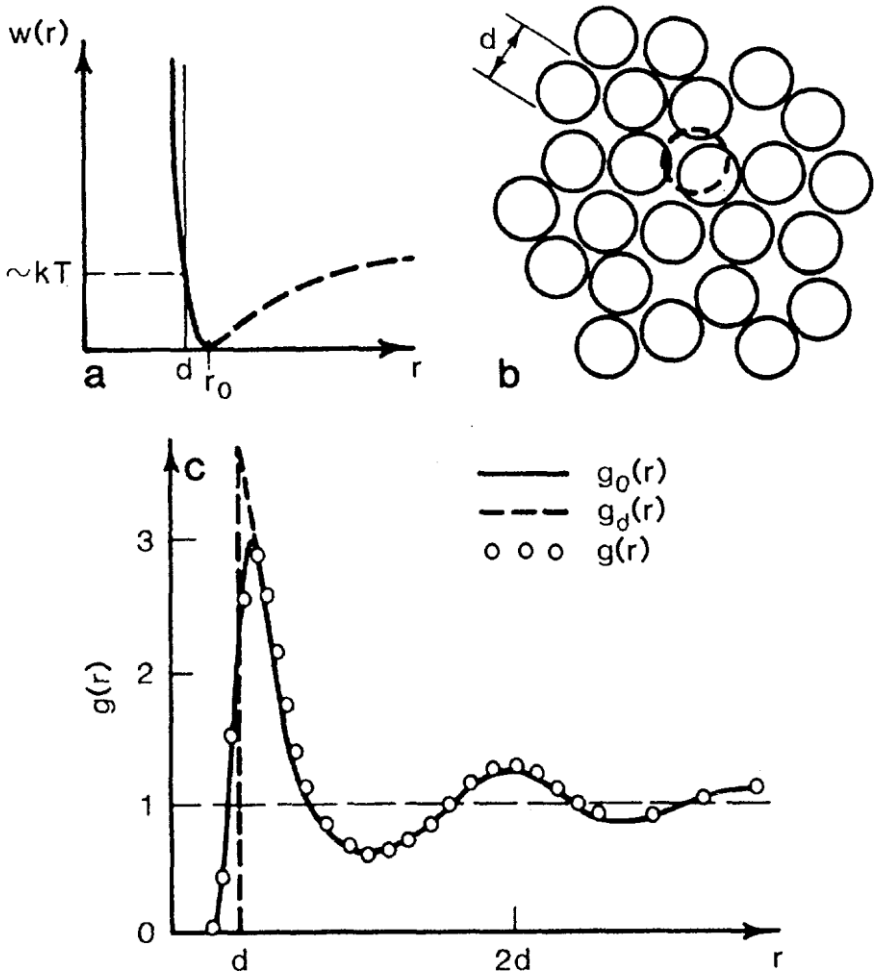
Recapitulation: Density operators

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



Recapitulation: the compressibility χ and the equation of state:

$$n\,kT\,\chi = \frac{kT}{\partial p/\partial n} = 1 + n\int d^3r(g-1)$$

$$P = nkT - n^2\int d^3r\; g(r)r\frac{\partial U\quad(r\quad)}{\partial r}/6$$

Pair correlation function can be measured experimentally

- Pair correlation function $\mathrm{g}(\mathrm{r},\mathrm{r}') = \frac{n(r,r')}{n(r)n(r')}$
- In scattering experiments, one can meassure
- $S(k) = \sum \exp\left(ik \cdot r_{jl}\right)/N$
- $S(k) =$
  $\int \frac{drdr'}{N} < n(r)n(r') > e^{i\,k(r-r')} = 1 + n \quad [\cancel{\delta(k)} + \int (g-1)e^{i\,k(r-r')}]$
- The compressibility $n\,kT\,\chi = \frac{kT}{\partial p/\partial n} = 1 + n\int d^3r(g-1)$ can be realted to the zero q limit of S(q)!

Statistical physics of scattering, correlation, and structure

Scattering experiment

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Static structure factor
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Scattering divergence near critical point
Compressibility rule
Derivation of compressibility rule
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Average values
Variance of N
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Significance

- Let us now consider using scattering experiments to study a system described by the

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} u(r_{ij}).$$

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$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} u(r_{ij}).$$

- We prepare a collimated beam of probe particles (neutrons, X-rays, etc.) with probe coordinates $\vec{r}_p$ and momenta $\hbar\vec{k}$.

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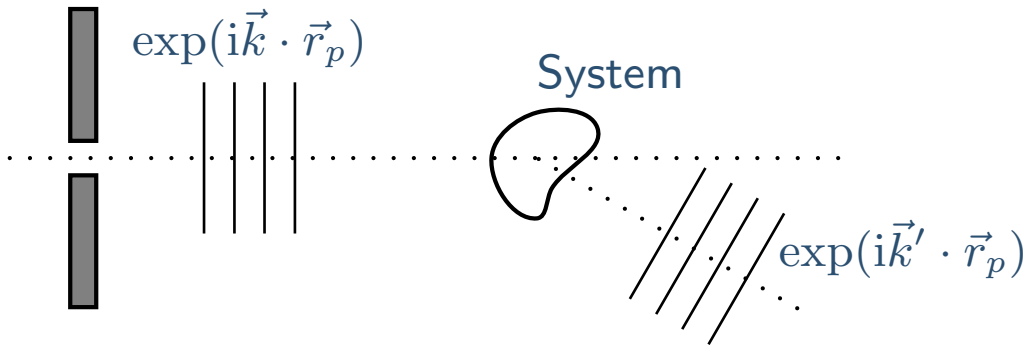
$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i<j} u(r_{ij}).$$

- We prepare a collimated beam of probe particles (neutrons, X-rays, etc.) with probe coordinates $\vec{r}_p$ and momenta $\hbar\vec{k}$.
- The incident beam is approximately in a plane-wave state $\exp(\mathrm{i}\vec{k}\cdot\vec{r}_p)$:



- The scattered beam is in a different plane-wave state $\exp(\mathrm{i}\vec{k}'\cdot\vec{r}_p)$, where $\hbar\vec{k}'$ is the final momentum of the scattered probe particles.

