

Lecture 7: Dynamics in Liquids

In the previous lecture we learnt how to characterise the static structure of a liquid through the pair distribution function $g(r)$ and its Fourier transform, the static structure factor $S(q)$. Those quantities captured the short-range ordering of atoms caused by the interatomic potential. We now turn to the dynamics of liquids — how atoms move, how correlations decay in time and space, and how these dynamical processes are probed experimentally. The liquid state sits midway between crystalline order and gaseous chaos, and the dynamical signatures of this “edge of chaos” will motivate many of the correlation functions we introduce below.

7.1 Edge of Chaos and Stability

Liquids exhibit a delicate balance between local stability and chaotic motion. On one hand, the interatomic potential still imposes a preferred separation distance r_0 that gives rise to the first coordination shell found in crystalline solids. On the other hand, thermal energy on the order of $k_B T$ is sufficient to continually rearrange these local motifs. As a result the structure is *short-range ordered* but constantly fluctuating.

Recent experiments comparing liquids to their crystalline counterparts show that high-frequency collective excitations reminiscent of solid phonons occur in liquids as well. The main difference is that these excitations are broadened due to disorder and relaxation processes, reflecting the distribution of local structures and the transient nature of the liquid environment. In other words, liquids display fingerprints of order and disorder: the average nearest-neighbour distances and coordination numbers are similar to those of the corresponding solids, yet local vibrations and collective modes are broadened because the environment is constantly being reconfigured.

This interplay between order and chaos can be viewed through the lens of “edge-of-chaos” concepts. In nonlinear dynamics, the edge of chaos refers to a transition region between order and disorder in which a system operates with bounded instability and constant dynamic interplay between the two. Complex adaptive systems often evolve toward this regime where complexity and adaptation are maximised. A liquid is a physical realisation of such a regime: structural forces try to maintain local order, while thermal fluctuations drive continual rearrangements. This leads to a variety of interesting dynamical processes such as diffusion, structural relaxation and dynamical heterogeneities.

Figure 1 illustrates the idea. A central particle (red) is surrounded by a ring of neighbours (orange) at the preferred distance r_0 , capturing short-range order, while more distant particles (light blue) are randomly distributed, representing chaotic motion. The boundaries between ordered shells and disordered regions blur continuously as atoms move and exchange partners.

7.2 van Hove Formalism

In order to characterize dynamics in solids, we considered the normal modes of the crystalline structure, which lead us to the concept of phonons. Phonons are characteristic of long-range

Edge of Chaos: Short-range order vs Random motion

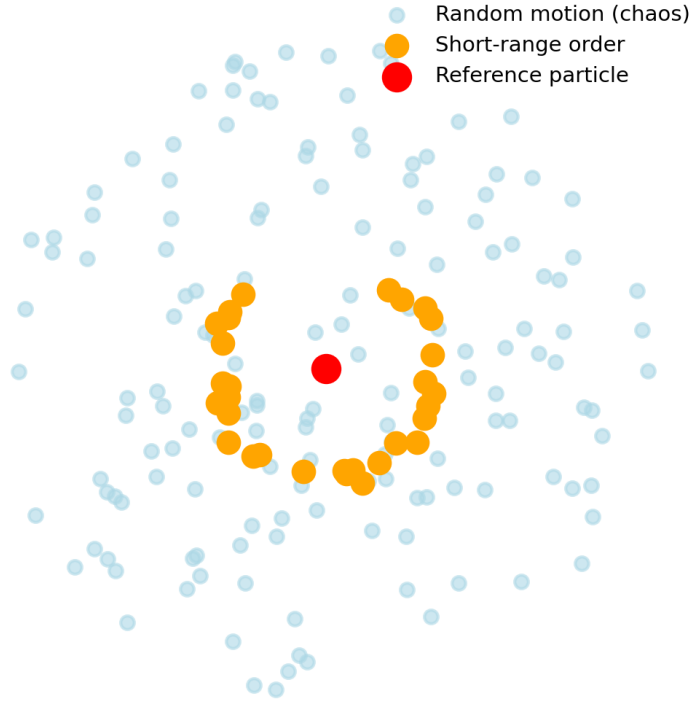


Figure 1: Conceptual representation of the liquid state at the “edge of chaos”. A reference particle (red) is surrounded by a first shell of neighbours at the preferred separation r_0 (orange), indicating short-range structural order, while more distant atoms move randomly (light blue) reflecting chaotic thermal motion. The interplay of these regimes gives rise to complex dynamics.

