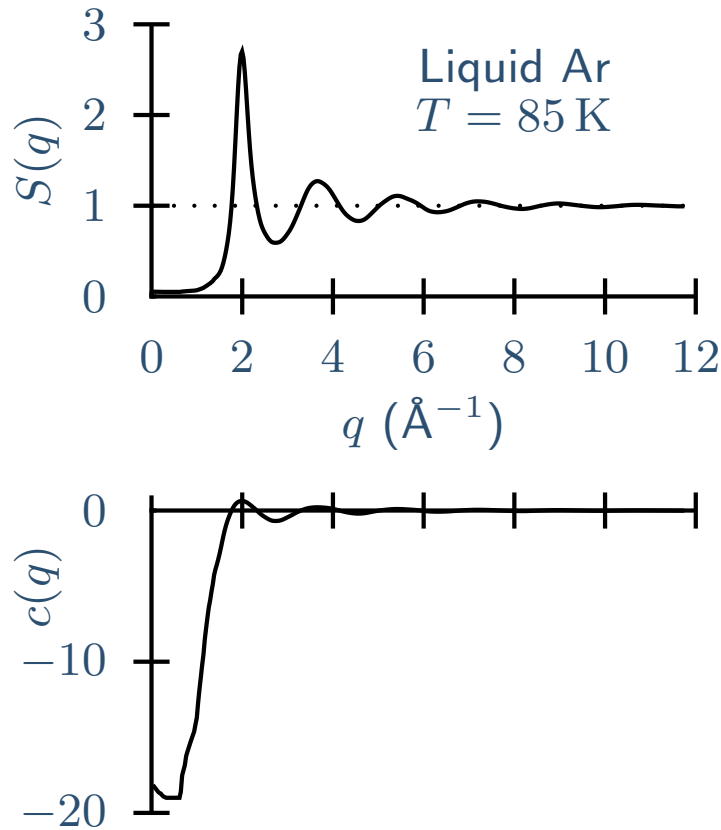


- That is,  $h$  can be written as an infinite series involving only the Ornstein–Zernike function  $c$ .



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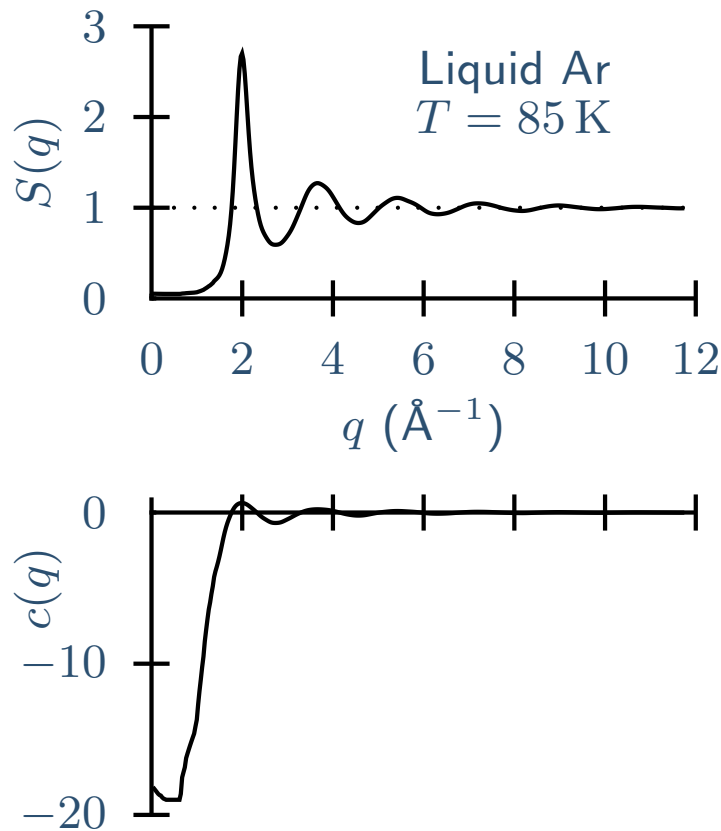
- What does experiment tell us?
- Consider the structure factor  $S(q)$  away from the critical point.
- We can use  $S(q)$  to find the Ornstein–Zernike function via

$$c(q) = 1 - \frac{1}{S(q)}.$$



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$$c(q) = 1 - \frac{1}{S(q)}.$$