Static structure factor

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- The experiments measure the static structure factor $S(\vec{q})$

$$S(\vec{q}) \equiv \frac{1}{N}\langle \hat{n}_1(\vec{q})\hat{n}_1(-\vec{q})\rangle - N\delta_{\vec{q},0},$$

  in which the last term is introduced for later convenience (recall that the scattered beam cannot be measured at exactly $\vec{q} = 0$).
- $S(\vec{q})$ is related to the pair distribution function $g(\vec{r})$ for a continuous phase by

$$S(\vec{q}) - 1 = \frac{N}{V}\int \mathrm{d}^3 r\, [g(\vec{r}) - 1] \exp(-\mathrm{i}\vec{q}\cdot\vec{r}).$$

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

Typical forms of $S(\vec{q})$

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- What do we expect to obtain from measurements of $S(\vec{q})$?
- Let us survey some typical results for gases, liquids, and crystals of spherically symmetric atoms.

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- In dilute gases, we can use a virial expansion to write

$$g(r) = \exp[-\beta u(r)]\{1 + n g_1(r) + n^2 g_2(r) + \cdots\}.$$

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$$g(r) = \exp[-\beta u(r)]\{1 + n g_1(r) + n^2 g_2(r) + \cdots\}.$$

- For hard spheres of diameter σ with no attractive interaction, the Fourier transform can be evaluated exactly to obtain[2]

$$S(q) = 1 - 4\pi n \left(\frac{\sin q\sigma - q\sigma \cos q\sigma}{q^3} \right) + O(n^2).$$

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$$S(q) = 1 - 4\pi n \left(\frac{\sin q\sigma - q\sigma \cos q\sigma}{q^3} \right) + O(n^2).$$

- In the limit of an ideal gas (i.e., $n \to 0$), we have

$$S(q) \to 1.$$

- Deviations of $S(q)$ from 1 therefore give a measure of how far the system deviates from an ideal gas.

[2] N. W. Ashcroft and N. H. March, *Proc. Roy. Soc. London A* **297**, 336 (1967).

Dilute gas

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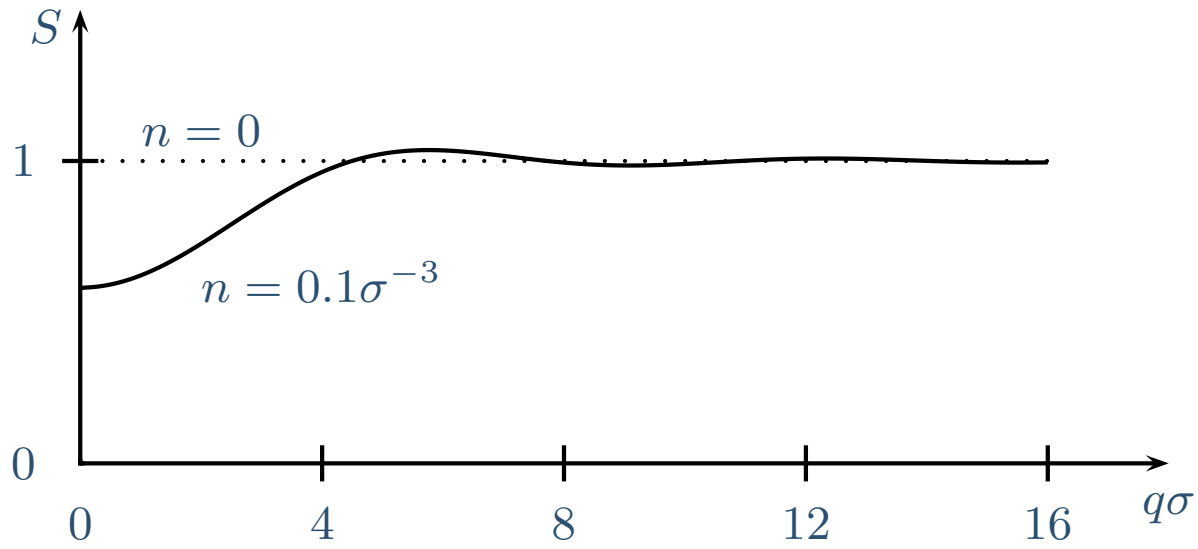
- The structure factor of a dilute gas of hard spheres is compared with that of an ideal gas in the figure below:



- The structure factor of a dilute gas therefore drops below one for small values of q.