ordering. However, in liquids, these collective modes cannot really exist, as long range ordering doesn't persist anymore. Therefore, the study of dynamics in liquids involves defining a more general formulation, which can help us picture the particles evolve dynamically. This can be achieved by quantifying correlations in both space and time, which is formulated using van Hove correlation function.

Just as in the formalism to describe the structure, we begin by defining the *microscopic number density field*, but additionally now, as function of time t and not just the coordinates \mathbf{r} ,

$$n(\mathbf{r}, t) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j(t)), \quad (7.2.1)$$

where $\mathbf{r}_j(t)$ is the position of particle j at time t . This generalises the microscopic density introduced in Lecture 6 to include time dependence.

7.2.1 Two-time density correlation function

We begin by considering the most general form of a density-density correlation function involving two distinct times,

$$G(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = \frac{1}{N} \langle n(\mathbf{r}_1, t_1) n(\mathbf{r}_2, t_2) \rangle, \quad (7.2.2)$$

which measures how a density fluctuation at (\mathbf{r}_1, t_1) correlates with another at (\mathbf{r}_2, t_2) . In equilibrium, the system is stationary: its statistical properties do not depend on the absolute choice of time origin. Consequently, G depends only on the *time difference* $t = t_2 - t_1$, and not on t_1 and t_2 separately. This allows us to invoke *time-translational invariance*,

$$G(\mathbf{r}_1, t_1; \mathbf{r}_2, t_2) = G(\mathbf{r}_1, \mathbf{r}_2; t_2 - t_1).$$

Without loss of generality we may therefore choose $t_1 = 0$ and write $t \equiv t_2$.

With this simplification, the correlation function becomes

$$G(\mathbf{r}_1, \mathbf{r}_2; t) = \frac{1}{N} \langle n(\mathbf{r}_1, 0) n(\mathbf{r}_2, t) \rangle, \quad (7.2.3)$$

which measures correlations between a density fluctuation at \mathbf{r}_1 at time 0 and another at \mathbf{r}_2 at time t . Inserting the microscopic definition of the density,

$$n(\mathbf{r}, t) = \sum_{j=1}^N \delta(\mathbf{r} - \mathbf{r}_j(t)),$$

we obtain

$$G(\mathbf{r}_1, \mathbf{r}_2; t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta(\mathbf{r}_1 - \mathbf{r}_i(0)) \delta(\mathbf{r}_2 - \mathbf{r}_j(t)) \right\rangle. \quad (7.2.4)$$

For a homogeneous system, the correlation depends only on the separation $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$. Integrating over the dummy variable \mathbf{r}_1 , we arrive at the *van Hove correlation function*,

$$G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta(\mathbf{r} - [\mathbf{r}_j(t) - \mathbf{r}_i(0)]) \right\rangle. \quad (7.2.5)$$

This function counts all particle pairs (i, j) whose separation vector at time t coincides with \mathbf{r} . At $t = 0$, the double sum splits into $i = j$ (self) and $i \neq j$ (distinct) contributions. Using translational invariance one recovers the familiar static limit,

$$G(\mathbf{r}, 0) = \delta(\mathbf{r}) + \langle n \rangle g(r), \quad (7.2.6)$$

so that the van Hove function provides a natural dynamical generalisation of the static radial distribution function $g(r)$. Thus the van Hove function generalises $g(r)$ to non-zero times.