- The direct correlation function  $c(r)$  is then given by the Fourier series

$$c(\vec{r}) = \frac{1}{nV} \sum_{\vec{q}} c(\vec{q}) \exp(i\vec{q} \cdot \vec{r}).$$

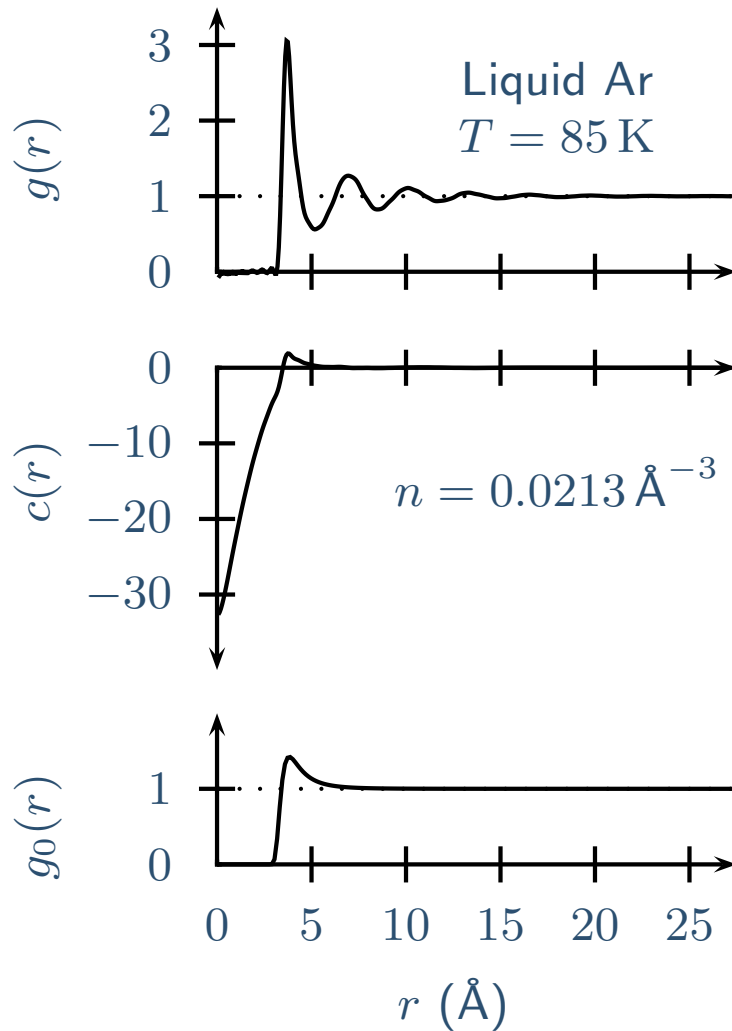
- In the thermodynamic limit  $V \rightarrow \infty$ , the sum becomes an integral:

$$c(\vec{r}) = \frac{1}{n(2\pi)^3} \int d^3q c(\vec{q}) \exp(i\vec{q} \cdot \vec{r}).$$