Liquid structure factor

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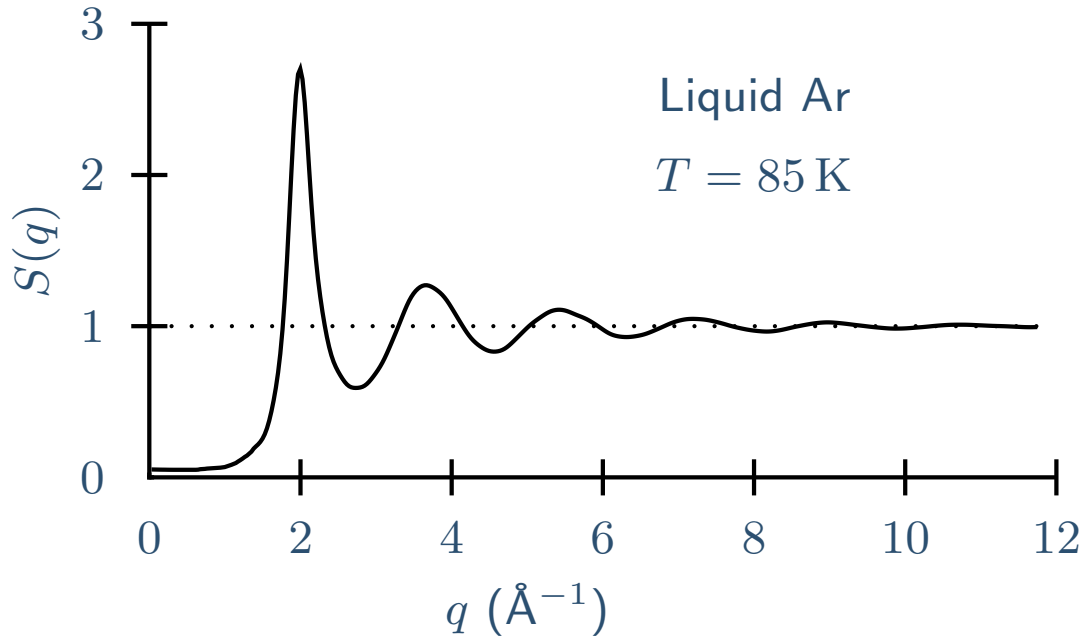
- By contrast, the measured structure factor of a liquid differs quite remarkably from that of an ideal gas:[3]



- The data shown here were taken far away from the critical point ($T_c = 151\,\mathrm{K}$, $P_c = 48.1\,\mathrm{atm}$).

[3] J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig, *Phys. Rev. A* **7**, 2130 (1973).

Distribution function

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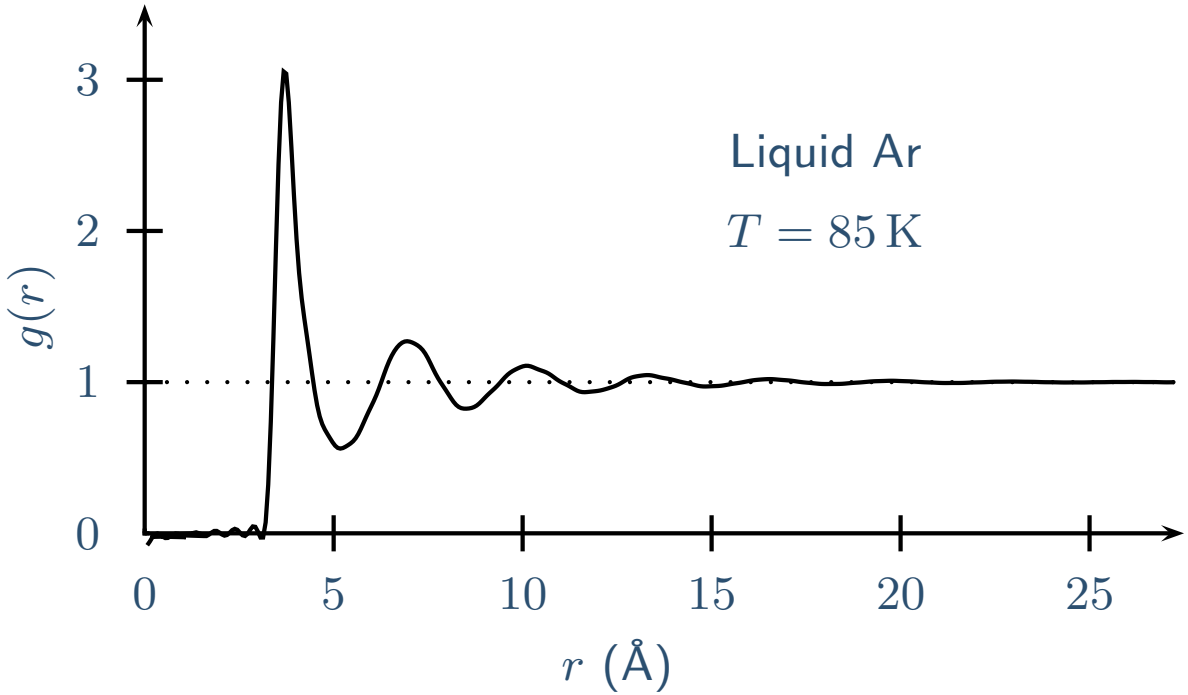
- The corresponding pair distribution function (obtained by Fourier transform) is shown below:



- The sharp peak at $r \simeq 3.7\,\text{Å}$ shows that there is a strong tendency for atoms to cluster together at this separation in liquid argon.
- Subsidiary peaks at greater r show that the correlations extend beyond nearest neighbors.

Critical point

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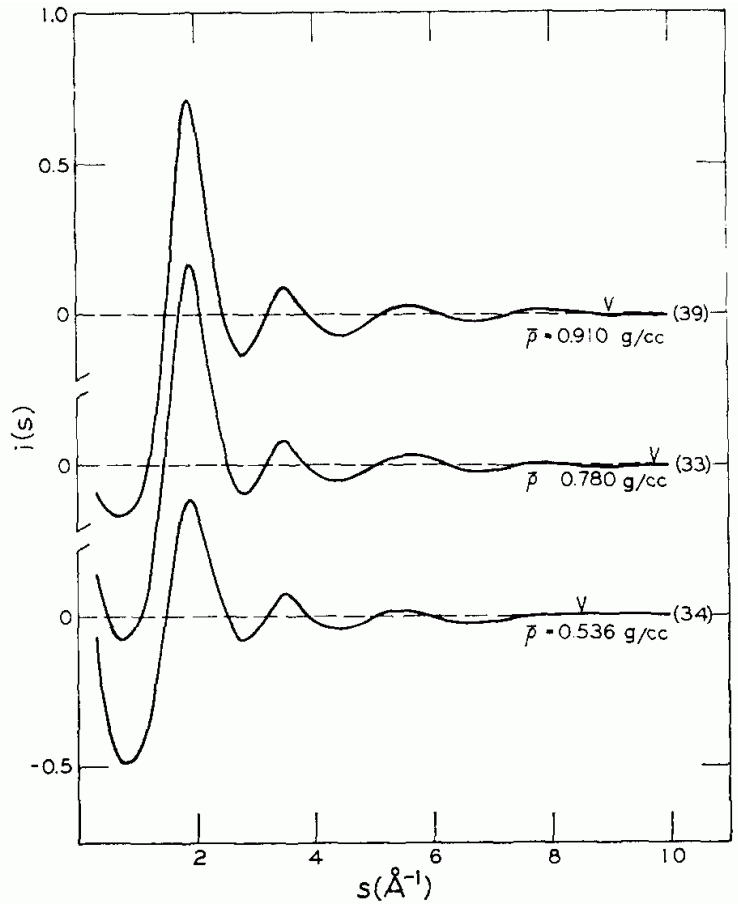

