

Statistical physics of systems out of equilibrium

Henk van Beijeren
Institute for Theoretical Physics, Utrecht University

and KIAS Seoul September 2011

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1 Hydrodynamic equations

1.1 Conservation laws

One-component systems (one kind of particles) in the simplest case are characterized by just three conserved densities: *mass density*, $\rho(\mathbf{r}, t)$, *momentum*

density, $\mathbf{G}(\mathbf{r}, t) \equiv \rho(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t)$, with $\mathbf{u}(\mathbf{r}, t)$ the *local mass velocity*, and *energy density*, $\epsilon(\mathbf{r}, t)$. Microscopically, for a system of N particles in an external potential $m\mathcal{V}(\mathbf{r}, t)$ and with pair potential $\phi(r_{ij})$, between each pair i, j of particles, these densities are defined through:

$$\rho^{mic}(\mathbf{r}, t) = \sum_i^N m\delta(\mathbf{r} - \mathbf{r}_i(t)), \quad (1)$$

$$\mathbf{G}^{mic}(\mathbf{r}, t) = \sum_i^N m\mathbf{v}_i(t)\delta(\mathbf{r} - \mathbf{r}_i(t)), \quad (2)$$

$$\begin{aligned} \rho^{mic}(\mathbf{r}, t)\epsilon^{mic}(\mathbf{r}, t) &= \sum_i^N [m\{\frac{1}{2}v_i^2(t) + \mathcal{V}(\mathbf{r}_i(t), t)\} + \\ &\quad \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}(t))]\delta(\mathbf{r} - \mathbf{r}_i(t)), \end{aligned} \quad (3)$$

with $r_{ij} \equiv |\mathbf{r}_{ij}| \equiv |\mathbf{r}_i - \mathbf{r}_j|$. From these the macroscopic densities may be obtained either by spatial averaging (integrate over a little sphere around \mathbf{r} and divide by its volume), or by ensemble averaging (average over a large collection of systems that are considered to be macroscopically equivalent according to some criterium, perhaps up to small fluctuations), or by taking a Fourier transform and keeping only the long-wave-length components. It is common to split the energy density into macroscopic contributions and an internal energy density, in the simplest case according to

$$\epsilon(\mathbf{r}, t) = [\frac{1}{2}u^2(\mathbf{r}, t) + \mathcal{V}(\mathbf{r}, t)] + \tilde{\epsilon}(\mathbf{r}, t), \quad (4)$$

with *microscopic* internal energy density satisfying

$$\rho^{mic}(\mathbf{r}, t)\tilde{\epsilon}^{mic}(\mathbf{r}, t) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t))[\frac{1}{2}m|\mathbf{v}_i(t) - \mathbf{u}(\mathbf{r}, t)|^2 + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}, t)]. \quad (5)$$

Often part of the interaction energy also is counted as macroscopic energy, e.g. elastic energy in the case of reversible bending of an elastic rod, or Coulomb energy in the case of a charged object. But in this assignment there is quite some arbitrariness.

Thermodynamics teaches that internal energy density and pressure $p(\mathbf{r}, t)$ can be expressed through equations of state,

$$\tilde{\epsilon}(\mathbf{r}, t) = \tilde{\epsilon}(T(\mathbf{r}, t), \rho(\mathbf{r}, t)), \quad (6)$$

$$p(\mathbf{r}, t) = p(T(\mathbf{r}, t), \rho(\mathbf{r}, t)). \quad (7)$$

For systems with very large gradients (or extremely long-ranged potentials) these relationships may have to be generalized to non-local ones.

1.2 Continuity equation

For an arbitrary volume the change of the mass contained can be expressed as

$$\frac{dM}{dt} = \int_V \frac{\partial \rho}{\partial t} d\mathbf{r}. \quad (8)$$

Because of mass conservation it may also be expressed as

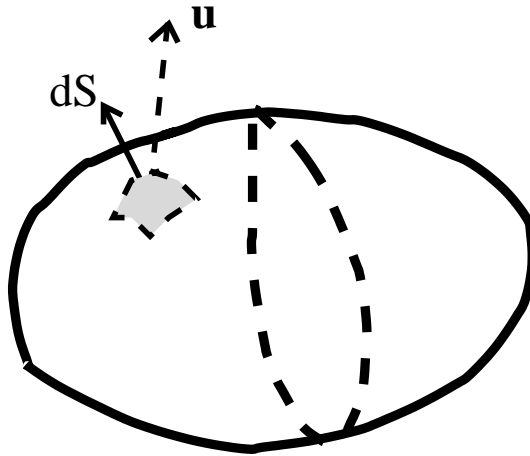


Figure 1: The mass flow through the surface element $d\mathbf{S}$ is $\rho \mathbf{u} d\mathbf{S}$

$$\begin{aligned} \frac{dM}{dt} &= - \int_S \rho \mathbf{u} \cdot d\mathbf{S}, \\ &= - \int_V \nabla \cdot (\rho \mathbf{u}) d\mathbf{r}, \end{aligned} \quad (9)$$

where Gauss' divergence theorem was used. Since (8) has to equal (9) for arbitrary V , the *continuity equation*

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{u}) \quad (10)$$

follows. After defining the comoving derivative

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{u} \cdot \nabla \quad (11)$$

we may rewrite this as

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{u} = 0. \quad (12)$$

A consequence is that *for an incompressible fluid*, where ρ is strictly constant, $\nabla \cdot \mathbf{u} = 0$.

1.3 Momentum current equation

In a similar way one may obtain the local momentum conservation law in the form

$$\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot \mathbf{J}_u - \mathbf{f}^{ext} \rho = 0, \quad (13)$$

with \mathbf{f}^{ext} the external force per unit mass. The momentum current is the sum of the macroscopic momentum current and the pressure tensor,

$$\mathbf{J}_u = \rho \mathbf{u} \mathbf{u} + \mathbf{P}. \quad (14)$$

Here $P_{\alpha\beta}$ is the flow per unit area of momentum in the α -direction, measured in the local rest frame, through a surface element normal to the β -direction, moving with the local velocity \mathbf{u} . This may alternatively be described as the force per unit area in the α -direction, exerted upon each other by the masses of fluid on either side of the surface element. For our system one can define a *microscopic pressure tensor*, describing this momentum flow for a specific configuration in phase space. It has the form

$$\begin{aligned} \mathbf{P}^{mic}(\mathbf{r}, t) &= \sum_i m(\mathbf{v}_i - \mathbf{u}(\mathbf{r}, t))(\mathbf{v}_i - \mathbf{u}(\mathbf{r}, t))\delta(\mathbf{r} - \mathbf{r}_i) \\ &+ \sum_{i < j} \int_0^1 d\lambda \mathbf{r}_{ij} \mathbf{F}_{ij} \delta(\mathbf{r} - \lambda \mathbf{r}_i - (1 - \lambda)\mathbf{r}_j). \end{aligned} \quad (15)$$

The continuity equation may be used to simplify (13) to

$$\rho \frac{D\mathbf{u}}{Dt} = \rho \mathbf{f}^{ext} - \nabla \cdot \mathbf{P}. \quad (16)$$

1.4 Energy equation

In the simplest case (no internal degrees of freedom, no long range interactions) the energy contained within a (small) volume V may be written as

$$E = \int_V \rho \left(\frac{1}{2} u^2 + \mathcal{V} + \hat{\epsilon} \right) d\mathbf{r}, \quad (17)$$

with ρ the (average) mass density within the volume, E the total energy contained within it, \mathcal{V} the external potential per unit mass and $\hat{\epsilon}(\mathbf{r}, t)$ the local internal energy per unit of mass. Energy conservation gives rise to the following equation:

$$\frac{dE}{dt} = - \int_S \mathbf{u} \cdot \mathbf{P} \cdot d\mathbf{S} + \int_V \rho \mathbf{u} \cdot \tilde{\mathbf{f}}^{ext} d\mathbf{r} - \int_S \rho \left(\frac{1}{2} u^2 + \mathcal{V} + \hat{\epsilon} \right) \mathbf{u} \cdot d\mathbf{S} - \int_S \mathbf{q} \cdot d\mathbf{S}, \quad (18)$$

with $\tilde{\mathbf{f}}^{ext} \equiv \mathbf{f}^{ext} + \nabla \mathcal{V}$ that part of the external force field that is not caused by the external potential (of course this may vanish). The first term on the rhs. describes the work done by displacing and deforming the mass within V . In case the pressure is uniform it may be identified with $-pdV$. The second term describes the average work done by external forces, the third one changes due to *convection* and the last term the contributions from the *heat current density* \mathbf{q} . Combining these two equations and using Gauss' divergence theorem one obtains

$$\frac{\partial [\rho (\frac{1}{2} u^2 + \mathcal{V} + \hat{\epsilon})]}{\partial t} = -\nabla \cdot [\mathbf{P} \cdot \mathbf{u} + \rho \mathbf{u} (\frac{1}{2} u^2 + \mathcal{V} + \hat{\epsilon})] + \rho \mathbf{u} \cdot \tilde{\mathbf{f}}^{ext} - \nabla \cdot \mathbf{q}. \quad (19)$$

By using both the continuity and the momentum current equation one may reduce this to

$$\rho \frac{D\hat{\epsilon}}{Dt} = -\mathbf{P} : \nabla \mathbf{u} - \nabla \cdot \mathbf{q}, \quad (20)$$

with the convention $\mathbf{A} : \mathbf{B} \equiv \sum_{ij} A_{ij} B_{ji}$. Further reformulations can be made by using e.g. the first and second law of thermodynamics to write

$$\frac{D\hat{\epsilon}}{Dt} = T \frac{D\hat{s}}{Dt} - p \frac{D\rho^{-1}}{Dt}, \quad (21)$$

with \hat{s} the entropy per unit mass.

Like for the momentum current equation one can define a microscopic heat current. The microscopic internal energy density satisfies equation (20) with \mathbf{P} and \mathbf{q} the microscopic pressure tensor and heat current density respectively.

1.5 Phenomenological laws

In order to obtain a set of closed hydrodynamic equations one has to express the currents in terms of the densities or of thermodynamically equivalent fields, such as temperature and chemical potential. For simple fluids the standard form for the heat current is *Fourier's law of heat conduction*,

$$\mathbf{q} = -\lambda \nabla T, \quad (22)$$

where λ is a *transport coefficient*, called the *heat conduction coefficient*. The standard phenomenological expression for the pressure tensor is

$$\mathbf{P} = [p - \kappa \nabla \cdot \mathbf{u}] \mathbf{I} - 2\eta \overset{\circ}{\nabla} \mathbf{u}. \quad (23)$$

Here p is the local equilibrium pressure, depending on e.g. local temperature and mass density the same way as in equilibrium; κ is called the *bulk viscosity* and η the *shear viscosity*. In this notation the tilde denotes a symmetric tensor, so one has $\tilde{A}_{ij} \equiv \frac{1}{2}(A_{ij} + A_{ji})$, and the dot denotes a traceless tensor, so in the end

$$(\overset{\circ}{\nabla} \mathbf{u})_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) - \frac{1}{3} \delta_{ij} \nabla \cdot \mathbf{u}. \quad (24)$$

The intuitive ideas behind this are: in a system of uniform temperature there should be no heat currents and in a system of uniform velocity there should be no momentum currents. For non-uniform systems the currents should depend on the gradients of temperature respectively velocity and the simplest assumptions one can make are linear relationships. Since ∇T is a vector, the heat current can simply be assumed being proportional to it. The velocity gradient is a second-degree tensor, the trace of which transforms as a scalar under coordinate transformations. In an isotropic system the trace of the pressure tensor and its traceless part transform independently; the former may be assumed to be proportional to the trace of the velocity gradient and the latter to the traceless part of this tensor. In addition, one can

easily see from the definition of the microscopic pressure tensor (15) that this tensor is symmetric (more generally this follows from angular momentum conservation), therefore it should be proportional to the *symmetrized* traceless velocity gradient. Note that for an incompressible fluid the bulk viscosity has to vanish because of (12). Inserting (23) into (16) and (22) plus (23) into (20) one obtains the hydrodynamic equations.

1.6 The diffusion equation

A much simpler case than the full hydrodynamic equations is the equation describing the transport of a dilute component in an inert background (often a fluid in equilibrium). Examples are Brownian motion and the diffusion of tracer particles (e.g. radioactive isotopes). If $\rho(\mathbf{r}, t)$ is the density of these tracer particles, this quantity satisfies again a continuity equation,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (25)$$

with $\mathbf{u}(\mathbf{r}, t)$ the average local velocity of the tracer component. But now the integral of $\rho \mathbf{u}$ is not conserved, as it is just the momentum of the tracer component alone. Instead it is a *diffusion current*, satisfying again a linear phenomenological equation, known as *Fick's first law*,

$$\rho \mathbf{u} = -D \nabla \rho. \quad (26)$$

D is called the *diffusion constant*. Combining (25) and (26) one obtains Fick's second law, or the linear *diffusion equation*

$$\frac{\partial \rho}{\partial t} = D \nabla^2 \rho. \quad (27)$$

In an infinite system with initial density $\rho(\mathbf{r}, 0)$ this equation can be solved easily, e.g. by using Fourier transform, with the result

$$\rho(\mathbf{r}, t) = \int d\mathbf{r}_0 G(\mathbf{r} - \mathbf{r}_0, t) \rho(\mathbf{r}_0, 0). \quad (28)$$

Here $G(\mathbf{r}, t)$ is the *diffusion Green function*,

$$G(\mathbf{r}, t) = \frac{e^{-\frac{r^2}{4Dt}}}{(4\pi Dt)^{d/2}}, \quad (29)$$

in d dimensions. As always, the Green function describes the decay of an initial delta function in space. For linear equations this suffices to describe the time evolution of an arbitrary initial distribution. An alternative for using the Green function is expanding the solution in terms of eigenfunctions. In the present case these are plane waves, $\exp(i\mathbf{k} \cdot \mathbf{r})$, with eigenvalue $-Dk^2$. For short times the Green function method converges faster (the Green function is still close to a δ function), but for long times the expansion in eigenfunctions is more efficient (only those that decay very slowly remain).