7.2.2 Self and distinct parts

It is useful to separate Eq. (7.2.5) into *self* and *distinct* contributions. The self part counts only the same particle at different times

$$G_s(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \delta(\mathbf{r} - (\mathbf{r}_i(t) - \mathbf{r}_i(0))) \right\rangle, \quad (7.2.7)$$

while the distinct part counts pairs of different particles

$$G_d(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i \neq j} \delta(\mathbf{r} - (\mathbf{r}_j(t) - \mathbf{r}_i(0))) \right\rangle. \quad (7.2.8)$$

At $t = 0$, G_s reduces to $\delta(\mathbf{r})$ and G_d reduces to $\rho g(r)$. The physical interpretations are clear:

- $G_s(\mathbf{r}, t)$ is the probability density of finding a given particle at displacement \mathbf{r} at time t knowing it was at the origin at $t = 0$. In homogeneous systems this is identical to the probability density of displacement for any particle and will be denoted $P(\mathbf{r}, t)$.
- $G_d(\mathbf{r}, t)$ is the probability density of finding a second particle at separation \mathbf{r} from the original particle after time t . At $t = 0$ this is just the static pair correlation $\rho g(r)$.

Normalization of these functions reads

$$\int d\mathbf{r} G_s(\mathbf{r}, t) = 1, \quad \int d\mathbf{r} G_d(\mathbf{r}, t) = N - 1, \quad (7.2.9)$$

reflecting that G_s counts one particle and G_d counts the other $N - 1$. At long times, G_s and G_d lose memory of the initial configuration and become uniform.

Figure 2 illustrates typical self and distinct parts. For a diffusive process the self part broadens from a sharp peak at $t = 0$ to a Gaussian at later times. The distinct part starts from $\rho g(r)$ at $t = 0$ and gradually decays toward the mean density ρ as the memory of initial correlations is lost.

7.2.3 van Hove functions for diffusive motion

In a simple diffusive liquid the motion of a tagged particle can be described by Brownian dynamics. In that case $P(\mathbf{r}, t)$ is a Gaussian

$$G_s(\mathbf{r}, t) = P(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right), \quad (7.2.10)$$

where D is the self-diffusion coefficient. The distribution broadens as $t^{1/2}$ and its variance increases linearly with time, a result we will revisit when discussing Brownian motion. The distinct part relaxes toward the uniform density on a time scale set by the structural relaxation time of the liquid. In dense liquids or glassy systems the decay of G_d may be non-exponential and exhibits *dynamic heterogeneity*, but such effects are beyond the scope of the present discussion.