FIG. 5. The argon intensity function $i(s)$ at $t = -120°C$.

- For a liquid close to the critical point, $S(q)$ diverges near $q = 0$, becoming more divergent as $(T, P) \to (T_c, P_c)$.[a]

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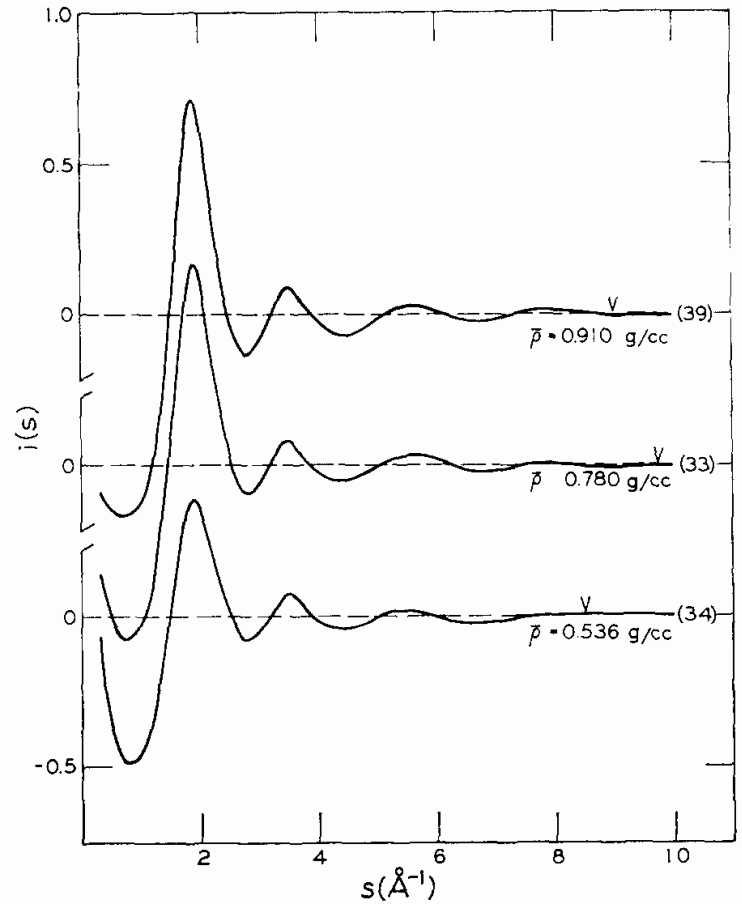

FIG. 5. The argon intensity function $i(s)$ at $t = -120°C$.

- For a liquid close to the critical point, $S(q)$ diverges near $q = 0$, becoming more divergent as $(T, P) \to (T_c, P_c)$.[a]
- This says that the quantity

$$\frac{1}{N}\langle \hat{n}_1(\vec{q})\hat{n}_1(-\vec{q})\rangle$$

  diverges as $\vec{q} \to 0$ and $(T, P) \to (T_c, P_c)$.
- Can you think of a reason why this would happen?

[a] P. G. Mikolaj and C. J. Pings, *J. Chem. Phys.* **46**, 1401 (1967).

Crystal structure factor

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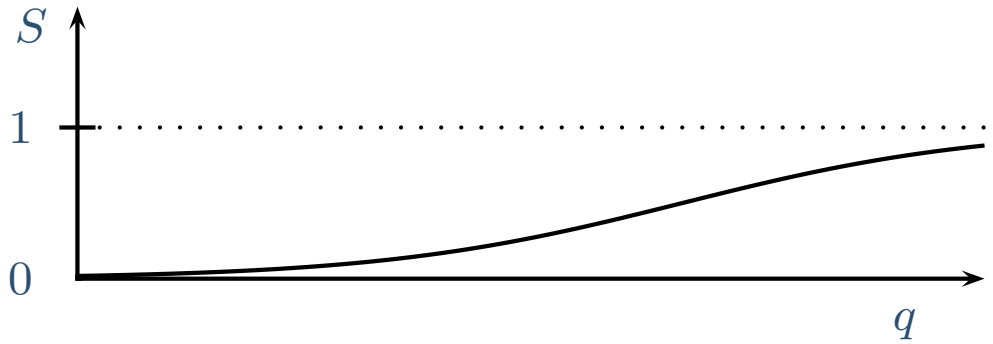
- For an arbitrary direction of $\vec{q}$, the structure factor of a crystal has the smooth form sketched below (due to thermal diffuse scattering by lattice vibrations):