[Question: what is a good criterium to separate these regimes?]

1.7 The Euler equations

The simplest form of the hydrodynamic equations is obtained by neglecting all *dissipative terms*, i.e. all terms containing transport coefficients. This leaves the *Euler equations*:

$$\begin{aligned}\frac{D\rho}{Dt} &= -\rho\nabla \cdot \mathbf{u}, \\ \frac{D\mathbf{u}}{Dt} &= \mathbf{f}^{ext} - \frac{1}{\rho}\nabla p, \\ \frac{D\hat{s}}{Dt} &= 0.\end{aligned}\tag{30}$$

The last equation is obtained by combining (20) and (21) with the continuity equation. It teaches us that entropy does not increase under the action of the Euler equations (the effect of throwing away all dissipative terms!). And for a system starting out in a homogeneous state, the entropy per unit mass remains homogeneous throughout.

Let us further restrict ourselves to stationary systems in which the external force satisfies $\mathbf{f}^{ext} = -\nabla\mathcal{V}$. Using the identity

$$(\mathbf{u} \cdot \nabla)\mathbf{u} = \frac{1}{2}\nabla u^2 - \mathbf{u} \times (\nabla \times \mathbf{u})$$

we can rewrite (30) as

$$\nabla\left(\frac{1}{2}u^2 + \mathcal{V}\right) + \frac{1}{\rho}\nabla p = \mathbf{u} \times (\nabla \times \mathbf{u}).\tag{31}$$

This may be simplified in two important cases:

1) For incompressible fluids ρ is constant and from (30) it follows, by taking the curl, that $\nabla \times \mathbf{u} \equiv 0$ if this is satisfied at the initial time. Then (31) reduces to *Bernoulli's equation*,

$$\nabla\left(\frac{1}{2}\rho u^2 + \rho\mathcal{V} + p\right) = 0. \quad (32)$$

Of course the curl term may be left on the rhs. if it does not vanish.

2) For initially homogeneous systems the thermodynamic relationship

$$d\hat{h} = Td\hat{s} + \frac{1}{\rho}dp \quad (33)$$

for the enthalpy per unit mass may be used to replace $\nabla p/\rho$ in (30) by $\nabla\hat{h}$, leading to

$$\nabla\left(\frac{1}{2}u^2 + \mathcal{V} + \hat{h}\right) = \mathbf{u} \times (\nabla \times \mathbf{u}), \quad (34)$$

where again the rhs. vanishes for curl-free flows.

The Euler equations may also be used to describe sound propagation, ignoring damping. Using again the condition of initial homogeneity, which in this case is completely natural, and assuming there is no external potential (or, its gradient is sufficiently weak), one may rewrite (30) now as

$$\frac{D\mathbf{u}}{Dt} = -\frac{1}{\rho}\nabla p = -\frac{1}{\rho}\left(\frac{\partial p}{\partial\rho}\right)_{\hat{s}}\nabla\rho, \quad (35)$$

as the additional $\nabla\hat{s}$ -term vanishes. Inserting this into the time derivative of the continuity equation and *linearizing* the resulting equations ¹ one obtains the *sound propagation equation*

$$\frac{d^2\rho}{dt^2} = \left(\frac{\partial p}{\partial\rho}\right)_{\hat{s}}\nabla^2\rho. \quad (36)$$

Taking the Fourier transform of this equation, one immediately finds that the eigenfunctions (the *sound modes*) are of the form

$$\rho(\mathbf{r}, t) = \exp(-i\omega t \pm i\mathbf{k} \cdot \mathbf{r}),$$

with $\omega = \pm ck$ and $c^2 = \left(\frac{\partial p}{\partial\rho}\right)_{\hat{s}}$.

¹Linearizing implies ignoring all terms that are of higher than linear order in deviations from equilibrium. Such deviations include gradients of hydrodynamic fields and non-vanishing local velocities

1.8 The Navier-Stokes equations

Keeping the dissipative terms, but assuming that the transport coefficients are constant (which is not really correct; they do depend on temperature, density etc. But the approximation is a good one in many cases) one obtains the *Navier-stokes equations*:

$$\begin{aligned}
 \frac{D\rho}{Dt} &= -\rho\nabla\cdot\mathbf{u} \\
 \rho\frac{D\mathbf{u}}{Dt} &= \rho\mathbf{f}^{ext} - \nabla p + \eta\nabla^2\mathbf{u} + \left(\kappa + \frac{1}{3}\eta\right)\nabla(\nabla\cdot\mathbf{u}), \\
 \rho\frac{D\hat{\epsilon}}{Dt} &= -p\nabla\cdot\mathbf{u} + \left(\kappa - \frac{2}{3}\eta\right)(\nabla\cdot\mathbf{u})^2 + \eta[(\partial_\alpha u_\beta)(\partial_\beta u_\alpha) + (\partial_\alpha u_\beta)(\partial_\alpha u_\beta)] \\
 &\quad + \lambda\nabla^2 T,
 \end{aligned} \tag{37}$$

with summation convention for repeated indices. In order to have a closed set of equations one has to supplement the Navier-Stokes equations with equations of state for p and $\hat{\epsilon}$. In most cases these are used to eliminate the energy density in favor of the temperature.

1.8.1 Simple solutions

In general the Navier-Stokes equations are hard to solve and require heavy numerical methods. In simple geometries and with simple boundary conditions analytical solutions (or approximate solutions) may be obtained. A few examples follow:

Couette flow

This is the case of two infinite parallel plates at temperature T , moving with constant velocity with respect to each other. The most common boundary conditions used are *stick boundary conditions*, requiring that at contact points the fluid moves with the same velocity as the plate it touches. Suppose the plates are parallel to the xy -plane, the lower one is at rest at $z = 0$ and the upper one moves at $z = z_0$ with velocity $v_0\hat{\mathbf{x}}$ (with $\hat{\mathbf{a}}$ the unit vector in the direction of the vector \mathbf{a}). Then the momentum equation is solved by

$$\mathbf{u}(\mathbf{r}) = \frac{z}{z_0}v_0\hat{\mathbf{x}}.$$

The pressure is constant. If the system is incompressible, Landau and Lifshitz show in [1] Ch. V that the energy equation may be reduced to an equation for the temperature of the form

$$\rho c_p \frac{DT}{Dt} = \lambda \nabla^2 T + P_{\alpha\beta}(\partial_\alpha u_\beta). \quad (38)$$

For Couette flow this gives rise to a temperature profile of the form

$$T(\mathbf{r}) = T_0 - \frac{\eta v_0^2}{2\lambda z_0^2} z (z_0 - z).$$

[Question: what changes if η depends on temperature? Hint: multiply Eq.(38) by $\partial T/\partial z$ and integrate in two steps.]

Poiseuille flow

In the case of Poiseuille flow the plates are kept at rest, but the fluid is driven forward between them by means of a constant homogeneous pressure gradient (to be specific: assume in the x -direction, with strength p_x). Under stick boundary conditions this gives rise to a stationary velocity field

$$\mathbf{u}(\mathbf{r}) = -\frac{p_x}{2\eta} z (z_0 - z) \hat{\mathbf{x}}.$$

The resulting temperature field now is of the form

$$T(\mathbf{r}) = T_0 - \frac{p_x^2}{12\eta\lambda} \left[\left(z - \frac{z_0}{2} \right)^4 - \left(\frac{z_0}{2} \right)^4 \right].$$

2 Green-Kubo formalism

See references[2, 3, 4, 5, 6, 7, 9]

2.1 Tracer diffusion and self diffusion

Tracer diffusion is the phenomenon of diffusion of a very dilute substance in a macroscopically homogeneous background. The background may be a

gaseous or a liquid system, but it may also be a crystal or amorphous solid. In case the tracer particles are mechanically identical to the surrounding particles constituting the background, but are distinguishable from these, e.g. through the orientation of their nuclear spin, one talks of *self diffusion*. In any case, mutual interactions between different tracer particles should be negligible.

As argued in subsection 1.6 tracer diffusion is described at the macroscopic level by the diffusion equation

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D\nabla^2 n(\mathbf{r}, t), \quad (39)$$

where, this time, I used the number density rather than the mass density. Microscopically, $n(\mathbf{r}, t)$ is a fluctuating field. Its *average behavior* (i.e. averaged either over many tracer particles, or over many macroscopically equivalent realizations of the process) is described by (39). On the other hand it should also satisfy

$$n(\mathbf{r}, t) = \sum_i P_i(\mathbf{r}, t), \quad (40)$$

where i runs over all tracer particles and $P_i(\mathbf{r}, t)$ is the probability density for finding particle i at \mathbf{r} at time t . Again, the probabilistic nature comes from averaging over macroscopically equivalent realizations of the initial state. From (40) and the linearity of the diffusion equation it follows that on macroscopic time and length scales also $P_i(\mathbf{r}, t)$ must satisfy the diffusion equation.

As stated before, the solution of the diffusion equation starting out from a δ -function in space as initial condition, in a d -dimensional system is of the form

$$G_D(\mathbf{r}, t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right). \quad (41)$$

Applied to $P_i(\mathbf{r}, t)$ this describes the probability density for a tracer particle to be displaced over \mathbf{r} during a time interval of length t . Hence, we may conclude that the *mean squared displacement* of a tracer particle as function

of time may be found as

$$\begin{aligned}
\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle &= \int d\mathbf{r} G_D(\mathbf{r}, t) r^2, \\
&= \int d\mathbf{r} \frac{r^2}{(4\pi Dt)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right), \\
&= 2dDt.
\end{aligned} \tag{42}$$

In physical processes the actual probability density will differ from the diffusion Green function, but for long enough times and large enough displacements it will approach to it. This implies that (42) will be valid asymptotically for $t \rightarrow \infty$. This is expressed by the famous *Einstein relation*

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{2dt}. \tag{43}$$

Under mild conditions this can be transformed in a few steps to a *Green-Kubo expression*:

$$\begin{aligned}
D &= \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle, \\
&\quad \text{(provided this limit exists)} \\
&= \lim_{t \rightarrow \infty} \frac{1}{d} \langle (\mathbf{r}(t) - \mathbf{r}(0)) \cdot \mathbf{v}(t) \rangle, \\
&= \lim_{t \rightarrow \infty} \frac{1}{d} \int_0^t d\tau \langle \mathbf{v}(\tau) \cdot \mathbf{v}(t) \rangle, \\
&= \lim_{t \rightarrow \infty} \frac{1}{d} \int_0^t d\tau \langle \mathbf{v}(0) \cdot \mathbf{v}(t - \tau) \rangle \\
&= \frac{1}{d} \int_0^\infty dt \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle.
\end{aligned} \tag{44}$$

In these expressions the brackets indicate averaging over an equilibrium ensemble (e.g. the canonical ensemble). This does not imply though that the diffusion constant is an equilibrium property that can be obtained from thermodynamics. It is crucial that the average involves products of phase space functions at different times (in this case just two velocities of the same particle). Equilibrium averages of such products are called *equilibrium time correlation functions*. The specific correlation function considered

here, $\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$, is known as the *velocity autocorrelation function*. In equilibrium, or more generally in stationary states, time correlation functions possess time translation invariance:

$$\langle A(t_1)B(t_2) \rangle = \langle A(t_1 + \tau)B(t_2 + \tau) \rangle = \langle A(0)B(t_2 - t_1) \rangle. \quad (45)$$

This has been used in the chain of simplifications leading to (44).

2.2 Frequency and wave number dependent diffusion coefficient

Fourier and Laplace transform of the diffusion equation leads to

$$\begin{aligned} (z + Dk^2)\tilde{n}(\mathbf{k}, z) &= n(\mathbf{k}, t = 0), & \text{or} \\ \tilde{n}(\mathbf{k}, z) &= G_D(\mathbf{k}, z)n(\mathbf{k}, t = 0), & \text{with} \\ G_D(\mathbf{k}, z) &= \frac{1}{z + Dk^2}. \end{aligned} \quad (46)$$

This should describe physical diffusive systems on large time and length scales, corresponding to the limit of both k and z tending to zero. Hence, it is reasonable to assume that the full Green function of such a system can be written in the form

$$G(\mathbf{k}, z) = \frac{1}{z + U(\mathbf{k}, z)k^2}, \quad (47)$$

$$\text{with} \quad D = \lim_{\substack{\mathbf{k} \rightarrow 0 \\ z \rightarrow 0^+}} U(\mathbf{k}, z). \quad (48)$$

The limit $D > 0$ should be independent of the direction from which the point $\mathbf{k}, z = \mathbf{0}, 0$ is approached, as long as $Re(z) > 0$.