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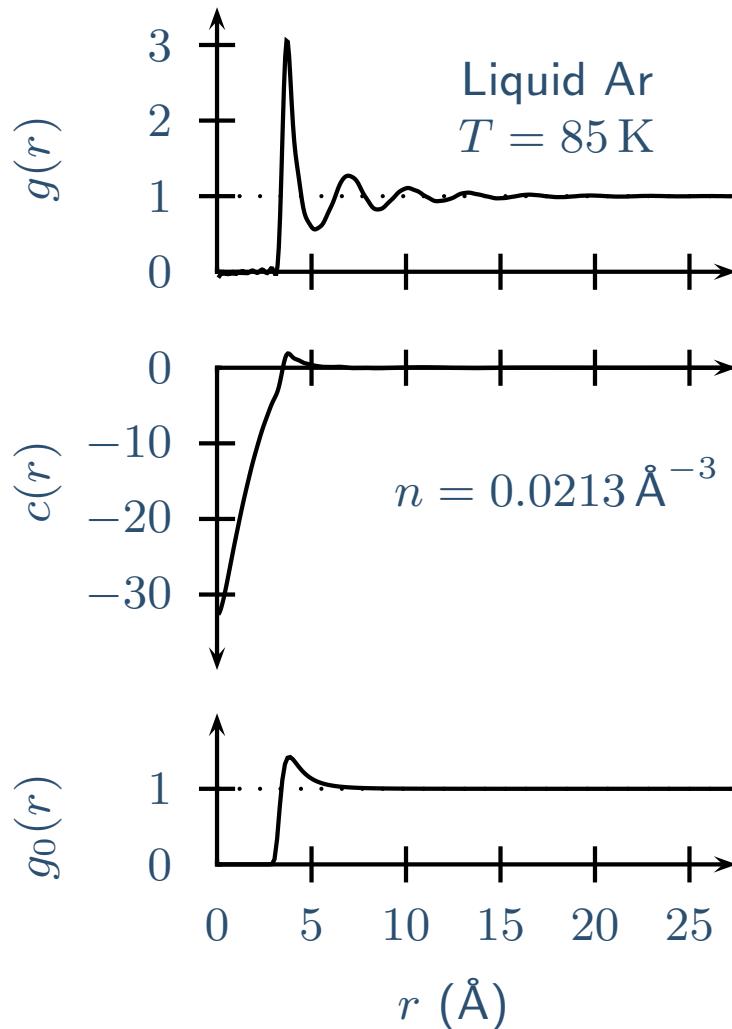


- The results for  $c(r)$  are compared with the measured  $g(r)$  in the figures on the left.

# Experimental $c(r)$



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- The results for  $c(r)$  are compared with the measured  $g(r)$  in the figures on the left.
- Also shown is the function

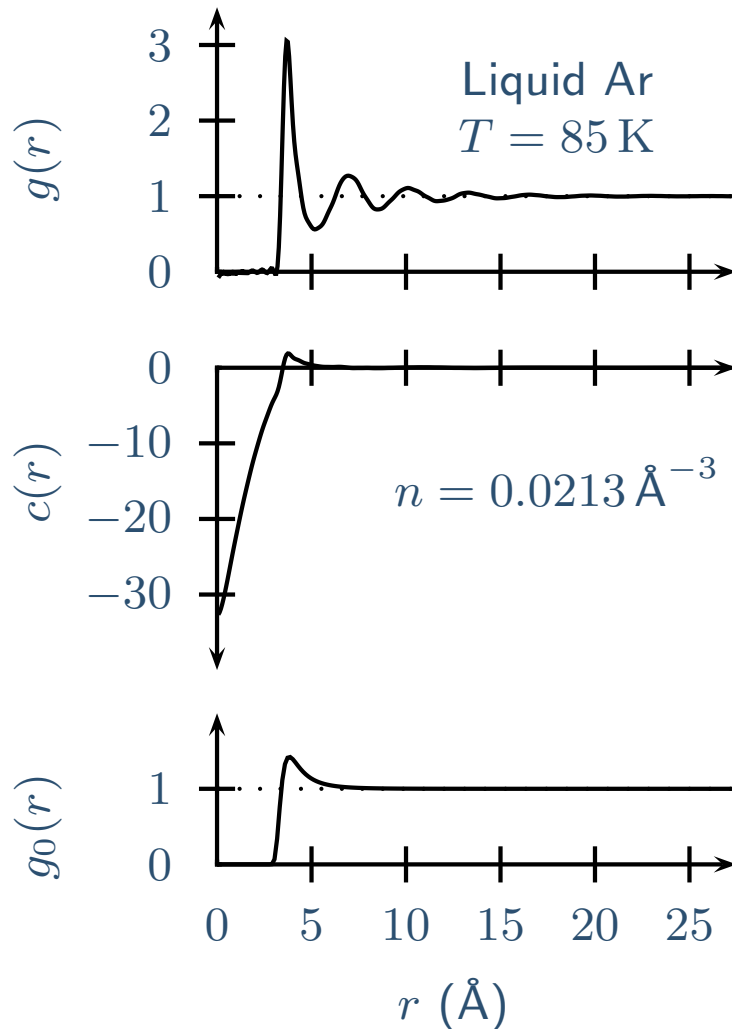
$$g_0(r) \equiv \exp[-\beta u(r)]$$

for the Lennard-Jones potential  $u(r)$ .