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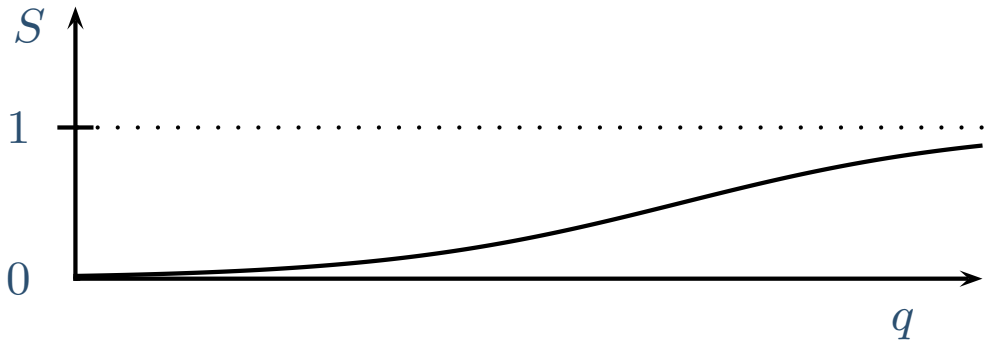
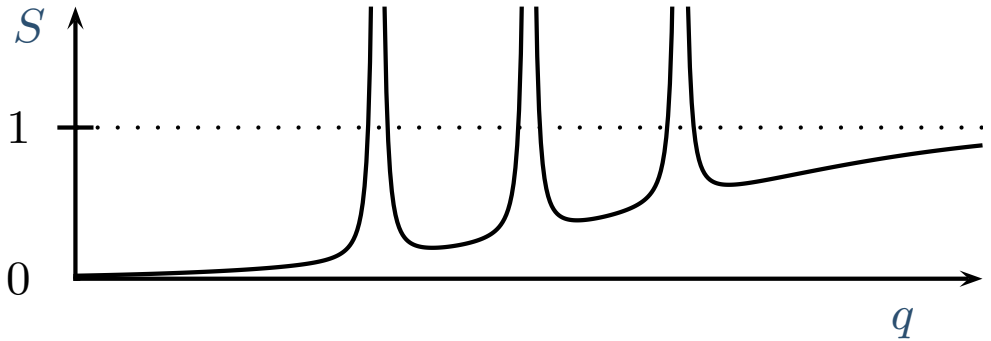


- However, for certain special directions of $\vec{q}$, there are sharp peaks (of order N):



Reciprocal lattice

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Significance

- The special values of $\vec{q}$ where the peaks occur are those values satisfying

$$\exp(\mathrm{i}\vec{q}\cdot\vec{R}) = 1$$

  for all lattice vectors $\vec{R}$ of the crystal lattice.
- These values of $\vec{q}$ are just the reciprocal lattice vectors $\vec{K}$.

Order parameter for solid

density $\rho(r) = \sum_i \delta(r - r_i)$

Fourier transform

$$\rho(q) = \int dr\, \rho(r) e^{iq\cdot r}/N = \sum_j e^{iq\cdot r_j}/N$$

For solids , there are vectors G so that $G \cdot R_j = 2\pi n$ for some integer n.

For example, in one dimension, for $R_j = ja$, G= $2\pi/a$

$\rho(G) = \sum_j e^{iG\cdot u_j}/N$ is a good order parameter.

$$\rho(G) = \sum_j e^{iG\cdot u_j}/N$$

Average of the order parameter

- $< \rho(G) > = \sum_j < e^{iG \cdot u_j} > / N$
- Use cumulant expansion:
- $< e^{if} > \cong e^{-\frac{<f^2>}{2} + \cdots}$ for any function f such that <f>=0.
- This can be seen by comparing the series expansion on both sides.
- $< \rho(G) > \cong \sum_j e^{-<[G \cdot u_j]^2>/2}$/N.
- For fluids $< u^2 > = \infty$, $< \rho(G) > = 0$

Fluctuation of the order parameter

- $< |\rho(G)|^2 > = \sum_{j,k} < e^{iG\cdot(u_j - u_k)} >$
- Use cumulant expansion:
- $< e^{if} > \cong e^{-\frac{<f^2>}{2}+\cdots}$ for any function f such that <f>=0.
- This can be seen by comparing the series expansion on both sides.
- $< |\rho(G)|^2 > /N^2 \cong \sum_j e^{-<[G\cdot(u_0 - u_j)]^2>}$/N

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- The special values of $\vec{q}$ where the peaks occur are those values satisfying

$$\exp(\mathrm{i}\vec{q}\cdot\vec{R}) = 1$$

  for all lattice vectors $\vec{R}$ of the crystal lattice.
- These $\vec{q}$ are called the reciprocal lattice vectors $\vec{K}$ of the crystal.
- A cumulant expansion with the lattice vibration gives the static structure has the form[4]

$$S(\vec{q}) = N\mathrm{e}^{-2W(\vec{q})}\sum_{\vec{K}}\delta_{\vec{q},\vec{K}}\ ,$$

  where W is a smoothly varying function of $\vec{q}$ and T known as the Debye–Waller factor.

[4] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976), pp. 790–795.

Temperature variation

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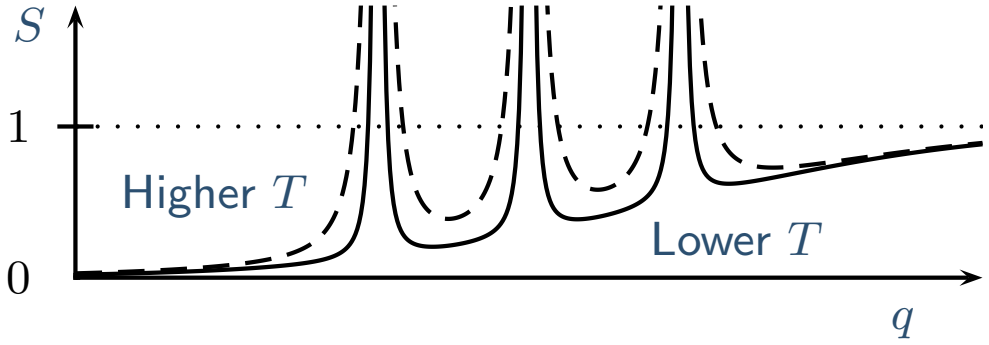
- As the temperature increases, the peaks become broader:



- This indicates a change in the motion of the system, but one that preserves the crystal symmetry.