$G(\mathbf{k}, z)$, and consequently $U(\mathbf{k}, z)$, may be expressed in terms of time corre-

lation functions:

$$\begin{aligned}
G(\mathbf{k}, z) &= \int_0^\infty dt e^{-zt} \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle \delta(\mathbf{r}_1(t) - \mathbf{r}_1(0) - \mathbf{r}) \rangle, \\
&= \int_0^\infty dt e^{-zt} \langle e^{-i\mathbf{k}\cdot(\mathbf{r}_1(t) - \mathbf{r}_1(0))} \rangle, \\
&= \left[\frac{-e^{-zt}}{z} \langle e^{-i\mathbf{k}\cdot(\mathbf{r}_1(t) - \mathbf{r}_1(0))} \rangle \right]_0^\infty + \frac{1}{z} \int_0^\infty dt e^{-zt} \langle -i\mathbf{k} \cdot \mathbf{v}_1(t) e^{-i\mathbf{k}\cdot(\mathbf{r}_1(t) - \mathbf{r}_1(0))} \rangle, \\
&= \frac{1}{z} + \int_0^\infty dt \frac{e^{-zt}}{z} \langle -i\mathbf{k} \cdot \mathbf{v}_1(0) e^{-i\mathbf{k}\cdot(\mathbf{r}_1(0) - \mathbf{r}_1(-t))} \rangle, \\
&= \frac{1}{z} - \left[\frac{1}{z^2} e^{-zt} \langle -i\mathbf{k} \cdot \mathbf{v}_1(t) e^{-i\mathbf{k}\cdot(\mathbf{r}_1(t) - \mathbf{r}_1(0))} \rangle \right]_0^\infty \\
&\quad - \frac{1}{z^2} \int_0^\infty dt e^{-zt} \langle (\mathbf{k} \cdot \mathbf{v}_1(0)) (\mathbf{k} \cdot \mathbf{v}_1(-t)) e^{-i\mathbf{k}\cdot(\mathbf{r}_1(0) - \mathbf{r}_1(-t))} \rangle, \\
G(\mathbf{k}, z) &= \frac{1}{z} - \frac{k^2}{z^2} \int_0^\infty dt e^{-zt} \langle (\hat{\mathbf{k}} \cdot \mathbf{v}_1(0)) (\hat{\mathbf{k}} \cdot \mathbf{v}_1(t)) e^{-i\mathbf{k}\cdot(\mathbf{r}_1(t) - \mathbf{r}_1(0))} \rangle, \tag{49} \\
&\equiv \frac{1}{z} - \frac{k^2}{z^2} C(\mathbf{k}, z). \tag{50}
\end{aligned}$$

Here the inverse Laplace transform of $C(\mathbf{k}, z)$ is the *wave number dependent velocity autocorrelation function*

$$C(\mathbf{k}, t) = \langle (\hat{\mathbf{k}} \cdot \mathbf{v}_1(0)) (\hat{\mathbf{k}} \cdot \mathbf{v}_1(t)) e^{-i\mathbf{k}\cdot(\mathbf{r}_1(t) - \mathbf{r}_1(0))} \rangle. \tag{51}$$

Some algebra yields

$$U(\mathbf{k}, z) = \frac{zC(\mathbf{k}, z)}{z - k^2C(\mathbf{k}, z)}, \tag{52}$$

$$\text{or } C(\mathbf{k}, z) = \frac{zU(\mathbf{k}, z)}{z + k^2U(\mathbf{k}, z)}. \tag{53}$$

From the regular behavior around $\mathbf{k}, z = \mathbf{0}, 0$ of $U(\mathbf{k}, z)$ we may conclude that the diffusion coefficient follows from $C(\mathbf{k}, z)$ as

$$D = \lim_{z \rightarrow 0} \lim_{k \rightarrow 0} C(\mathbf{k}, z). \tag{54}$$

This is again the Green-Kubo expression (44). But note that $C(\mathbf{k}, z)$ has a very discontinuous behavior near the origin! For example, one has

$$\lim_{k \rightarrow 0} C(k, \alpha k^2) = \frac{\alpha D}{\alpha + D}.$$

So far no physical details have been invoked yet. We only have seen statements of the type "If a system behaves diffusively on large time and length scales, its diffusion coefficient can be expressed as ...". To determine the actual properties of functions such as $U(\mathbf{k}, z)$ for some physical system one should in some way start from the equations of motion (classically or quantum mechanically) and derive from these the form of $U(\mathbf{k}, z)$. The expressions in terms of time correlation functions are a very convenient tool for reaching this goal, but basically no more than that.

Once the function $U(\mathbf{k}, z)$ is known explicitly one may rewrite the diffusion equation as a non-local equation (both in position and time) that takes full account of all information contained in $U(\mathbf{k}, z)$. The form of this equation is

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = \nabla^2 \int d\mathbf{r}' \int_0^t dt' u(\mathbf{r}', t') n(\mathbf{r} - \mathbf{r}', t - t'). \quad (55)$$

Here $u(\mathbf{r}, t)$ is the inverse Fourier and Laplace transform of $U(\mathbf{k}, z)$. If the density changes only on time and length scales that are large compared to the ranges in time and space of $u(\mathbf{r}, t)$, this equation reduces to the ordinary diffusion equation, with indeed, $D = \int d\mathbf{r} \int_0^\infty dt u(\mathbf{r}, t) = U(\mathbf{0}, 0)$.

Remark: Instead of the Laplace transform one often uses the Fourier transform with respect to time, defined through

$$\hat{f}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} f(t).$$

For even functions f this is simply related to the Laplace transform through $\hat{f}(\omega) = \tilde{f}(i\omega) + \tilde{f}(-i\omega)$. Autocorrelation functions $\langle f(0)f(t) \rangle$ are even because of time translation invariance.

2.3 Projection operator formalism

The projection operator method has been introduced in Green-Kubo theory by Zwanzig[10] and Mori[11]. It can be avoided, but there are a number of advantages in using it:

- 1) The connections between Green-Kubo formalism for hydrodynamic fluctuations and linear response theory become more transparent.
- 2) The structure of equations remains simpler in more complicated situations, such as the description of hydrodynamic fluctuations in liquids,
- 3) The physical ideas underlying the method are interesting and illuminating.
- 4) It appears very frequently in the physics literature, so it is useful knowing it.

As preliminaries we first introduce a Hilbert space of square integrable functions on phase space under the inner product

$$\langle f | g \rangle = \sum_N \int d\Gamma \rho_G(\Gamma) (f(\Gamma) - \langle f(\Gamma) \rangle)^* (g(\Gamma) - \langle g(\Gamma) \rangle). \quad (56)$$

Here $\Gamma \equiv (\mathbf{r}_1 \cdots \mathbf{r}_N, \mathbf{p}_1 \cdots \mathbf{p}_N)$ and ρ_G denotes the grand canonical density.

The time evolution of phase functions (i.e. functions depending on the position and momentum coordinates of the particles in the system) may be described formally through the action of the *Liouville operator*, i.e.

$$\frac{df(\Gamma)}{dt} = \mathcal{L}f(\Gamma) = \sum_{i=1}^N \left\{ \frac{\mathbf{p}_i}{m} \cdot \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial V(\mathbf{r}_1 \cdots \mathbf{r}_N)}{\partial \mathbf{r}_i} \cdot \frac{\partial}{\partial \mathbf{p}_i} \right\} f(\Gamma), \quad (57)$$

$$f(\Gamma(t)) = e^{\mathcal{L}t} f(\Gamma). \quad (58)$$

In addition the time evolution of an ensemble in phase space is described by²

$$\frac{\partial \rho(\Gamma)}{\partial t} = -\mathcal{L}\rho(\Gamma), \quad (59)$$

$$\rho(\Gamma, t) = e^{-\mathcal{L}t} \rho(\Gamma, 0) = \rho(e^{-\mathcal{L}t} \Gamma, 0). \quad (60)$$

For infinite systems or systems with periodic boundary conditions, without external potential, \mathcal{L} commutes with the *translation operator* $T(\mathbf{a})$, defined through

$$T(\mathbf{a})f(\mathbf{r}_1 \cdots \mathbf{r}_N, \mathbf{p}_1 \cdots \mathbf{p}_N) = f(\mathbf{r}_1 + \mathbf{a} \cdots \mathbf{r}_N + \mathbf{a}, \mathbf{p}_1 \cdots \mathbf{p}_N). \quad (61)$$

²Here Γ denotes an arbitrary point in phase space and *not* the set of coordinates of all particles, as in (57).

The reason for this is that in these cases the potential depends on relative coordinates only and therefore is invariant under the action of $T(\mathbf{a})$. Then the Hilbert space can be decomposed into Fourier components consisting of functions of the form

$$e^{-i\mathbf{k}\cdot\mathbf{R}}f(\boldsymbol{\rho}_1\cdots\boldsymbol{\rho}_N,\mathbf{p}_1\cdots\mathbf{p}_N)$$

with \mathbf{R} the center of mass and $\boldsymbol{\rho}_i = \mathbf{r}_i - \mathbf{R}$. The operator $e^{\mathcal{L}t}$ maps each Fourier component onto itself³

Let us assume that the system contains exactly one tracer particle, which we will label as particle 1. Consider all square integrable functions under the inner product (56) of its coordinates, $\mathbf{r}_1, \mathbf{p}_1$ and their equilibrium averages $\langle f(\mathbf{r}_1, \mathbf{p}_1) \rangle$. They can be decomposed into functions of the form $\exp(-i\mathbf{k}\cdot\mathbf{r}_1)P_n(\mathbf{p}_1)$, with P_n a complete set of orthogonal polynomials under the inner product (56). Note that the equilibrium averages vanish for all non-zero \mathbf{k} . One may investigate how the averages of all these functions over a *non-equilibrium ensemble* evolve in time. For $k \rightarrow 0$ one should expect this decay is very slow for the averages $\langle \exp(-i\mathbf{k}\cdot\mathbf{r}_1) \rangle$, since these are the Fourier components of the tagged particle density, which ought to satisfy a diffusion equation. There is no reason to expect an independent slow decay for any of the other functions of particle 1, since the distribution of its momentum, if not an equilibrium distribution initially, will approach such a distribution rapidly. Averages of other phase space functions of particle 1 may have a small component that decays diffusively as well, because the microscopic function that on average decays according to the diffusion equation is not entirely identical to $\exp(-i\mathbf{k}\cdot\mathbf{r}_1)$. But these slow decays are not independent of the decay of $\langle \exp(-i\mathbf{k}\cdot\mathbf{r}_1) \rangle$ and in the projection operator formalism it is the latter that is entirely representing them. There could in principle be phase space functions involving other particles that would decay slowly, but for the time being we will assume that the "bath" consisting of these particles is perfectly in equilibrium, or at most shows small deviations that are determined completely again by the tagged particle density $\langle \exp(-i\mathbf{k}\cdot\mathbf{r}_1) \rangle$.

³One may also describe the momenta in the center of mass frame, in other words set the total momentum equal to zero. For the decomposition into Fourier components this is not necessary, but in doing so-called *molecular dynamics* simulations it is the standard choice.

We now introduce the projection operator^{4 5} with the idea that the average time evolution of the set of functions $n_t(\mathbf{k})$ will determine the slowly decaying part of an arbitrary function $f(\mathbf{r}_1, \mathbf{p}_1)$. In addition we define

$$\mathcal{P}_\perp = 1 - \mathcal{P} \quad (62)$$

and

$$\widehat{\mathcal{L}} = \mathcal{P}_\perp \mathcal{L} \mathcal{P}_\perp. \quad (63)$$

Let the system to be considered be described by an ensemble of the form

$$\rho(t) = \rho_0(1 + \Delta(t)) = \rho_0(1 + \mathcal{P}\Delta(t) + \mathcal{P}_\perp\Delta(t)), \quad (64)$$

with ρ_0 the Grand canonical distribution. The time evolution of this is described by Liouville's equation (59)

$$\frac{\partial \rho(t)}{\partial t} = -\mathcal{L}\rho(t) = -\rho_0 \mathcal{L}\Delta(t), \quad (65)$$

where the identity $\mathcal{L}\rho_0 = 0$ was used. This may be worked out into the two equations

$$\frac{\partial \mathcal{P}\Delta(t)}{\partial t} = -\mathcal{P}\mathcal{L}\mathcal{P}_\perp\Delta(t), \quad (66)$$

$$\frac{\partial \mathcal{P}_\perp\Delta(t)}{\partial t} = -\mathcal{P}_\perp\mathcal{L}\mathcal{P}_\perp\Delta(t) - \mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(t). \quad (67)$$

In deriving (66) we used $\mathcal{P}\mathcal{L}\mathcal{P} = 0$, following from $\langle n_t(\mathbf{k}) | \mathcal{L} | n_t(\mathbf{k}) \rangle = 0$. Eq. (67) can be solved for $\mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(t)$, as

$$\mathcal{P}_\perp\Delta(t) = -\int_0^t d\tau e^{-\widehat{\mathcal{L}}(t-\tau)} \mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(\tau) + e^{-\widehat{\mathcal{L}}t} \mathcal{P}_\perp\Delta(0). \quad (68)$$

Substitution into (66) results into

$$\frac{\partial \mathcal{P}\Delta(t)}{\partial t} = \int_0^t d\tau \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\widehat{\mathcal{L}}\tau} \mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(t-\tau) - \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\widehat{\mathcal{L}}t} \mathcal{P}_\perp\Delta(0). \quad (69)$$

⁴There is no need here to subtract the averages of phase space functions, as is done in (56). For $\mathbf{k} \neq 0$ the averages all vanish. For $\mathbf{k} = 0$ $n_t(\mathbf{k})$ reduces to a constant, so its time evolution is trivial.