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- The results for  $c(r)$  are compared with the measured  $g(r)$  in the figures on the left.
- Also shown is the function

$$g_0(r) \equiv \exp[-\beta u(r)]$$

for the Lennard-Jones potential  $u(r)$ .

- Although the range of  $g(r)$  extends significantly beyond that of  $u(r)$ , the range of  $c(r)$  is about the same as that of  $u(r)$ .
- Hence, the direct correlation function  $c(r)$  seems to have a much shorter range than the pair distribution function  $g(r)$ .



# Physical meaning of OZ function

- To understand this, let's take another look at the iterated form of the Ornstein–Zernike equation:

$$\begin{array}{c}
 \text{O} \text{---} \text{wavy line} \text{---} \text{O} = \text{O} \text{---} \text{dashed line} \text{---} \text{O} + \text{O} \text{---} \text{dashed line} \text{---} \bullet \text{---} \text{dashed line} \text{---} \text{O} \\
 + \text{O} \text{---} \text{dashed line} \text{---} \bullet \text{---} \text{dashed line} \text{---} \bullet \text{---} \text{dashed line} \text{---} \text{O} + \dots
 \end{array}$$

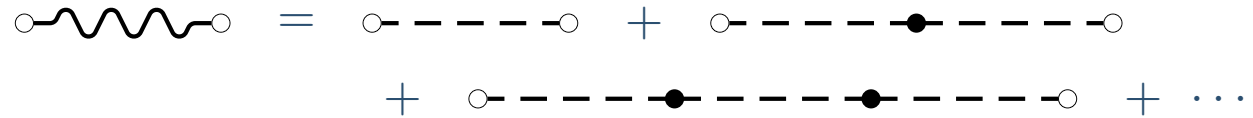
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- To understand this, let's take another look at the iterated form of the Ornstein–Zernike equation:



- On the left side, we have a function  $h(r) = g(r) - 1$  with a range of correlations that extends out to many  $\sigma$ .



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- On the left side, we have a function  $h(r) = g(r) - 1$  with a range of correlations that extends out to many  $\sigma$ .
- On the right side, there is a series of interactions:
  - (i) The first term [i.e.,  $c(r)$ ] describes the direct correlation between two particles.



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$$\begin{aligned}
 \text{wavy line} &= \text{dashed line} + \text{dashed line with 1 dot} \\
 &+ \text{dashed line with 2 dots} + \dots
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- On the left side, we have a function  $h(r) = g(r) - 1$  with a range of correlations that extends out to many  $\sigma$ .
- On the right side, there is a series of interactions:
  - (i) The first term [i.e.,  $c(r)$ ] describes the direct correlation between two particles.
  - (ii) The second term describes a correlation between two particles that is indirectly transmitted by a third particle.



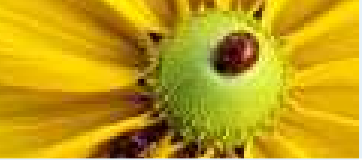
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- On the right side, there is a series of interactions:
  - (i) The first term [i.e.,  $c(r)$ ] describes the direct correlation between two particles.
  - (ii) The second term describes a correlation between two particles that is indirectly transmitted by a third particle.
  - (iii) The third term describes a correlation between two particles that is indirectly transmitted by two intermediate particles.
- Hence, the Ornstein–Zernike equation allows us to express arbitrarily long-ranged total correlations  $h(r)$  in terms of the short-ranged direct correlation  $c(r)$ .



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- The direct correlation  $c(r)$  is particularly useful near the critical point, where the range of the total correlation  $h(r)$  diverges.