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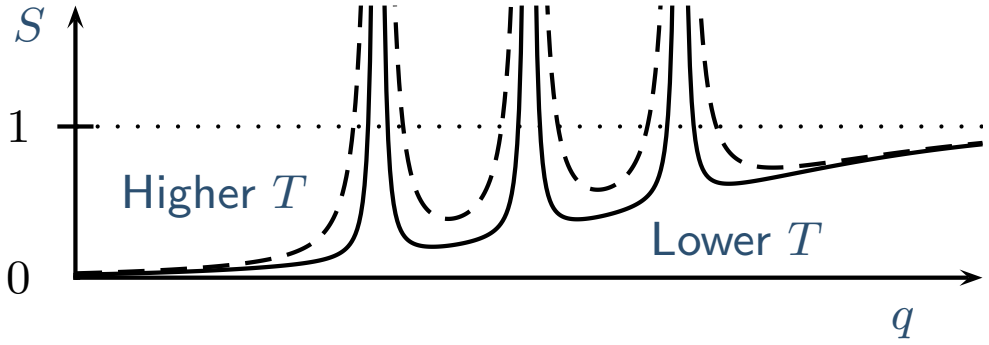

- This indicates a change in the motion of the system, but one that preserves the crystal symmetry.
- When T finally exceeds the melting temperature, the $O(N)$ peaks of the crystal are reduced to the $O(1)$ peaks of the liquid.
- However, the liquid still shows significant order even though it is a continuous phase.

Molecular dynamics

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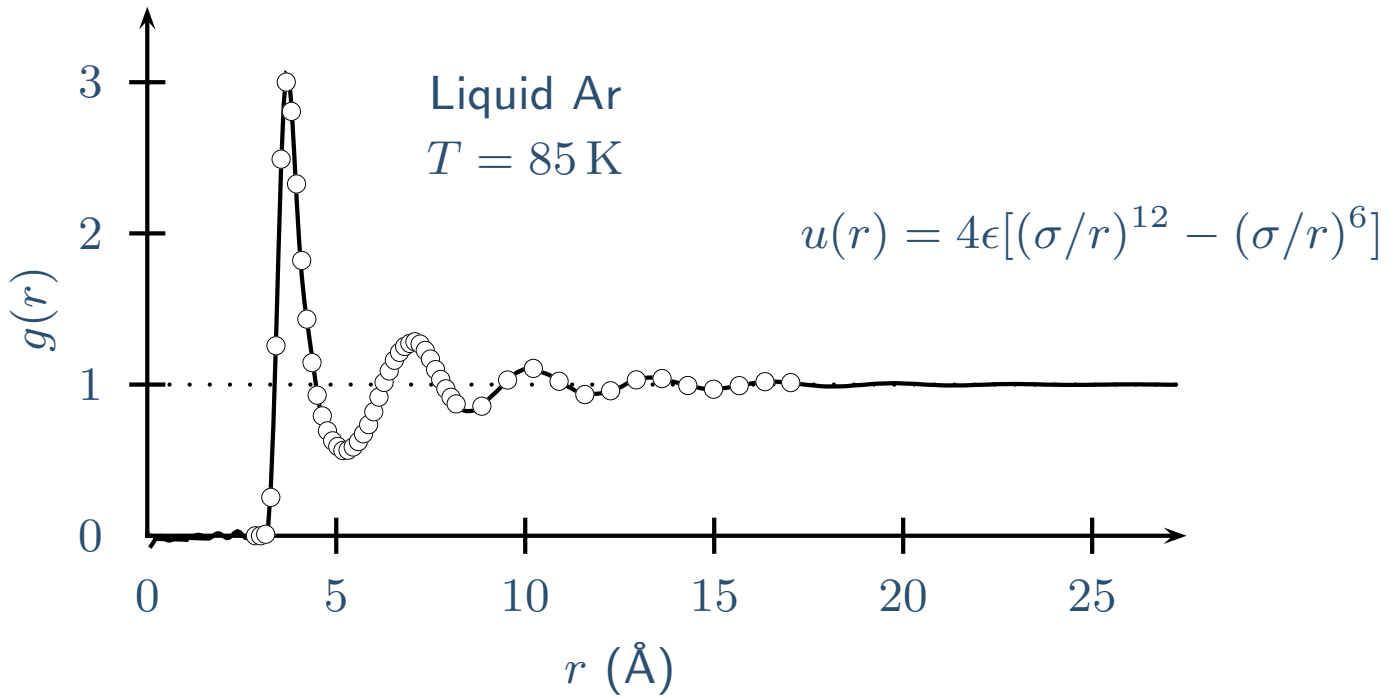
Significance

- Molecular dynamics simulations based on a Lennard-Jones potential[5] are in excellent agreement with the measured $g(r)$ of liquid argon:[6]



- The circles in the figure are Verlet's simulation data for $k_\mathrm{B}T = 0.719\epsilon$ and $n = 0.850\sigma^{-3}$, where $\epsilon/k_\mathrm{B} = 119.8\,\mathrm{K}$ and $\sigma = 3.405\,\text{Å}$.

[5] L. Verlet, *Phys. Rev.* **165**, 201 (1968).
[6] J. L. Yarnell, M. J. Katz, R. G. Wenzel, and S. H. Koenig, *Phys. Rev. A* **7**, 2130 (1973).