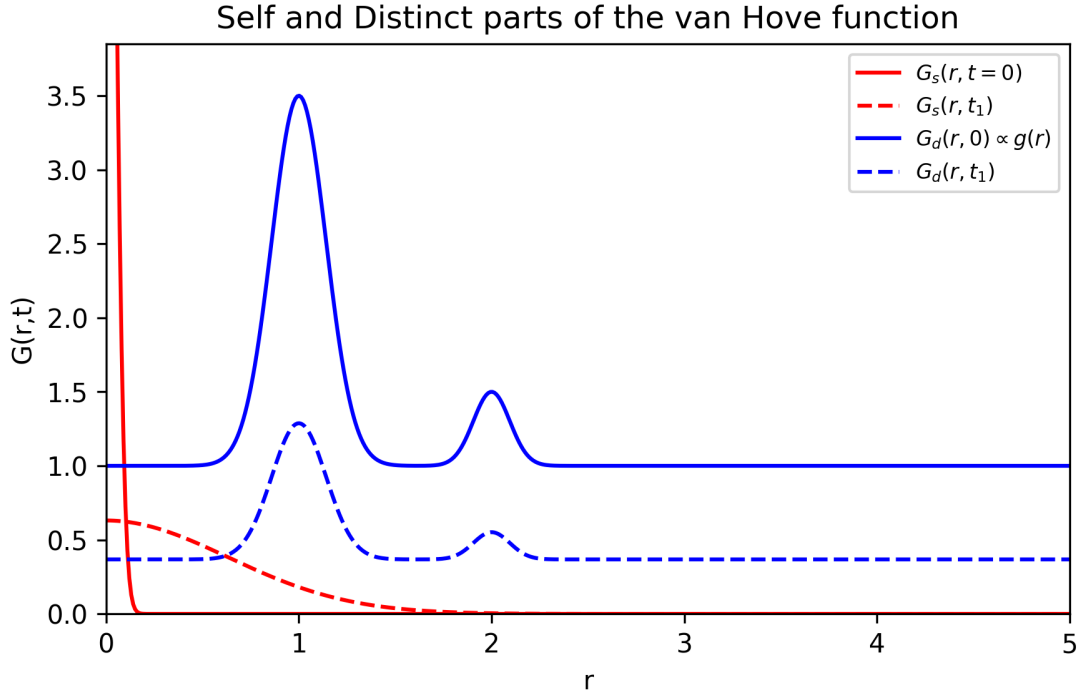


Figure 2: Schematic self (G_s) and distinct (G_d) parts of the van Hove function. At $t = 0$ the self part is a Dirac peak at $r = 0$ (approximated by a narrow Gaussian), while the distinct part is proportional to the static radial distribution function $g(r)$. At later times the self part broadens (red dashed) and the distinct part decays toward the mean density (blue dashed). These curves are representative of a diffusive liquid and were generated for illustration.

7.3 Measurements with Neutron Scattering

The van Hove function becomes experimentally accessible through its space and time Fourier transforms. We begin by introducing the time-dependent Fourier transform of the microscopic density,

$$n(\mathbf{q}, t) = \int d\mathbf{r} e^{-i\mathbf{q}\cdot\mathbf{r}} n(\mathbf{r}, t) = \sum_{j=1}^N e^{-i\mathbf{q}\cdot\mathbf{r}_j(t)}. \quad (7.3.1)$$

The corresponding two-time correlation of these modes defines the *intermediate scattering function*,

$$F(\mathbf{q}, t) = \frac{1}{N} \langle n(\mathbf{q}, t) n(-\mathbf{q}, 0) \rangle. \quad (7.3.2)$$

Using Eq. (7.2.4), one finds that $F(\mathbf{q}, t)$ is simply the spatial Fourier transform of the van Hove function,

$$F(\mathbf{q}, t) = \int d\mathbf{r} G(\mathbf{r}, t) e^{-i\mathbf{q}\cdot\mathbf{r}}. \quad (7.3.3)$$

The decomposition of G into self and distinct parts carries over directly:

$$F_s(\mathbf{q}, t) = \int d\mathbf{r} G_s(\mathbf{r}, t) e^{-i\mathbf{q}\cdot\mathbf{r}}, \quad (7.3.4)$$

$$F_d(\mathbf{q}, t) = \int d\mathbf{r} G_d(\mathbf{r}, t) e^{-i\mathbf{q}\cdot\mathbf{r}}. \quad (7.3.5)$$

Coherent and incoherent neutron scattering

In neutron scattering, the measured signal depends on the fluctuations of the *scattering length* of each particle. If the scattering length varies from particle to particle (as in many hydrogenous systems), then the measured signal contains two distinct contributions:

- **Coherent scattering** arises from correlations between *different* particles. It is therefore sensitive to the *distinct* part $G_d(\mathbf{r}, t)$ and probes collective density fluctuations.
- **Incoherent scattering** arises from fluctuations of the *self* scattering length of individual particles. It isolates the *self* part $G_s(\mathbf{r}, t)$ and therefore probes single-particle dynamics.

Thus the intermediate scattering functions have a direct experimental interpretation:

$$\text{coherent neutrons} \longrightarrow F(\mathbf{q}, t) \quad (\text{dominantly from } F_d),$$

$$\text{incoherent neutrons} \longrightarrow F_s(\mathbf{q}, t) \quad (\text{self correlations only}).$$

This is the experimental realisation of the mathematical decomposition of the van Hove function.

Static limit and dynamical information

At $t = 0$ the intermediate scattering function reduces to the static structure factor,

$$F(\mathbf{q}, 0) = S(\mathbf{q}) = 1 + \rho \int d\mathbf{r} [g(r) - 1] e^{-i\mathbf{q}\cdot\mathbf{r}}, \quad (7.3.6)$$

as derived in Lecture 6. For $t > 0$, the decay of $F(\mathbf{q}, t)$ describes the relaxation of density fluctuations.