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- To see what the precise range of  $h(r)$  is, let us return to the definitions

$$c(q) = 1 - \frac{1}{S(q)}, \quad S(q) = \frac{1}{1 - c(q)}.$$





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$$c(q) = 1 - \frac{1}{S(q)}, \quad S(q) = \frac{1}{1 - c(q)}.$$

- For small values of  $q$  (i.e., long wavelengths), we can use the compressibility rule:

$$\lim_{q \rightarrow 0} S(q) = \frac{K_T}{K_T^{\text{id}}}, \quad \therefore \lim_{q \rightarrow 0} c(q) = 1 - \frac{K_T^{\text{id}}}{K_T}.$$



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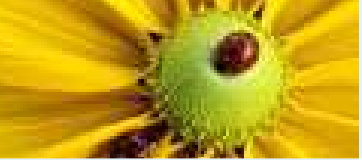
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- Even if  $S(q)$  diverges as  $q \rightarrow 0$  (when  $K_T \rightarrow \infty$ ),  $c(q)$  remains finite.
- We can therefore expand  $c(q)$  in the power series

$$c(q) = c_0 + c_2 q^2 + c_4 q^4 + \dots, \quad c_0 = 1 - \frac{K_T^{\text{id}}}{K_T},$$

where the restriction to even powers of  $q$  comes from the rotational and translational invariance of the fluid.



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$$c(\vec{q}) = n \int \exp(-i\vec{q} \cdot \vec{r}) c(\vec{r}) d^3r.$$



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$$c(\vec{q}) = n \int \exp(-i\vec{q} \cdot \vec{r}) c(\vec{r}) d^3r.$$

- For spherically symmetric  $c(r)$ , this reduces to

$$\begin{aligned} c(q) &= 4\pi n \int_0^\infty r^2 \frac{\sin qr}{qr} c(r) dr \\ &= 4\pi n \int_0^\infty r^2 \left( 1 - \frac{q^2 r^2}{3!} + \frac{q^4 r^4}{5!} - \dots \right) c(r) dr. \end{aligned}$$



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- The coefficient of the quadratic term in the power series is then

$$c_2 = -R^2, \quad R^2 \equiv \frac{4\pi}{6} n \int_0^\infty r^4 c(r) dr.$$



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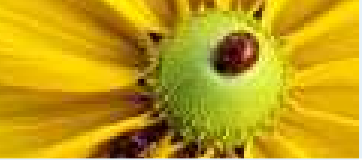
$$\begin{aligned} c(q) &= 4\pi n \int_0^\infty r^2 \frac{\sin qr}{qr} c(r) dr \\ &= 4\pi n \int_0^\infty r^2 \left( 1 - \frac{q^2 r^2}{3!} + \frac{q^4 r^4}{5!} - \dots \right) c(r) dr. \end{aligned}$$

- The coefficient of the quadratic term in the power series is then

$$c_2 = -R^2, \quad R^2 \equiv \frac{4\pi}{6} n \int_0^\infty r^4 c(r) dr.$$

- We can therefore write the power series as

$$c(q) = 1 - \frac{K_T^{\text{id}}}{K_T} - q^2 R^2 + O(q^4).$$



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$$S(q) = \frac{1}{1 - c(q)} \approx \frac{1}{K_T^{\text{id}} / K_T + q^2 R^2}.$$



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$$\int \frac{\exp(-\alpha r)}{r} \exp(-i\vec{q} \cdot \vec{r}) d^3 r = \frac{4\pi}{\alpha^2 + q^2}.$$





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- Near the critical point, we have  $K_T \rightarrow \infty$ , so  $S(q)$  becomes very large for small  $q$ , and we can write

$$S(q) \approx S(q) - 1 \approx \frac{1}{4\pi R^2} \frac{4\pi}{\alpha^2 + q^2}.$$



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- But  $S(q) - 1$  is just the Fourier transform of  $nh(r) = n[g(r) - 1]$ , so the total correlation function has the asymptotic behavior

$$h(r) \sim \frac{1}{4\pi n R^2} \frac{\exp(-r/\xi)}{r} \quad (r \rightarrow \infty),$$

where  $\xi = \alpha^{-1}$  is the **correlation length**

$$\xi = R \left( \frac{K_T}{K_T^{\text{id}}} \right)^{1/2}.$$



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- Hence, the correlation length  $\xi$  diverges near the critical point, because  $K_T \rightarrow \infty$  there.
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- This is the essential result of Ornstein and Zernike.
- Physically, the divergence of  $\xi$  is related to the divergence of particle number fluctuations, since