⁵In order to have \mathcal{P} to project onto slowly decaying functions only one should specify an upper cut-off on the value of k . The choice of this is somewhat arbitrary. Fortunately, since the time evolution in the present case does not couple different values of \mathbf{k} this does not really matter. For any value of \mathbf{k} the projection operator projects onto a single function within the corresponding set.

Next use:

$$\mathcal{L}n_t(\mathbf{k}) = \mathcal{L}e^{-i\mathbf{k}\cdot\mathbf{r}_1} = -i\mathbf{k} \cdot \frac{\mathbf{p}_1}{m_1} e^{-i\mathbf{k}\cdot\mathbf{r}_1} \equiv -ikj_t(\mathbf{k}). \quad (70)$$

Insert this into (69) letting the first \mathcal{L} act to the left. This yields

$$\frac{\partial \mathcal{P}\Delta(t)}{\partial t} = - \sum_{\mathbf{k}} k^2 \int_0^t d\tau \langle j_t(\mathbf{k}) | e^{-\hat{\mathcal{L}}\tau} j_t(\mathbf{k}) \rangle \mathcal{P}\Delta(t-\tau) - \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\hat{\mathcal{L}}t} \mathcal{P}_\perp \Delta(0). \quad (71)$$

Let us denote the average tracer density by $\bar{n}_t(\mathbf{k}, t)$. It is given by

$$\begin{aligned} \bar{n}_t(\mathbf{k}, t) &= \sum_N \int d\Gamma \rho_0 [1 + \Delta(t)] n_t(\mathbf{k}) \\ &= \delta_{\mathbf{k}0} + \langle \Delta(t) | n_t(\mathbf{k}) \rangle \end{aligned} \quad (72)$$

With this notation we may rewrite the adjoint of (71) as

$$\frac{\partial \bar{n}_t(\mathbf{k}, t)}{\partial t} = -k^2 \int_0^t d\tau \langle j_t(\mathbf{k}) | e^{\hat{\mathcal{L}}\tau} j_t(\mathbf{k}) \rangle \bar{n}_t(\mathbf{k}, t-\tau) + \langle \Delta(0) | \mathcal{P}_\perp e^{\hat{\mathcal{L}}t} \mathcal{P}_\perp \mathcal{L}n_t(\mathbf{k}) \rangle, \quad (73)$$

where we used that $-\hat{\mathcal{L}}$ is the adjoint of $\hat{\mathcal{L}}$. We expect that for the perturbations under consideration (only particle 1 out of equilibrium) the propagator $e^{\hat{\mathcal{L}}t}$ induces a rapid decay to zero⁶. Then the second term on the rhs. of (73) may be neglected and we recover the generalized diffusion equation

$$\frac{\partial \bar{n}_t(\mathbf{k}, t)}{\partial t} = -k^2 \int_0^t d\tau u(\mathbf{k}, \tau) \bar{n}_t(\mathbf{k}, t-\tau). \quad (74)$$

with now

$$u(\mathbf{k}, t) = \langle j_t(\mathbf{k}) | e^{\hat{\mathcal{L}}t} j_t(\mathbf{k}) \rangle. \quad (75)$$

From (74) we see that $\langle j_t(\mathbf{k}) | e^{\hat{\mathcal{L}}\tau} j_t(\mathbf{k}) \rangle$ describes the response of $\partial n_t(\mathbf{k}, t)/\partial t$ to $n_t(\mathbf{k}, t-\tau)$. The orthogonal projection in $e^{\hat{\mathcal{L}}\tau}$ prevents double counting of

⁶The assumption underlying this is that it is true for $\mathbf{k} = 0$, where all functions depend on \mathbf{p}_1 only. The function $n_t(0)$ is just unity and does not decay. The averages of all functions of \mathbf{p}_1 orthogonal to this under the inner product (56) are expected to decay rapidly to their equilibrium value, which is zero, because it is just the inner product with the unit function). Then it will remain true for small k , because the spectrum of $\hat{\mathcal{L}}$ depends smoothly on \mathbf{k} .

the response to $n_t(\mathbf{k}, \tau')$, with $t - \tau < \tau' < t$. In the limit $k \rightarrow 0$ $n_t(\mathbf{k}, \tau')$ is not excited and $e^{\hat{\mathcal{L}}\tau}$ becomes identical to $e^{\mathcal{L}\tau}$, as follows from (53).

We may also use the projection operator technique for deriving (53) in an alternative way. First note the identity

$$C(\mathbf{k}, z) = \langle j_t(\mathbf{k}) | (z - \mathcal{L})^{-1} j_t(\mathbf{k}) \rangle. \quad (76)$$

Next we need a chain of algebraic operator identities:

$$\mathcal{P}_\perp (z - \mathcal{L})^{-1} \mathcal{P}_\perp = \mathcal{P}_\perp \left[(z - \hat{\mathcal{L}})^{-1} + (z - \hat{\mathcal{L}})^{-1} (\mathcal{P}\mathcal{L}\mathcal{P}_\perp + \mathcal{P}_\perp \hat{\mathcal{L}}\mathcal{P}) (z - \mathcal{L})^{-1} \right] \mathcal{P}_\perp,$$

again using $\mathcal{P}\mathcal{L}\mathcal{P} = 0$. Next use $\mathcal{P}_\perp (z - \hat{\mathcal{L}})^{-1} \mathcal{P} = 0$ to obtain

$$\mathcal{P}_\perp (z - \mathcal{L})^{-1} \mathcal{P}_\perp = \mathcal{P}_\perp (z - \hat{\mathcal{L}})^{-1} \left[1 + \mathcal{P}_\perp \mathcal{L}\mathcal{P} \left\{ (z - \hat{\mathcal{L}})^{-1} + (z - \hat{\mathcal{L}})^{-1} \mathcal{P}\mathcal{L}\mathcal{P}_\perp (z - \mathcal{L})^{-1} \right\} \right] \mathcal{P}_\perp,$$

The same identity has been used again for $(z - \mathcal{L})^{-1}$, plus $\mathcal{P}(z - \hat{\mathcal{L}})^{-1} \mathcal{P}_\perp = 0$.

Using this once more leads to

$$\mathcal{P}_\perp (z - \mathcal{L})^{-1} \mathcal{P}_\perp = \mathcal{P}_\perp (z - \hat{\mathcal{L}})^{-1} \left[1 - |ikj_t(\mathbf{k})\rangle \langle n_t(\mathbf{k}) | (z - \hat{\mathcal{L}})^{-1} n_t(\mathbf{k}) \rangle ikj_t(\mathbf{k}) | (z - \mathcal{L})^{-1} \right] \mathcal{P}_\perp. \quad (77)$$

Next use $(z - \hat{\mathcal{L}})^{-1} n_t(\mathbf{k}) = n_t(\mathbf{k})/z$ and take the inner product $\langle j_t(\mathbf{k}) | \cdots j_t(\mathbf{k}) \rangle$ on both sides. This reproduces eq. (52);

$$C(\mathbf{k}, z) = U(\mathbf{k}, z) \left(1 - \frac{k^2}{z} C(\mathbf{k}, z) \right).$$

An important remark to be made here is that the tagged particle density-density time correlation function satisfies exactly the same generalized diffusion equation (73) as the tagged particle density itself. This follows from the identities

$$\begin{aligned} \langle n_t(\mathbf{k}) | n_t(\mathbf{k}, t) \rangle &= \langle n_t(\mathbf{k}) | e^{\mathcal{L}t} n_t(\mathbf{k}) \rangle, \\ \text{and} \quad \langle \Delta(t) | n_t(\mathbf{k}) \rangle &= \langle e^{-\mathcal{L}t} \Delta(0) | n_t(\mathbf{k}) \rangle = \langle \Delta(0) | e^{\mathcal{L}t} n_t(\mathbf{k}) \rangle. \end{aligned}$$

The right hand sides are identical in case $\mathcal{P}_\perp \Delta(0) = 0$. This demonstrates *Onsager's regression hypothesis*: Thermally excited fluctuations in an equilibrium system *on average* decay in exactly the same way as small macroscopic deviations from equilibrium. The decay of the probability distribution $P(\mathbf{r}, t)$ for the position of a tagged particle according to the (generalized) diffusion equation is just one example of this.

2.4 Hydrodynamic equations for a simple fluid

In this section I will represent the hydrodynamic fields of a simple fluid primarily by number density, momentum density and energy density. Their Fourier components are given, microscopically, by

$$\hat{n}(\mathbf{k}) = \sum_{i=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i}, \quad (78)$$

$$\hat{\mathbf{G}}(\mathbf{k}) = \sum_{i=1}^N \mathbf{p}_i e^{-i\mathbf{k}\cdot\mathbf{r}_i}, \quad (79)$$

$$\hat{\epsilon}(\mathbf{k}) = \sum_{i=1}^N \epsilon_i e^{-i\mathbf{k}\cdot\mathbf{r}_i}, \quad (80)$$

with

$$\epsilon_i = \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}). \quad (81)$$

Since we will only consider small deviations from total equilibrium we need not define the densities in a local comoving frame, as in (2,3). Other hydrodynamic fields may be defined as linear combinations of the above ones. For example the temperature field may be introduced as

$$T(\mathbf{r}, t) = T_0(\mathbf{r}, t) + \left(\frac{\partial T}{\partial n} \right)_{\epsilon} \delta n(\mathbf{r}, t) + \left(\frac{\partial T}{\partial \epsilon} \right)_{n} \delta \epsilon(\mathbf{r}, t), \quad (82)$$

with $\delta n(\mathbf{r}, t) = n(\mathbf{r}, t) - n_0(\mathbf{r}, t)$ and $\delta \epsilon(\mathbf{r}, t) = \epsilon(\mathbf{r}, t) - \epsilon_0(\mathbf{r}, t)$ the deviations of number and energy density from their equilibrium values. For the Fourier components this leads to

$$\hat{T}(\mathbf{k}, t) = \left(\frac{\partial T}{\partial n} \right)_{\epsilon} \hat{n}(\mathbf{k}, t) + \left(\frac{\partial T}{\partial \epsilon} \right)_{n} \hat{\epsilon}(\mathbf{k}, t). \quad (83)$$

This has to be generalized slightly as \mathbf{k} is increased; in fact the dependence of temperature on density and energy density exhibits mild non-local effects due to the interactions between particles. In Appendix A it is shown how these effects can be taken into account. On our Hilbert space we may introduce the projection operator P , projecting for each \mathbf{k} onto the $d+2$ (five in three

dimensions) densities specified above. For a compact description of this it is useful introducing the $d + 2$ -dimensional vector

$$\boldsymbol{\psi}(\mathbf{k}) = \begin{pmatrix} \widehat{n}(\mathbf{k}) \\ \widehat{\mathbf{G}}(\mathbf{k}) \\ \widehat{\boldsymbol{\epsilon}}(\mathbf{k}) \end{pmatrix} \quad (84)$$

plus the adjoint vector

$$\boldsymbol{\phi}(\mathbf{k}) = \boldsymbol{\psi}(\mathbf{k}) \circ \boldsymbol{\chi}^{-1}(\mathbf{k}). \quad (85)$$

Here \circ denotes the simple inner product $\mathbf{a} \circ \mathbf{b} = \sum_i a_i b_i$ in the $(d + 2)$ -dimensional space spanned by $\boldsymbol{\psi}(\mathbf{k})$. In other words,

$$\phi_i(\mathbf{k}) = \sum_j \psi_j(\mathbf{k}) \chi_{ji}^{-1}(\mathbf{k}).$$

The matrix $\boldsymbol{\chi}$ is defined through

$$\chi_{ij}(\mathbf{k}) = \langle \psi_i(\mathbf{k}) | \psi_j(\mathbf{k}) \rangle, \quad (86)$$

from which one immediately obtains the identities

$$\langle \psi_i(\mathbf{k}) | \phi_j(\mathbf{k}) \rangle = \langle \phi_i(\mathbf{k}) | \psi_j(\mathbf{k}) \rangle = \delta_{ij}.$$

In terms of these vectors the projection operator may be expressed as

$$\mathcal{P} = \sum_{\mathbf{k}} |\boldsymbol{\psi}(\mathbf{k})\rangle \circ \langle \boldsymbol{\phi}(\mathbf{k})|, \quad (87)$$

$$= \sum_{\mathbf{k}} |\boldsymbol{\phi}(\mathbf{k})\rangle \circ \langle \boldsymbol{\psi}(\mathbf{k})|. \quad (88)$$

This may be rewritten in a physically more appealing form as

$$\mathcal{P} = \frac{1}{V} \sum_{\mathbf{k}} \left[|\widehat{n}(\mathbf{k})\rangle \langle \widehat{\nu}(\mathbf{k})| + \frac{\beta_0}{mn_0} |\widehat{\mathbf{G}}(\mathbf{k})\rangle \cdot \langle \widehat{\mathbf{G}}(\mathbf{k})| - |\widehat{\boldsymbol{\epsilon}}(\mathbf{k})\rangle \langle \widehat{\boldsymbol{\beta}}(\mathbf{k})| \right]. \quad (89)$$