Range of correlations

Scattering experiment
Nature of experiment
Interaction between probe and system
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One-particle density
Static structure factor
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Pair distribution function
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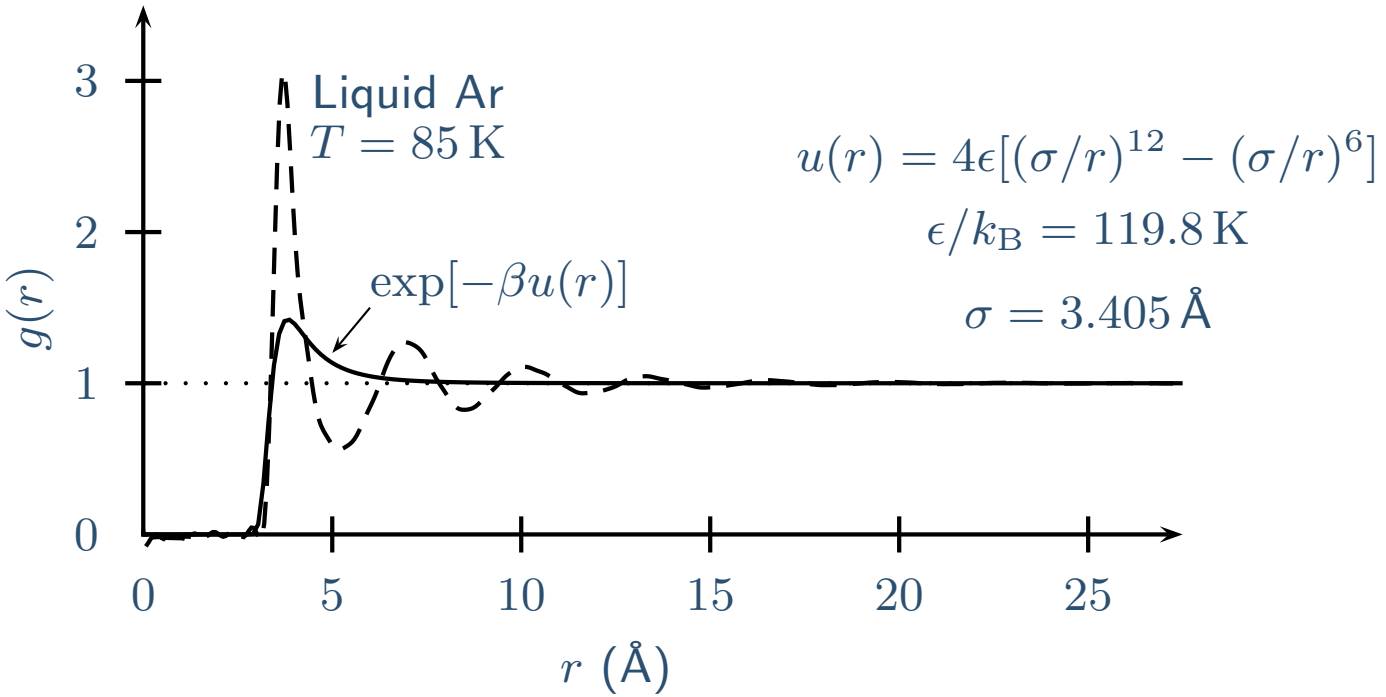
Significance

- How well does the measured distribution function of a liquid agree with the approximation $g(r) \approx \exp[-\beta u(r)]$ valid for a dilute gas?



- Notice that the correlations in $\exp[-\beta u(r)]$ die out quickly for $r > \sigma$, but those in the measured $g(r)$ continue out to many σ.

Scattering divergence near critical point

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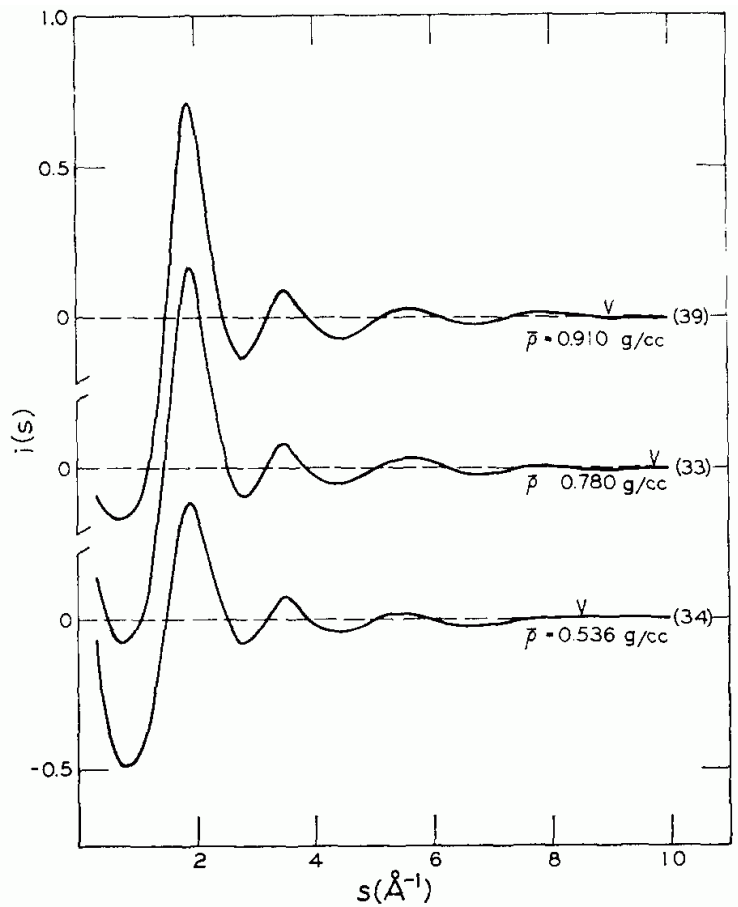

FIG. 5. The argon intensity function $i(s)$ at $t = -120°C$.