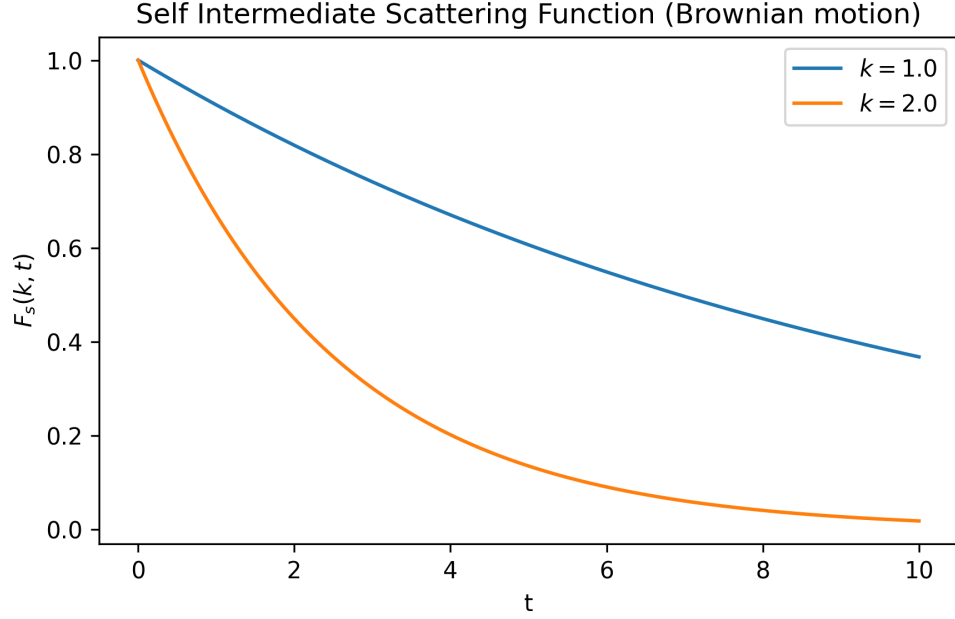


Figure 3: Self intermediate scattering function $F_s(q, t)$ for two wavenumbers (dimensionless units). For Brownian motion F_s decays exponentially as $\exp(-Dq^2t)$; larger q values decay faster because they probe shorter length scales.

For Brownian diffusion, inserting the self part of the van Hove correlation function from Eq. (7.2.10) into Eq. (7.3.4) immediately yields

$$F_s(\mathbf{q}, t) = e^{-Dq^2t}, \quad (7.3.7)$$

a simple exponential decay whose rate grows with q^2 . This behaviour is shown in Fig. 3.

Dynamic structure factor and diffusion from incoherent scattering

Going one step further, the incoherent *dynamic structure factor* measured in inelastic neutron scattering is the time Fourier transform of $F_s(\mathbf{q}, t)$,

$$S_{inc}(\mathbf{q}, \omega) = \int_{-\infty}^{\infty} dt F_s(\mathbf{q}, t) e^{i\omega t}. \quad (7.3.8)$$

For diffusive systems, the self part produces the well-known Lorentzian:

$$S_{inc}(\mathbf{q}, \omega) = \frac{1}{\pi} \frac{Dq^2}{(Dq^2)^2 + \omega^2}, \quad (7.3.9)$$

whose half-width at half-maximum is Dq^2 .

Since **incoherent neutrons measure only the self part**, this Lorentzian line shape provides a direct route to determining the diffusion coefficient D experimentally. By fitting the quasi-elastic broadening of $S_s(q, \omega)$, one extracts D without needing any information about the distinct part.