Here we introduced the fields β and ν . These are defined through

$$\beta(\mathbf{r}, t) = \frac{1}{k_B T(\mathbf{r}, t)}, \quad (90)$$

$$\nu(\mathbf{r}, t) = \beta(\mathbf{r}, t) \mu(\mathbf{r}, t), \quad (91)$$

with μ the chemical potential. Precise definitions and a derivation of (89) are given in Appendix A. An alternative for (89) may be obtained by replacing the energy density $\hat{\epsilon}(\mathbf{k})$ and the variable $\hat{v}(\mathbf{k})$ by \mathbf{k} -dependent generalizations of the entropy per unit mass, $\hat{\sigma}(\mathbf{k})$ and the pressure, $\hat{p}(\mathbf{k})$ (Appendix A). This yields

$$\mathcal{P} = \frac{\beta_0}{Vn_0} \sum_{\mathbf{k}} \left[|\hat{n}(\mathbf{k})\rangle\langle\hat{p}(\mathbf{k})| + \frac{1}{m} |\hat{\mathbf{G}}(\mathbf{k})\rangle \cdot \langle\hat{\mathbf{G}}(\mathbf{k})| + n_0^2 |\hat{\sigma}(\mathbf{k})\rangle\langle\hat{T}(\mathbf{k})| \right]. \quad (92)$$

Now we are ready to formulate the hydrodynamic equations linearized around a total equilibrium state in a homogeneous system. Set again

$$\rho(t) = \rho_0[1 + \mathcal{P}\Delta(t) + \mathcal{P}_\perp\Delta(t)]. \quad (93)$$

Like in the case of tracer diffusion the equation for the time evolution can be split up as

$$\frac{\partial\mathcal{P}\Delta(t)}{\partial t} = -\mathcal{P}\mathcal{L}\mathcal{P}\Delta(t) - \mathcal{P}\mathcal{L}\mathcal{P}_\perp\Delta(t), \quad (94)$$

$$\frac{\partial\mathcal{P}_\perp\Delta(t)}{\partial t} = -\mathcal{P}_\perp\mathcal{L}\mathcal{P}_\perp\Delta(t) - \mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(t), \quad (95)$$

from which $\mathcal{P}_\perp\Delta(t)$ can be solved as

$$\mathcal{P}_\perp\Delta(t) = -\int_0^t d\tau e^{-\hat{\mathcal{L}}(t-\tau)}\mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(\tau) + e^{-\hat{\mathcal{L}}t}\mathcal{P}_\perp\Delta(0). \quad (96)$$

Now substitution into (94) gives

$$\begin{aligned} \frac{\partial\mathcal{P}\Delta(t)}{\partial t} &= -\mathcal{P}\mathcal{L}\mathcal{P}\Delta(t) + \int_0^t d\tau\mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\hat{\mathcal{L}}\tau}\mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(t-\tau) \\ &\quad -\mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\hat{\mathcal{L}}t}\mathcal{P}_\perp\Delta(0). \end{aligned} \quad (97)$$

Set $\bar{\psi}(\mathbf{k}, t) = \langle\Delta(t) | \psi(\mathbf{k})\rangle = \langle\psi(-\mathbf{k}) | \Delta(t)\rangle$. Using (88) and neglecting the last term in (97) one obtains

$$\begin{aligned} \frac{\partial\bar{\psi}(\mathbf{k}, t)}{\partial t} &= \bar{\phi}(\mathbf{k}, t) \circ \langle\psi(\mathbf{k}) | \mathcal{L}\psi(\mathbf{k})\rangle \\ &\quad + \int_0^t d\tau\bar{\phi}(\mathbf{k}, t-\tau) \circ \langle\psi(\mathbf{k}) | \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{\hat{\mathcal{L}}\tau}\mathcal{P}_\perp\mathcal{L}\mathcal{P}\psi(\mathbf{k})\rangle. \end{aligned} \quad (98)$$

Next we have to introduce some further notation:

$$\Omega(\mathbf{k}) = \frac{-1}{ikV} \langle \boldsymbol{\psi}(\mathbf{k}) | \mathcal{L}\boldsymbol{\psi}(\mathbf{k}) \rangle, \quad (99)$$

$$\mathcal{U}(\mathbf{k}, t) = \frac{-1}{k^2V} \langle \boldsymbol{\psi}(\mathbf{k}) | \mathcal{L}\mathcal{P}_\perp e^{\hat{\mathcal{L}}t} \mathcal{P}_\perp \mathcal{L}\boldsymbol{\psi}(\mathbf{k}) \rangle. \quad (100)$$

These matrices may be reexpressed in terms of the *currents*,

$$\mathbf{J}(\mathbf{k}) = \frac{\mathcal{L}\boldsymbol{\psi}(\mathbf{k})}{-ik}, \quad (101)$$

which are called this way in view of the conservation laws⁷

$$\frac{d\psi_i(\mathbf{k})}{dt} = -i\mathbf{k} \cdot \mathbf{J}_i(\mathbf{k}). \quad (102)$$

In terms of these we have

$$\Omega(\mathbf{k}) = \frac{1}{V} \langle \boldsymbol{\psi}(\mathbf{k}) | \mathbf{J}(\mathbf{k}) \rangle, \quad (103)$$

$$\mathcal{U}(\mathbf{k}, t) = \frac{1}{V} \langle \mathbf{J}(\mathbf{k}) | e^{\hat{\mathcal{L}}t} \mathbf{J}(\mathbf{k}) \rangle. \quad (104)$$

We can now rewrite (98) in terms of the generalized hydrodynamic equations

$$\frac{\partial \bar{\boldsymbol{\psi}}(\mathbf{k}, t)}{\partial t} = V \left[-ik\bar{\boldsymbol{\phi}}(\mathbf{k}, t) \circ \Omega(\mathbf{k}) - k^2 \int_0^t d\tau \bar{\boldsymbol{\phi}}(\mathbf{k}, t - \tau) \circ \mathcal{U}(\mathbf{k}, \tau) \right]. \quad (105)$$

The Laplace transform of this equation reads

$$z\tilde{\boldsymbol{\psi}}(\mathbf{k}, z) = V\tilde{\boldsymbol{\phi}}(\mathbf{k}, z) \circ \Omega \left[-ik\Omega(\mathbf{k}) - k^2\mathcal{U}(\mathbf{k}, z) \right] + \bar{\boldsymbol{\psi}}(\mathbf{k}, t = 0). \quad (106)$$

These equations are still very general. They provide a good description of the macroscopic time evolution of a fluid close to equilibrium, whenever all slow variations in the long-wave-length Fourier components of our Hilbert space can be parameterized by the behavior of number density, momentum density and energy density alone. In order to have them reducing to the ordinary (linearized) hydrodynamic equations on macroscopic time and length scales, the limit $\lim_{\mathbf{k} \rightarrow 0} \mathcal{U}(\mathbf{k}, z)$ has to exist (and be positive definite!), just like in the case of the diffusion equation.

⁷for the interpretation of (102) as a set of conservation laws it is crucial that the limit of $\mathbf{J}(\mathbf{k})$ for $\mathbf{k} \rightarrow 0$ exists, implying $d\boldsymbol{\psi}(0)/dt = 0$.

2.4.1 Specific form of the hydrodynamic equations

To appreciate that indeed (105,106) represent the hydrodynamic equations as we have seen them, one has to work out the matrices Ω and \mathcal{U} more explicitly. First of all, we specify the hydrodynamic densities and currents in more detail:

$$\mathcal{L}m\hat{n}(\mathbf{k}) = -i\mathbf{k} \cdot \hat{\mathbf{G}}(\mathbf{k}), \quad (107)$$

$$\mathcal{L}\hat{\mathbf{G}}(\mathbf{k}) = -i\mathbf{k} \cdot \hat{\mathbf{P}}(\mathbf{k}), \quad (108)$$

$$T_0\mathcal{L}\hat{\sigma}(\mathbf{k}) = -i\mathbf{k} \cdot \hat{\mathbf{J}}_q(\mathbf{k}). \quad (109)$$

Here $\hat{\mathbf{G}}(\mathbf{k})$ was defined in (79). The Fourier components of the microscopic pressure tensor $\hat{\mathbf{P}}(\mathbf{k})$ are defined as

$$\hat{\mathbf{P}}(\mathbf{k}) = \sum_i \frac{\mathbf{p}_i \mathbf{p}_i}{m} e^{-i\mathbf{k} \cdot \mathbf{r}_i} - \sum_{i < j} \frac{e^{-i\mathbf{k} \cdot \mathbf{r}_i} - e^{-i\mathbf{k} \cdot \mathbf{r}_j}}{i\mathbf{k} \cdot \mathbf{r}_{ij}} \mathbf{r}_{ij} \mathbf{F}_{ij}. \quad (110)$$

From this the \mathbf{k} -dependent pressure is obtained as

$$\hat{p}(\mathbf{k}) = \mathcal{P} \hat{\mathbf{k}} \hat{\mathbf{k}} : \hat{\mathbf{P}}(\mathbf{k}). \quad (111)$$

The Fourier components of the microscopic density of entropy per particle follow from the conditions

$$\langle \hat{\sigma}(\mathbf{k}) | \hat{p}(\mathbf{k}) \rangle = 0 \quad (112)$$

plus

$$\lim_{k \rightarrow 0} \hat{\sigma}(\mathbf{k}) = \frac{1}{n_0 T_0} \left[\hat{\epsilon}(\mathbf{k}) - \frac{p_0 + \epsilon_0}{n_0} \hat{n}(\mathbf{k}) \right]. \quad (113)$$

As shown in Appendix A this leads to

$$\hat{\sigma}(\mathbf{k}) = \frac{1}{n_0 T_0} [\hat{\epsilon}(\mathbf{k}) - h_0(\mathbf{k}) \hat{n}(\mathbf{k})], \quad (114)$$

with $h_0(\mathbf{k})$ the \mathbf{k} -dependent enthalpy density (defined there). From this the heat current is obtained as

$$\hat{\mathbf{J}}_q(\mathbf{k}) = \frac{-T_0}{ik} \mathcal{L} \hat{\sigma}(\mathbf{k}). \quad (115)$$

Notice that, thanks to (112), $\mathcal{P}\hat{\mathbf{J}}_q = 0$. The matrix elements of \mathcal{L} may now be worked out as

$$\begin{aligned}\langle \hat{n}(\mathbf{k}) | \mathcal{L}\hat{n}(\mathbf{k}) \rangle &= \langle \hat{n}(\mathbf{k}) | \mathcal{L}\hat{\epsilon}(\mathbf{k}) \rangle = \langle \hat{\epsilon}(\mathbf{k}) | \mathcal{L}\hat{\epsilon}(\mathbf{k}) \rangle \\ &= \langle \hat{\epsilon}(\mathbf{k}) | \mathcal{L}\hat{n}(\mathbf{k}) \rangle = 0,\end{aligned}\quad (116)$$

$$\langle \hat{\mathbf{G}}(\mathbf{k}) | \mathcal{L}\hat{\mathbf{G}}(\mathbf{k}) \rangle = \mathbf{0}, \quad (117)$$

$$\begin{aligned}\langle \hat{n}(\mathbf{k}) | \mathcal{L}\hat{\mathbf{G}}(\mathbf{k}) \rangle &= \langle \hat{\mathbf{G}}(\mathbf{k}) | \mathcal{L}\hat{n}(\mathbf{k}) \rangle = -\frac{1}{m}\langle \hat{\mathbf{G}}(\mathbf{k}) | i\mathbf{k} \cdot \hat{\mathbf{G}}(\mathbf{k}) \rangle \\ &= \frac{-i\mathbf{k}Vn_0}{\beta_0},\end{aligned}\quad (118)$$

$$\langle \hat{\mathbf{G}}(\mathbf{k}) | \mathcal{L}\hat{\sigma}(\mathbf{k}) \rangle = \langle \hat{\sigma}(\mathbf{k}) | \mathcal{L}\hat{\mathbf{G}}(\mathbf{k}) \rangle = i\mathbf{k}\langle \hat{\sigma}(\mathbf{k}) | \hat{p}(\mathbf{k}) \rangle = 0. \quad (119)$$

The wave number and frequency dependent linearized hydrodynamic equations may now be cast in more explicit form. The continuity equation becomes

$$\frac{\partial \bar{n}(\mathbf{k}, t)}{\partial t} = -\frac{i\mathbf{k}}{m} \cdot \bar{\mathbf{G}}(\mathbf{k}, t) = -i\mathbf{k} \cdot n_0 \mathbf{u}(\mathbf{k}, t), \quad (120)$$

with $\mathbf{u}(\mathbf{k}, t)$ again the Fourier transform of the local velocity. The "Navier-Stokes equation" becomes

$$\begin{aligned}\frac{\partial \bar{\mathbf{G}}(\mathbf{k}, t)}{\partial t} &= -i\mathbf{k}\bar{p}(\mathbf{k}, t) \\ &- \frac{k^2}{n_0 m} \int_0^t d\tau \left[\eta(\mathbf{k}, \tau) \bar{\mathbf{G}}(\mathbf{k}, t - \tau) + \{ \kappa(\mathbf{k}, \tau) + \frac{1}{3}\eta(\mathbf{k}, \tau) \} \hat{\mathbf{k}}\hat{\mathbf{k}} \cdot \bar{\mathbf{G}}(\mathbf{k}, t - \tau) \right] \\ &- \frac{k^2 n_0 \beta_0^2 \hat{\mathbf{k}}}{V} \int_0^t d\tau \left\langle \mathcal{P}_\perp(\hat{\mathbf{k}}\hat{\mathbf{k}}:\hat{\mathbf{P}}(\mathbf{k}) | e^{\hat{\mathcal{L}}\tau} \mathcal{P}_\perp \hat{\mathbf{k}} \cdot \hat{\mathbf{J}}_q(\mathbf{k}) \right\rangle k_B \bar{T}(\mathbf{k}, t - \tau).\end{aligned}\quad (121)$$