- How can we understand the divergence in scattering for a fluid near the critical point?

Scattering divergence near critical point

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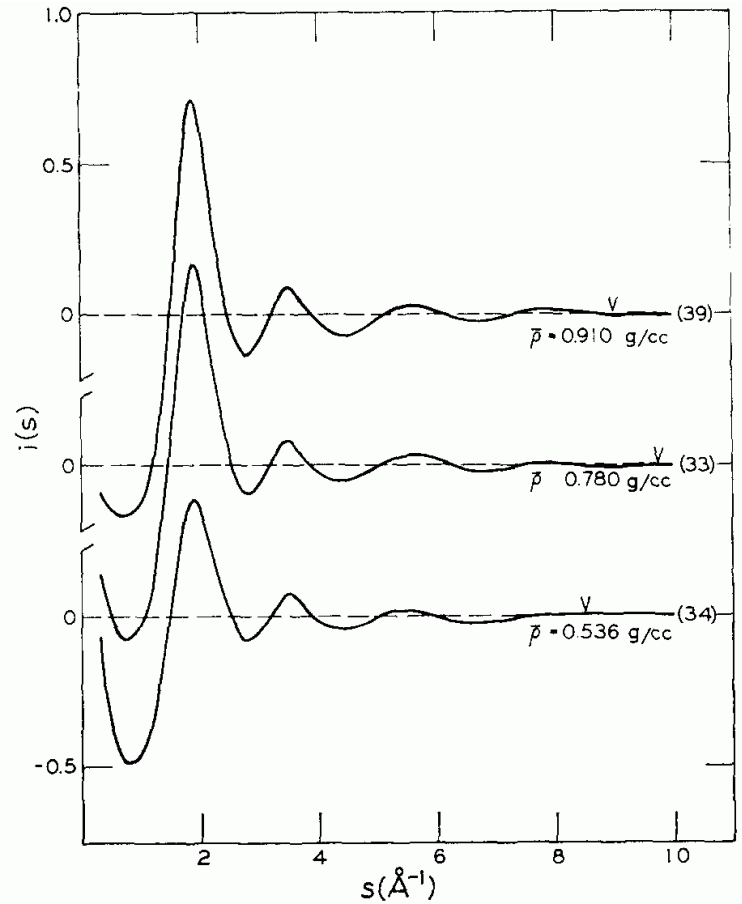

FIG. 5. The argon intensity function $i(s)$ at $t = -120°C$.

- How can we understand the divergence in scattering for a fluid near the critical point?
- We have proved the following theorem for the structure factor at long wavelengths:

$$\lim_{q \to 0} S(q) = n k_{\mathrm{B}} T \, K_T,$$

where K_T is the isothermal compressibility

$$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$$

- This is just the inverse of the isothermal bulk modulus

$$B_T \equiv -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{K_T}.$$

Compressibility rule

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- The compressibility rule can also be written as

$$\lim_{q\to 0} S(q) = \frac{K_T}{K_T^{\mathrm{id}}} = \frac{B_T^{\mathrm{id}}}{B_T},$$

where K_T^{id} is the compressibility of an ideal gas at the same density n and temperature T:

$$K_T^{\mathrm{id}} = \frac{1}{nk_{\mathrm{B}}T}.$$

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$$K_T^{\mathrm{id}} = \frac{1}{nk_{\mathrm{B}}T}.$$

- In an ordinary liquid far from the critical point, the order of magnitude of these quantities is

$$B_T \sim 30000\,\mathrm{atm}, \quad B_T^{\mathrm{id}} \sim 1000\,\mathrm{atm}; \qquad \therefore \lim_{q\to 0} S(q) \sim 0.03.$$

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- However, at the critical point (T_c, P_c), we have $\partial P/\partial V = 0$ and thus $B_T = 0$ (i.e., $K_T \to \infty$); consequently,

$$\lim_{q\to 0} S(q) = \infty.$$

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- What is the significance of this result?

$$\lim_{q \to 0} S(q) = \frac{K_T}{K_T^{\mathrm{id}}}$$

- On the left side, $S(q)$ is a microscopic quantity describing the structural order in a fluid.
- On the right side are thermodynamic quantities.

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- However, it diverges near the critical point, where $K_T \to \infty$.

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- On the right side are thermodynamic quantities.
- In a typical liquid far from the critical point, the value of this ratio is much less than one.
- However, it diverges near the critical point, where $K_T \to \infty$.
- Since $S(q) - 1$ is the Fourier transform of $n[g(r) - 1]$, a divergence of $S(q)$ at long wavelengths

$$\lambda = \frac{2\pi}{q}$$

Pair correlation function can be measured experimentally

- Pair correlation function $\mathrm{g}(\mathrm{r},\mathrm{r}') = \frac{n(r,r')}{n(r)n(r')}$
- In scattering experiments, one can meassure
- $S(k) = \sum \exp\left(ik \cdot r_{jl}\right)/N$
- $S(k) =$
  $\int \frac{drdr'}{N} < n(r)n(r') > e^{i\,k(r-r')} = 1 + n \quad [\cancel{\delta(k)} + \int (g-1)e^{i\,k(r-r')}]$
- The compressibility $n\,kT\,\chi = \frac{kT}{\partial p/\partial n} = 1 + n\int d^3r(g-1)$ can be realted to the zero q limit of S(q)!

- Current plan for the last two weeks in class.is to have students form groups by themselves, perform simulations with the computer programs I shall give them and present their results during class in either Chinese or English.

Do you know how to compile and run a computer program

- (1) Yes
- (2) No

Do you know the programming language

- (1) Fortran
- (2) C
- (3) others
- (4) no

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