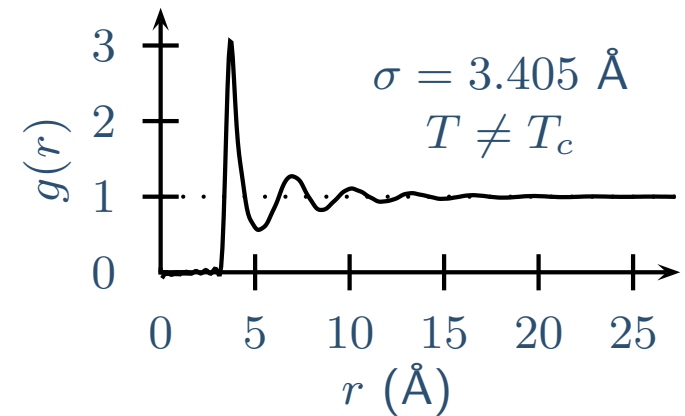
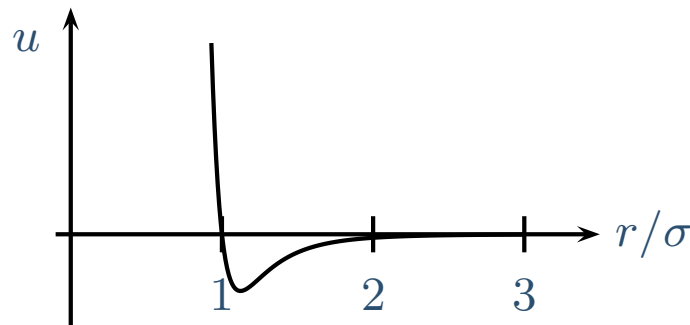
$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} = \frac{K_T}{K_T^{\text{id}}}.$$



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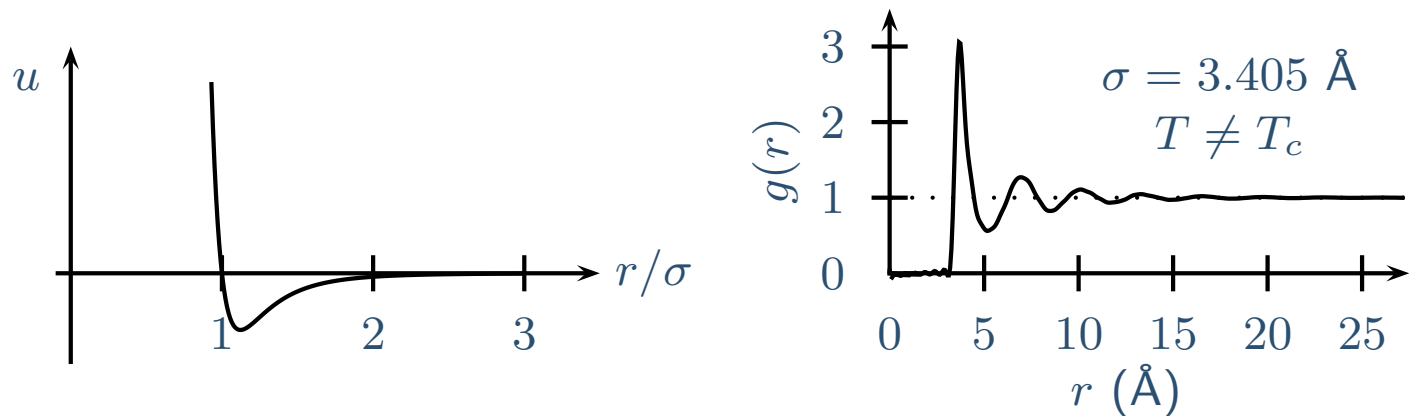
- In summary, the range of the microscopic pair potential is defined by the Lennard-Jones parameter  $\sigma$ .
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- However, near the critical point, the range of correlations diverges, since

$$h(r) \sim \frac{\exp(-r/\xi)}{r}, \quad \xi = R \left( \frac{K_T}{K_T^{\text{id}}} \right)^{1/2}, \quad K_T \rightarrow \infty.$$

- In a small neighborhood of the critical point, the atoms of the fluid are correlated over the entire macroscopic volume  $V$ .