Here the transport kernels η and κ are defined as

$$\eta(\mathbf{k}, t) = \frac{\beta_0}{V} \left\langle \hat{\mathbf{k}}\hat{\mathbf{l}}:\hat{\mathbf{P}}(\mathbf{k}) | e^{\hat{\mathcal{L}}t} \hat{\mathbf{k}}\hat{\mathbf{l}}:\hat{\mathbf{P}}(\mathbf{k}) \right\rangle, \quad (122)$$

$$\kappa(\mathbf{k}, t) + \frac{2(d-1)}{d}\eta(\mathbf{k}, t) = \frac{\beta_0}{V} \left\langle \mathcal{P}_\perp \hat{\mathbf{k}}\hat{\mathbf{k}}:\hat{\mathbf{P}}(\mathbf{k}) | e^{\hat{\mathcal{L}}t} \mathcal{P}_\perp \hat{\mathbf{k}}\hat{\mathbf{k}}:\hat{\mathbf{P}}(\mathbf{k}) \right\rangle, \quad (123)$$

with $\hat{\mathbf{l}}$ an arbitrary unit vector perpendicular to $\hat{\mathbf{k}}$. The equation of heat conduction, finally, is of the form

$$\begin{aligned}\frac{\partial \bar{\sigma}(\mathbf{k}, t)}{\partial t} &= -\frac{k^2}{n_0 T_0} \int_0^t d\tau \lambda(\mathbf{k}, \tau) \bar{T}(\mathbf{k}, t - \tau) \\ &- \frac{k_B \beta_0^2 k^2}{mn_0 V} \int_0^t d\tau \left\langle \mathcal{P}_\perp \hat{\mathbf{k}} \cdot \hat{\mathbf{J}}_q(\mathbf{k}) | e^{\hat{\mathcal{L}}\tau} \mathcal{P}_\perp \hat{\mathbf{k}}\hat{\mathbf{k}}:\hat{\mathbf{P}}(\mathbf{k}) \right\rangle \hat{\mathbf{k}} \cdot \bar{\mathbf{G}}(\mathbf{k}, t - \tau),\end{aligned}\quad (124)$$

with

$$\lambda(\mathbf{k}, t) = \frac{n_0^2 k_B \beta_0^2}{V} \left\langle \mathcal{P}_\perp \hat{\mathbf{k}} \cdot \hat{\mathbf{J}}_q(\mathbf{k}) \mid e^{\hat{\mathcal{L}}t} \mathcal{P}_\perp \hat{\mathbf{k}} \cdot \hat{\mathbf{J}}_q(\mathbf{k}) \right\rangle. \quad (125)$$

Like in the case of tracer diffusion the \mathbf{k} - and z -dependent transport coefficients may also be expressed in terms of current-current correlation functions with unprojected time evolution operators. Setting

$$\mathcal{U}(\mathbf{k}, z) = \frac{1}{V} \left\langle \mathcal{P}_\perp \mathbf{J}(\mathbf{k}) \mid (z - \hat{\mathcal{L}})^{-1} \mathcal{P}_\perp \mathbf{J}(\mathbf{k}) \right\rangle \quad (126)$$

$$\mathcal{C}(\mathbf{k}, z) = \frac{1}{V} \left\langle \mathcal{P}_\perp \mathbf{J}(\mathbf{k}) \mid (z - \mathcal{L})^{-1} \mathcal{P}_\perp \mathbf{J}(\mathbf{k}) \right\rangle \quad (127)$$

one has the relationship

$$\mathcal{U}(\mathbf{k}, z) = \mathcal{C}(\mathbf{k}, z) \left[\mathbf{I} + k^2 \left\{ \frac{\langle \psi(\mathbf{k}) \mid \psi(\mathbf{k}) \rangle}{V} z + ik\Omega - k^2 \mathcal{C}(\mathbf{k}, z) \right\}^{-1} \mathcal{C}(\mathbf{k}, z) \right]. \quad (128)$$

In the limit $\mathbf{k} \rightarrow 0$ \mathcal{U} and \mathcal{C} become equal again. In this limit we obtain the standard Green-Kubo expressions for the hydrodynamic transport coefficients. For the shear and bulk viscosity,

$$\eta = \frac{\beta_0}{V} \int_0^\infty dt \left\langle \hat{\mathbf{k}} \hat{\mathbf{l}} : \mathbf{P}(0) \hat{\mathbf{k}} \hat{\mathbf{l}} : \mathbf{P}(t) \right\rangle, \quad (129)$$

$$\kappa = \frac{\beta_0}{V} \int_{-\infty}^\infty dt \left\langle \frac{1}{d} \text{Tr}[\mathbf{P}(0)] - \left(\frac{\partial p}{\partial e} \right)_n (H - \langle H \rangle) - \left(\frac{\partial p}{\partial n} \right)_e (N - \langle N \rangle) - pV \mid \right. \quad (130)$$

$$\left. \frac{1}{d} \text{Tr}[\mathbf{P}(t)] - \left(\frac{\partial p}{\partial e} \right)_n (H - \langle H \rangle) - \left(\frac{\partial p}{\partial n} \right)_e (N - \langle N \rangle) - pV \right\rangle. \quad (131)$$

Here $\mathbf{P}(t)$ is $\frac{1}{d} \text{Tr} \hat{\mathbf{P}}(\mathbf{k} = 0)$ evaluated as function of the particle coordinates at time t . In (131) we have used (111) and subtracted $pV = \langle \hat{p}(\mathbf{k} = 0) \rangle$. By combining Eqs. (125), (115), (112) and (107) one finds that the heat conduction coefficient becomes

$$\lambda = \frac{\beta_0}{dVT_0} \int_0^\infty dt \left\langle \mathbf{J}_e(0) - \frac{h_0}{m} \mathbf{G} \mid \cdot \mathbf{J}_e(t) - \frac{h_0}{m} \mathbf{G} \right\rangle. \quad (132)$$

Here the energy current is

$$\mathbf{J}_e(\Gamma) = \sum_i \epsilon_i \frac{\mathbf{p}_i}{m} + \frac{1}{2} \sum_{i < j} \left(\frac{\mathbf{p}_i}{m} \cdot \mathbf{F}_{ij} \right) \mathbf{r}_{ij} \quad (133)$$

and \mathbf{G} is the total momentum.

2.4.2 Positivity of transport coefficients

For $\text{Re}(z) > 0$ the real parts of $\eta(\mathbf{k}, z)$, $\lambda(\mathbf{k}, z)$ and $\kappa(\mathbf{k}, z) + 2(d-1)\eta(\mathbf{k}, z)/d$ are positive. This follows from the antihermiticity of $\mathcal{P}_\perp \hat{\mathcal{L}} \mathcal{P}_\perp$: the operator $(z - \hat{\mathcal{L}})$ (and therefore also its inverse) has a spectrum with a positive real part. For $z = i\omega$ Forster[3] gives the following, more subtle argument: one has

$$I \equiv \left\langle \int_{-T}^T dt_1 e^{\hat{\mathcal{L}}t_1} J(\mathbf{k}) e^{-i\omega t_1} \mid \int_{-T}^T dt_2 e^{\hat{\mathcal{L}}t_2} J(\mathbf{k}) e^{-i\omega t_2} \right\rangle \geq 0. \quad (134)$$

Time translation invariance allows rewriting I as

$$I = T \int_0^{2T} d\tau \left(1 - \frac{\tau}{2T}\right) \left[\left\langle J(\mathbf{k}) \mid e^{\hat{\mathcal{L}}\tau} J(\mathbf{k}) \right\rangle e^{-i\omega\tau} + cc \right]. \quad (135)$$

Here $\tau = t_2 - t_1$ and an integration has been performed over $(t_1 + t_2)/2$. If $\left\langle J(\mathbf{k}) \mid e^{\hat{\mathcal{L}}\tau} J(\mathbf{k}) \right\rangle = o(1/\tau)$ for $\tau \rightarrow \infty$ the contribution of the term with $\tau/(2T)$ will vanish in the limit $T \rightarrow \infty$. In this case the remaining term approaches combinations such as $[\eta(k, i\omega) + \eta(k, -i\omega)]$. From (134) it follows that this is ≥ 0 . The possibility that transport coefficients are 0 or infinite remains open! For both possibilities there exist ample examples.

2.4.3 Mixtures

It is straightforward extending the Green-Kubo formalism to mixtures of s species of particles with masses $m_1 \cdots m_s$ and interparticle potentials $\phi_{ln}(r_{ij})$, depending on the species l and n of the particles i and j . The hydrodynamic space is now represented by the mass densities

$$\hat{\rho}_l(\mathbf{k}) \equiv m_l \sum_{j=1}^{N_l} e^{-i\mathbf{k}\cdot\mathbf{r}_j}, \quad (136)$$

together with momentum density and energy density, which are defined as before, except that masses and potentials now depend on particle species. The matrix χ has to be generalized to an $(s+4) \times (s+4)$ dimensional matrix with matrix elements

$$\chi_{ln}(\mathbf{k}) = \langle \hat{\rho}_l(\mathbf{k}) \mid \hat{\rho}_n(\mathbf{k}) \rangle; \quad \chi_{le}(\mathbf{k}) = \langle \hat{\rho}_l(\mathbf{k}) \mid \epsilon(\mathbf{k}) \rangle \quad (137)$$

etc. The fields adjoint to the mass densities are $\tilde{\nu}_l(\mathbf{k}) = \hat{\nu}_l(\mathbf{k})/m_l$, with μ_l the chemical potential of species l . The other adjoint fields do not change. The matrix Ω now has matrix elements

$$\Omega_{lG} = \Omega_{Gl} = \rho_{l_0} k_B T_0, \quad (138)$$

between mass densities and the $\hat{\mathbf{k}}$ -component of the momentum density, in addition to the matrix elements between $\hat{\epsilon}(\mathbf{k})$ and $\hat{\mathbf{G}}(\mathbf{k}) \cdot \hat{\mathbf{k}}$. For simplicity we now concentrate on the equations in the limit of $\mathbf{k}, z \rightarrow 0$. These become

$$\frac{\partial \bar{\rho}_l(\mathbf{k}, t)}{\partial t} = -\frac{\rho_{l_0}}{\rho_0} i\mathbf{k} \cdot \bar{\mathbf{G}}(\mathbf{k}, t) - k^2 \left[\sum_n L_{ln} \bar{\nu}_n(\mathbf{k}, t) - L_{le} \bar{\beta}(\mathbf{k}, t) \right] \quad (139)$$

$$\frac{\partial \bar{\epsilon}(\mathbf{k}, t)}{\partial t} = -\frac{p_0}{\rho_0} i\mathbf{k} \cdot \bar{\mathbf{G}}(\mathbf{k}, t) - k^2 \left[\frac{1}{n_0} \lambda \bar{T}(\mathbf{k}, t) + \sum_n L_{en} \bar{\nu}_n(\mathbf{k}, t) \right] \quad (140)$$

$$\frac{\partial \bar{\mathbf{G}}(\mathbf{k}, t)}{\partial t} = -ik\bar{p}(\mathbf{k}, t) - k^2 \left[\eta \bar{\mathbf{G}}(\mathbf{k}, t) + \left(\kappa + \frac{d-2}{d} \eta \right) \hat{\mathbf{k}} \hat{\mathbf{k}} : \bar{\mathbf{G}}(\mathbf{k}, t) \right] \quad (141)$$

Here the *Onsager coefficients* were introduced, defined as

$$\begin{aligned} L_{ln} &= \lim_{\mathbf{k} \rightarrow 0} \frac{-1}{k^2} \int_0^\infty dt \langle \mathcal{P}_\perp \mathcal{L} \rho_l(\mathbf{k}) | e^{\mathcal{L}t} \mathcal{P}_\perp \mathcal{L} \rho_n(\mathbf{k}) \rangle, \\ &= \frac{1}{d} \int_0^\infty dt \langle \mathbf{J}_l(0) \cdot \mathbf{J}_n(t) \rangle, \end{aligned} \quad (142)$$

$$L_{le} = \frac{1}{d} \int_0^\infty dt \langle \mathbf{J}_l(0) \cdot \mathbf{J}_q(t) \rangle, \quad (143)$$

$$L_{el} = \frac{1}{d} \int_0^\infty dt \langle \mathbf{J}_q(0) \cdot \mathbf{J}_l(t) \rangle. \quad (144)$$

Here the currents \mathbf{J}_l are given explicitly by

$$\mathbf{J}_l = \sum_{j=1}^{N_l} \mathbf{p}_j - \frac{\rho_{l_0}}{\rho_0} \mathbf{G}. \quad (145)$$

Notice that a mass-current of species l is not only driven by a gradient in the mass density of this species, but may also result from gradients in the other mass densities as well as from a temperature gradient. Similarly, a heat current may also be the result of gradients in the densities. Notice further

that the Onsager coefficients are not linearly independent. From Eqs. (142-144) and (145) one obtains the relationships

$$\sum_l L_{ln} = \sum_n L_{ln} = 0, \quad (146)$$

$$\sum_l L_{le} = \sum_l L_{el} = 0. \quad (147)$$

2.4.4 Onsager relations

Onsager was the first one to note the symmetry relations

$$L_{ln} = L_{nl}, \quad (148)$$

$$L_{le} = L_{el}. \quad (149)$$

These are a direct consequence of *time reversal invariance* of the equations of motion. The Green-Kubo formalism makes this particularly transparent. Define the time-reversal operator \mathcal{T} by its action on an arbitrary phase function;

$$\mathcal{T}f(\mathbf{r}_1 \cdots \mathbf{r}_N, \mathbf{p}_1 \cdots \mathbf{p}_N) = f(\mathbf{r}_1 \cdots \mathbf{r}_N, -\mathbf{p}_1 \cdots -\mathbf{p}_N). \quad (150)$$

Obviously $\mathcal{T}^2 = 1$ and for a Hamiltonian that is even in the momenta⁸ one has

$$\mathcal{T}\mathcal{L}\mathcal{T} = -\mathcal{L}, \quad (151)$$

$$\mathcal{T}e^{\mathcal{L}t}\mathcal{T} = e^{-\mathcal{L}t}. \quad (152)$$

On the basis of this, one obtains

$$\begin{aligned} \langle J_1 | e^{\mathcal{L}t} J_2 \rangle &= \langle \mathcal{T} J_1 | \mathcal{T} e^{\mathcal{L}t} \mathcal{T} \mathcal{T} J_2 \rangle, \\ &= \langle \mathcal{T} J_1 | e^{-\mathcal{L}t} \mathcal{T} J_2 \rangle, \\ &= \langle \mathcal{T} J_2 | e^{\mathcal{L}t} \mathcal{T} J_1 \rangle. \end{aligned} \quad (153)$$

If J_1 and J_2 have the same, definite parity in the momenta the time reversal operators in the last equality may be taken out by replacing \mathbf{p}_i by $-\mathbf{p}_i$ in the equilibrium average $\langle \cdot \rangle$. This is the basis of all the Onsager symmetries contained in (142-143).