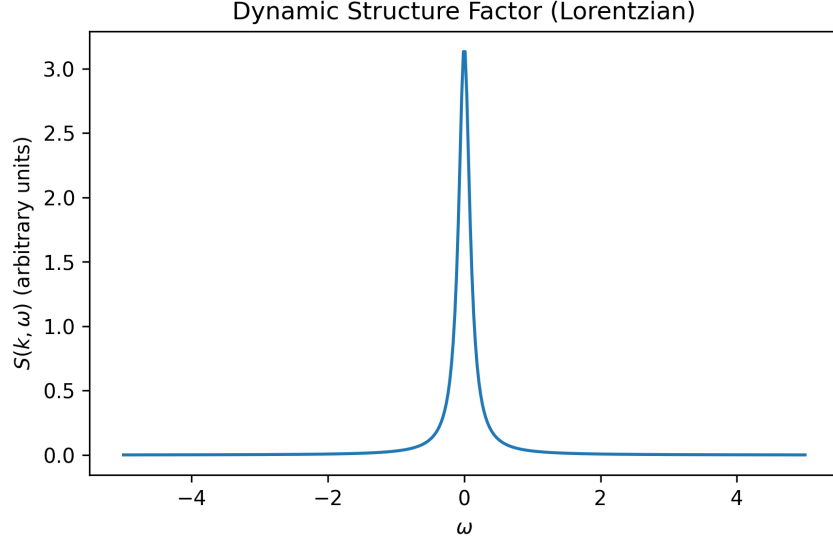


Figure 4: Dynamic structure factor in diffusion-dominated dynamics. The incoherent part $S_{inc}(q, \omega)$ is a Lorentzian whose width determines the diffusion coefficient.

7.4 Connection to Probability Density

For homogeneous fluids the self part of the van Hove function has a simple probabilistic interpretation. Equation (7.2.7) shows that $G_s(\mathbf{r}, t)$ is the probability density of displacement of a tagged particle after time t . In other words,

$$P(\mathbf{r}, t) \equiv G_s(\mathbf{r}, t) = \langle \delta(\mathbf{r} - [\mathbf{r}_i(t) - \mathbf{r}_i(0)]) \rangle, \quad (7.4.1)$$

where the average is over all particles i and over the equilibrium ensemble. This probability density fully characterises the statistics of single-particle displacements. Its Fourier transform with respect to \mathbf{r} is exactly the self intermediate scattering function: $F_s(\mathbf{q}, t)$ is the characteristic function of the displacement distribution. Consequently, knowledge of F_s at all \mathbf{q} is equivalent to knowing $P(\mathbf{r}, t)$.

In the long-time diffusive regime, $P(\mathbf{r}, t)$ becomes Gaussian and $F_s(\mathbf{q}, t)$ decays as $\exp(-Dq^2t)$, as shown earlier. However, deviations from Gaussian behaviour (for example, exponential tails in $P(\mathbf{r}, t)$) signal anomalous diffusion or dynamic heterogeneity. The van Hove formalism thus provides a bridge between microscopic dynamics and probability theory, and sets the stage for our next lecture on Brownian motion.

7.5 Summary

- Liquids reside at the edge of chaos: short-range structural order coexists with rapid, thermally driven rearrangements. This interplay manifests in broadened collective excitations and relaxation processes .
- The van Hove function $G(\mathbf{r}, t)$ quantifies density-density correlations in space and time. It reduces to $\delta(\mathbf{r}) + \rho g(r)$ at $t = 0$ and splits into a self part G_s (probability density of displacement) and a distinct part G_d (probability density of finding another particle at a given separation).

- The intermediate scattering function $F(\mathbf{q}, t)$ is the spatial Fourier transform of $G(\mathbf{r}, t)$ and is accessible via neutron scattering. Its self and distinct parts correspond to incoherent and coherent scattering respectively.
- The dynamic structure factor $S(\mathbf{q}, \omega)$ is the time Fourier transform of $F(\mathbf{q}, t)$ and reveals relaxation processes and collective excitations. For a diffusive self part it takes a Lorentzian form with width Dq^2 .
- The self part $G_s(\mathbf{r}, t)$ is the probability density of a particle's displacement. Its Fourier transform $F_s(\mathbf{q}, t)$ is the characteristic function of that probability distribution. This link to probability theory underpins the discussion of Brownian motion in the next lecture.