⁸This means in practice that the forces do not depend on velocities. In the presence of a magnetic field time reversal requires reversal of this field in addition to the momenta.

2.5 Linear response theory

The Green-Kubo formalism may also be used to describe the response of densities to small driving fields. Also in this case Einstein's treatment of Brownian motion has been ground laying.

2.5.1 Einstein relation between conductivity and diffusion coefficient

Einstein considered the electrical current of charged tracer particles in an equilibrium background due to a driving field on the one hand and to density gradients on the other. Phenomenologically these may be written as

$$\mathbf{j}_{el} = -\sigma \nabla \Phi, \quad (154)$$

$$\mathbf{j}_{diff} = -De_t \nabla n_t, \quad (155)$$

with Φ the Coulomb potential, e_t the charge of a tracer particle and $n_t(\mathbf{r}, t)$ the number density of these particles. He noted that in equilibrium both of these contributions would still be present, but ought to cancel each other. Therefore, if one can establish a relationship between $\nabla \Phi$ and ∇n_t in an equilibrium state, this will translate into a relationship between σ and D . Ensemble theory allows one to establish just such a relationship. First of all, we want to use the canonical ensemble to find out how the chemical potential changes if a system is placed in an external potential. For simplicity, first look at the case that species $1 \cdots s$ are subjected to uniform potentials (per particle) $\phi_1 \cdots \phi_s$. This leads to a canonical partition function

$$Z(T, V, N_i, \phi_i) = \exp\left(-\sum_i N_i \beta \phi_i\right) Z(T, V, N_i), \quad (156)$$

with $Z(T, V, N_i)$ the partition function in absence of external potentials. From this one finds

$$\mu_i(T, V, N_i, \phi_i) = \frac{\partial(-k_B T \ln Z)}{\partial N_i} = \phi_i + \tilde{\mu}_i(T, V, N_i), \quad (157)$$

with $\tilde{\mu}_i$ the *intrinsic chemical potential* of species i . For a nonuniform system with gradients on macroscopic length scales this may be generalized to a local

relationship⁹

$$\mu_i(T(\mathbf{r}), n_i(\mathbf{r}), \phi_i(\mathbf{r})) = \phi_i(\mathbf{r}) + \tilde{\mu}_i(T, n_i(\mathbf{r})). \quad (158)$$

In an equilibrium system μ_i should be uniform, hence

$$\nabla \tilde{\mu}_i(T, n_i(\mathbf{r})) = -\nabla \phi_i(\mathbf{r}). \quad (159)$$

In a system where only the tracer density is nonuniform one has

$$\nabla \tilde{\mu}_t = \frac{\partial \mu_t}{\partial n_t} \nabla n_t. \quad (160)$$

Substitution of (158-159) into (154-155), using $\phi_t = e_t \Phi$, and requiring the vanishing of the sum of these currents leads to the Einstein relation

$$\frac{\sigma}{e_t^2} = D \left(\frac{\partial n_t}{\partial \mu_t} \right)_{T, n_b}. \quad (161)$$

For the tracer particles the derivative $\left(\frac{\partial n_t}{\partial \mu_t} \right)_{T, n_b}$ may be worked out in detail by using the Grand canonical ensemble: since tracer particles do not interact it follows that the Grand canonical partition function for a system containing some tracer particles assumes the form

$$\begin{aligned} \Xi(\mu_t, \mu_b, T, V) &= \Xi_0(\mu_b, T, V) \left[1 + \sum_{n_t=1}^{\infty} \exp n_t \beta \mu_t \frac{\Delta(\mu_b, T, V)^{n_t}}{n_t!} \right] \\ &= \Xi_0 \exp\{\exp[\beta \mu_t] \Delta(\mu_b, T, V)\}, \end{aligned} \quad (162)$$

where $\Delta(\mu_b, T, V)$ is the ratio of the Grand partition function in the presence of one tracer particle and that without any. From this one obtains for the average tracer density

$$n_t = \frac{1}{V} \frac{(\partial k_B T \log \Xi)}{\partial \mu_t} = \exp[\beta \mu_t] \Delta(\mu_b, T, V), \quad (163)$$

leading to the identity

$$\left(\frac{\partial n_t}{\partial \mu_t} \right)_{T, n_b} = \beta n_t, \quad (164)$$

⁹Adequate generalizations are also known in the case of strong gradients[12].

solved by $n_t = C \exp \beta \mu_t$. Substituting this into the Einstein relation (161) one obtains

$$\sigma = \frac{n_t e_t^2 D}{k_B T}. \quad (165)$$

Linear response theory allows one to generalize this to a frequency and wave number dependent relationship. Set

$$H = H_0 + \Delta H(t) \quad (166)$$

with $\Delta H(t) = e_t \sum_{j=1}^{\langle N_t \rangle} \Phi(\mathbf{r}_j, t) = \frac{e_t}{V} \sum_{\mathbf{k}} \Phi(\mathbf{k}, t) n_t(-\mathbf{k}, t)$ and, for the time being, $\Delta H(t) = 0$ for $t < 0$. The corresponding Liouville operator, the time dependent phase space density and the Liouville equation may be split up similarly as

$$\mathcal{L} = \mathcal{L}_0 + \Delta \mathcal{L}(t), \quad (167)$$

$$\rho = \rho_0(1 + \Delta(t)), \quad (168)$$

$$\frac{\partial \rho}{\partial t} = -(\mathcal{L}_0 + \Delta \mathcal{L}(t))\rho. \quad (169)$$

Linearization of the Liouville equation yields

$$\frac{\partial \Delta(t)}{\partial t} = -\mathcal{L}_0 \Delta(t) - \Delta \mathcal{L}(t) \log \rho_0. \quad (170)$$

Under the projection operator formalism $\Delta(t)$ is split up again as

$$\Delta(t) = \mathcal{P} \Delta(t) + \mathcal{P}_\perp \Delta(t) \quad (171)$$

and $\mathcal{P}_\perp \Delta(t)$ can be solved as

$$\mathcal{P}_\perp \Delta(t) = - \int_0^t d\tau e^{-\hat{\mathcal{L}}_0(t-\tau)} [\mathcal{P}_\perp \mathcal{L}_0 \mathcal{P} \Delta(\tau) + \mathcal{P}_\perp \Delta \mathcal{L}(\tau) \log \rho_0], \quad (172)$$

leaving for $\mathcal{P} \Delta(t)$ the equation

$$\begin{aligned} \frac{\partial \mathcal{P} \Delta(t)}{\partial t} &= -\mathcal{P} \mathcal{L}_0 \mathcal{P} \Delta(t) - \mathcal{P} \Delta \mathcal{L} \log \rho_0 \\ &+ \int_0^t d\tau \mathcal{P} \mathcal{L}_0 \mathcal{P}_\perp \exp(-\hat{\mathcal{L}}_0 \tau) [\mathcal{P}_\perp \mathcal{L}_0 \mathcal{P} \Delta(t-\tau) + \mathcal{P}_\perp \Delta \mathcal{L}(t-\tau) \log \rho_0]. \end{aligned} \quad (173)$$

Let us now apply this to the case of tracer diffusion in an external electric field. In this case we have

$$\mathcal{P} = \frac{1}{\langle\langle N_t \rangle\rangle} \sum_{\mathbf{k}} |n_t(\mathbf{k})\rangle \langle n_t(\mathbf{k})|, \quad (174)$$

$$\Delta\mathcal{L}(t) = \sum_j e_t \mathbf{E}(\mathbf{r}_j, t) \cdot \frac{\partial}{\partial \mathbf{p}_j}, \quad (175)$$

with $\mathbf{E}(\mathbf{r}, t) = -\nabla\Phi(\mathbf{r}, t)$. Applying $\Delta\mathcal{L}(t)$ to the Grand canonical distribution we obtain

$$\begin{aligned} \Delta\mathcal{L}(t) \log \rho_0 &= - \sum_{j=1}^{N_t} \frac{\beta \mathbf{p}_j}{m} \cdot e_t \mathbf{E}(\mathbf{r}_j, t), \\ &= -\beta \int d\mathbf{r} \mathbf{j}_t(\mathbf{r}) \cdot e_t \mathbf{E}(\mathbf{r}, t), \\ &= -\frac{\beta}{V} \sum_{\mathbf{k}} \mathbf{j}_t(\mathbf{k}) \cdot e_t \mathbf{E}(-\mathbf{k}, t), \end{aligned} \quad (176)$$

with $\mathbf{j}_t(\mathbf{r}) = \sum_{i=1}^{N_t} (\mathbf{p}_i/m_t) \delta(\mathbf{r} - \mathbf{r}_i)$. In the case of tracer diffusion $\mathcal{P} \Delta\mathcal{L} \log \rho_0$ vanishes. Inserting (174) and (176) into (174) we obtain

$$\begin{aligned} \frac{\partial \mathcal{P} \Delta(t)}{\partial t} &= \sum_{\mathbf{k}} \int_0^t d\tau \frac{|n_t(\mathbf{k})\rangle}{\langle N_t \rangle} \frac{\langle \hat{\mathbf{k}} \cdot \mathbf{j}_t(\mathbf{k}) | \exp(-\hat{\mathcal{L}}_0 \tau) \hat{\mathbf{k}} \cdot \mathbf{j}_t(\mathbf{k}) \rangle}{\langle N_t \rangle} \\ &\quad \left[-k^2 \langle n_t(\mathbf{k}) | \Delta(t - \tau) \rangle - \frac{\beta \langle N_t \rangle}{V} e_t i \mathbf{k} \cdot \mathbf{E}(-\mathbf{k}, t - \tau) \right] \end{aligned} \quad (177)$$

The second term between square brackets describes the "direct response" of $\Delta(t)$ to the electric field, the first term the "indirect response" due to diffusive decay of the density field resulting from the action of the electric field at preceding times. From this one obtains the hydrodynamic equation for the tracer density as

$$\begin{aligned} \frac{\partial \bar{n}_t(\mathbf{k}, t)}{\partial t} &= \left\langle \frac{\partial \mathcal{P} \Delta(t)}{\partial t} \middle| n_t(\mathbf{k}) \right\rangle \\ &= \int_0^t d\tau \mathcal{U}(\mathbf{k}, \tau) \left[-k^2 \bar{n}_t(\mathbf{k}, t - \tau) + \beta e_t n_{t_0} i \mathbf{k} \cdot \mathbf{E}(\mathbf{k}, t - \tau) \right]. \end{aligned} \quad (178)$$

The Laplace transform of this reads

$$z\bar{\tilde{n}}_t(\mathbf{k}, z) = \tilde{U}(\mathbf{k}, z) \left[-k^2\bar{\tilde{n}}_t(\mathbf{k}, z) + \beta e_t n_{t_0} i\mathbf{k} \cdot \tilde{\mathbf{E}}(\mathbf{k}, z) \right] + n_t(\mathbf{k}, t=0). \quad (179)$$

2.5.2 Linear response theory for full hydrodynamics

It is straightforward now extending the above derivations to the case of the full hydrodynamic equations. First of all we have to evaluate the term $\mathcal{P}\Delta\mathcal{L}\log\rho_0$. From (176) this immediately follows as

$$\mathcal{P}\Delta\mathcal{L}\log\rho_0 = \frac{\beta}{M} i\mathbf{k} \cdot \mathbf{G}(\mathbf{k}) \sum_l [n_{l_0} \phi_l(-\mathbf{k}, t)], \quad (180)$$

with M the average total mass. This contributes an external force term to the Navier-Stokes equations. Furthermore, as follows from (177), the external potentials have the effect of consistently replacing $\nabla\nu_l$ by the sum of the gradients of the intrinsic $\tilde{\nu}_l$ and of $\beta\phi_l$. In summary, the linearized hydrodynamic equations in presence of external potentials become

$$\frac{\partial\bar{\rho}(\mathbf{k}, t)}{\partial t} = -i\mathbf{k} \cdot \bar{\mathbf{G}}(\mathbf{k}, t), \quad (181)$$

$$\begin{aligned} \frac{\partial\bar{\mathbf{G}}(\mathbf{k}, t)}{\partial t} &= -i\mathbf{k} \left[\bar{\mathbf{p}}(\mathbf{k}, t) + \sum_l n_{l_0} \phi_l(\mathbf{k}, t) \right] \\ &\quad - \frac{k^2}{n_0 m} \int_0^t d\tau \left[\eta(\mathbf{k}, \tau) \bar{\mathbf{G}}(\mathbf{k}, t - \tau) + \left\{ \kappa(\mathbf{k}, \tau) + \frac{d-2}{d} \eta(\mathbf{k}, \tau) \right\} \hat{\mathbf{k}}\hat{\mathbf{k}} \cdot \bar{\mathbf{G}}(\mathbf{k}, t - \tau) \right] \\ &\quad - \frac{k^2 n_0 \beta_0^2 \hat{\mathbf{k}}}{V} \int_0^t d\tau \left\langle \mathcal{P}_\perp(\hat{\mathbf{k}}\hat{\mathbf{k}}: \hat{\mathbf{P}}(\mathbf{k}) \mid e^{\hat{\mathcal{L}}\tau} \mathcal{P}_\perp \hat{\mathbf{k}} \cdot \hat{\mathbf{J}}_q(\mathbf{k}) \right\rangle k_B \bar{\mathbf{T}}(\mathbf{k}, t - \tau). \end{aligned} \quad (182)$$

$$\begin{aligned} \frac{\partial\bar{\sigma}(\mathbf{k}, t)}{\partial t} &= -\frac{k^2}{n_0 T_0} \int_0^t d\tau \left[\lambda(\mathbf{k}, \tau) \bar{\mathbf{T}}(\mathbf{k}, t - \tau) + \sum_l L_{el}(\mathbf{k}, \tau) [\bar{\nu}_l(\mathbf{k}, t - \tau) + \beta\phi_l(\mathbf{k}, t - \tau)] \right] \\ &\quad - \frac{k_B \beta_0^2 k^2}{m n_0 V} \int_0^t d\tau \left\langle \mathcal{P}_\perp \hat{\mathbf{k}} \cdot \hat{\mathbf{J}}_q(\mathbf{k}) \mid e^{\hat{\mathcal{L}}\tau} \mathcal{P}_\perp \hat{\mathbf{k}}\hat{\mathbf{k}}: \hat{\mathbf{P}}(\mathbf{k}) \right\rangle \hat{\mathbf{k}} \cdot \bar{\mathbf{G}}(\mathbf{k}, t - \tau), \end{aligned} \quad (183)$$

$$\begin{aligned} \frac{\partial\bar{\rho}_l(\mathbf{k}, t)}{\partial t} - \frac{\rho_{l_0}}{\rho_0} \frac{\partial\bar{\rho}(\mathbf{k}, t)}{\partial t} &= -k^2 \int_0^t d\tau \sum_n L_{ln}(\mathbf{k}, \tau) [\bar{\nu}_n(\mathbf{k}, t - \tau) + \beta\phi_n(\mathbf{k}, t - \tau)] \\ &\quad + k^2 \int_0^t d\tau L_{le}(\mathbf{k}, \tau) \bar{\beta}(\mathbf{k}, t - \tau). \end{aligned} \quad (184)$$

2.5.3 Quantum mechanical linear response theory

Let the Hamiltonian of a quantum mechanical system be given by

$$\mathcal{H} = \mathcal{H}_0 - \Delta\mathcal{H} = \mathcal{H}_0 - \sum_j A_j \phi_j(t). \quad (185)$$

The density operator describing this system satisfies

$$\frac{\partial \rho}{\partial t} = \frac{i}{\hbar} [\rho, \mathcal{H}]. \quad (186)$$

Set $\rho(t) = \rho_0 + \Delta\rho(t)$ and linearize (186). This leads to

$$\frac{\partial \Delta\rho}{\partial t} = \frac{i}{\hbar} \left\{ [\Delta\rho, \mathcal{H}_0] - \sum_j [\rho_0, A_j] \phi_j(t) \right\}. \quad (187)$$

This is solved by

$$\begin{aligned} \Delta\rho(t) &= - \int_0^t d\tau e^{-\frac{i(t-\tau)\mathcal{H}_0}{\hbar}} \frac{i}{\hbar} \sum_j [\rho_0, A_j] e^{\frac{i(t-\tau)\mathcal{H}_0}{\hbar}} \phi_j(\tau), \\ &\equiv - \int_0^t d\tau e^{-\mathcal{L}_0(t-\tau)} \frac{i}{\hbar} \sum_j [\rho_0, A_j] \phi_j(\tau). \end{aligned} \quad (188)$$

The operator \mathcal{L} now is defined through

$$\mathcal{L}A = -\frac{i}{\hbar} [A, \mathcal{H}] = \frac{dA}{dt}. \quad (189)$$

This is solved by

$$A(t) = e^{\mathcal{L}t} A \equiv e^{\frac{i\mathcal{H}t}{\hbar}} A e^{-\frac{i\mathcal{H}t}{\hbar}}. \quad (190)$$

For the expectation value (under linearized dynamics) of an operator B one finds

$$\begin{aligned} \langle B(t) \rangle &= Tr(\Delta\rho B) = -\frac{i}{\hbar} \int_0^t d\tau Tr \left[B e^{-\mathcal{L}_0(t-\tau)} \sum_j [\rho_0, A_j] \phi_j(\tau) \right], \\ &= -\frac{i}{\hbar} \int_0^t d\tau Tr \left[\sum_j [\rho_0, A_j] e^{\mathcal{L}_0(t-\tau)} B \phi_j(\tau) \right] \\ &= -\frac{i}{\hbar} \int_0^t d\tau Tr \left[\sum_j [\rho_0, A_j] B(t-\tau) \phi_j(\tau) \right] \\ &= -\frac{i}{\hbar} \int_0^t d\tau Tr \left[\sum_j \rho_0 [A_j, B(t-\tau)] \phi_j(\tau) \right] \end{aligned}$$

This may be abbreviated to

$$\langle B(t) \rangle = 2i \int_0^t d\tau \sum_j \mathbf{M}_{BA_j}(t - \tau) \phi_j(\tau), \quad (191)$$

with

$$\begin{aligned} \mathbf{M}_{BA}(t) &= \frac{-1}{2\hbar} \text{Tr} \{ [\rho_0, A] e^{\mathcal{L}_0 t} B \}, \\ &= \frac{-1}{2\hbar} \text{Tr} \{ \rho_0 [A, e^{\mathcal{L}_0 t} B] \}, \\ &= \frac{-1}{2\hbar} \langle [A, e^{\mathcal{L}_0 t} B] \rangle_0. \end{aligned} \quad (192)$$

In the canonical ensemble, with $\rho_0 = e^{-\beta \mathcal{H}_0}$, $[\rho_0, A]$ is expressible by the Kubo-identity

$$\begin{aligned} [e^{-\beta \mathcal{H}_0}, A] &= \int_0^\beta d\lambda e^{-(\beta-\lambda)\mathcal{H}_0} [A, \mathcal{H}_0] e^{-\lambda \mathcal{H}_0} \\ &\equiv -\frac{\hbar}{i} \int_0^\beta d\lambda e^{-(\beta-\lambda)\mathcal{H}_0} \dot{A} e^{-\lambda \mathcal{H}_0}. \end{aligned} \quad (193)$$

One may define a scalar product, *the Kubo product* as

$$\langle A | B \rangle = \frac{1}{\beta} \int_0^\beta d\lambda \langle A^\dagger e^{-\lambda \mathcal{H}_0} B e^{\lambda \mathcal{H}_0} \rangle_0. \quad (194)$$

In terms of this \mathbf{M}_{BA} may be expressed as

$$\mathbf{M}_{BA}(t) = \frac{\beta}{2i} \langle \dot{A}^\dagger | B(t) \rangle. \quad (195)$$

For $\beta \rightarrow 0$ ($T \rightarrow \infty$) the Kubo product $\langle A | B \rangle$ approaches the correlation function $\langle A^\dagger B \rangle$.

2.5.4 Response of tracer density to an external field

For a system with a single tracer particle the tracer density now is represented by the *operator*

$$n_t(\mathbf{k}) = \exp(-i\mathbf{k} \cdot \mathbf{r}_1). \quad (196)$$

In the Heisenberg representation the time evolution of this operator in the absence of an external field is generated by

$$\dot{n}_t(\mathbf{k}) = -\frac{i}{\hbar}[n_t(\mathbf{k}), \mathcal{H}_0] = -i\mathbf{k} \cdot \mathbf{j}_t(\mathbf{k}), \quad (197)$$

with

$$\mathbf{j}_t(\mathbf{k}) = \frac{1}{2} \left\{ \frac{\mathbf{p}_1}{m}, n_t(\mathbf{k}) \right\}. \quad (198)$$

Consider a perturbation of the Hamilton operator for $t > 0$ of the form

$$\Delta\mathcal{H} = -\frac{1}{V} \sum_{\mathbf{k}} e_t n_t(-\mathbf{k}) \Phi(\mathbf{k}, t). \quad (199)$$

Note, first of all, the identity

$$\begin{aligned} \sum_{\mathbf{k}} \dot{n}_t(-\mathbf{k}) \Phi(\mathbf{k}, t) &= \sum_{\mathbf{k}} i\mathbf{k} \cdot \mathbf{j}_t(-\mathbf{k}) \Phi(\mathbf{k}, t), \\ &= -\sum_{\mathbf{k}} \mathbf{j}_t(-\mathbf{k}) \cdot \mathbf{E}(\mathbf{k}, t). \end{aligned} \quad (200)$$

From (191), (195) and (200) one finds

$$\begin{aligned} \bar{n}_t(\mathbf{k}, t) &= 2i \int_0^t d\tau \frac{\beta e_t}{2iV} \mathbf{E}(\mathbf{k}, \tau) \cdot \langle \mathbf{j}_t(\mathbf{k}) | n_t(\mathbf{k}, t - \tau) \rangle, \\ &= n_t e_t \beta \int_0^t d\tau \mathbf{E}(\mathbf{k}, \tau) \cdot \langle \mathbf{j}_t(\mathbf{k}) | \exp[\mathcal{L}_0(t - \tau)] n_t(\mathbf{k}) \rangle, \\ \frac{\partial \bar{n}_t(\mathbf{k}, t)}{\partial t} &= -n_t e_t \beta \int_0^t d\tau i\mathbf{k} \mathbf{E}(\mathbf{k}, \tau) \cdot \langle \mathbf{j}_t(\mathbf{k}) | \exp[\mathcal{L}_0(t - \tau)] \mathbf{j}_t(\mathbf{k}) \rangle, \end{aligned} \quad (201)$$

where the identity $n_t = 1/V$ was used for the equilibrium tracer density. Introduce again the projection operator on the tracer density. Now this has the form

$$\mathcal{P} = \sum_{\mathbf{k}} \frac{|n_t(\mathbf{k})\rangle \langle n_t(\mathbf{k})|}{\langle n_t(\mathbf{k}) | n_t(\mathbf{k}) \rangle}. \quad (202)$$

Note that in the classical limit $\beta \rightarrow 0$ the inner product $\langle n_t(\mathbf{k}) | n_t(\mathbf{k}) \rangle$ reduces to unity. With the aid of this the streaming operator may be decomposed again as

$$\exp(\mathcal{L}_0 t) = \exp(\widehat{\mathcal{L}}_0 t) + \int_0^t d\tau \exp[\mathcal{L}_0(t - \tau)] (\mathcal{P} \mathcal{L} \mathcal{P}_\perp + \mathcal{P}_\perp \mathcal{L} \mathcal{P}) \exp(\widehat{\mathcal{L}}_0 \tau). \quad (203)$$

Substitution into (201) reproduces the equation

$$\frac{\partial \bar{n}_t(\mathbf{k}, t)}{\partial t} = -i\mathbf{k} \cdot \int_0^t d\tau U(\mathbf{k}, \tau) \left[n_t e_t \beta \mathbf{E}(\mathbf{k}, t - \tau) - i\mathbf{k} \frac{n_t(\mathbf{k}, t - \tau)}{\langle n_t(\mathbf{k}) | n_t(\mathbf{k}) \rangle} \right], \quad (204)$$

with

$$U(\mathbf{k}, t) = \langle \mathbf{j}_t(\mathbf{k}) \cdot \hat{\mathbf{k}} | \exp(\hat{\mathcal{L}}t) \mathbf{j}_t(\mathbf{k}) \cdot \hat{\mathbf{k}} \rangle. \quad (205)$$

2.5.5 Correlation functions

The Kubo product between densities at different times satisfies the same equations as the correlation function in the classical case. E.g. in absence of a driving field one has

$$\frac{\partial \langle n_t(\mathbf{k}) | n_t(\mathbf{k}, t) \rangle}{\partial t} = -k^2 \int_0^t d\tau \frac{U(\mathbf{k}, \tau)}{\langle n_t(\mathbf{k}) | n_t(\mathbf{k}) \rangle} \langle n_t(\mathbf{k}) | n_t(\mathbf{k}, t - \tau) \rangle. \quad (206)$$

But the Kubo product for finite temperatures is not the same as the correlation function. Under a few mild conditions the two may be related to each other. For this we first of all need the identities

$$\begin{aligned} & \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle (A - \langle A \rangle_0)(B(t) - \langle B \rangle_0) \rangle_0 \\ &= Tr \int_{-\infty}^{\infty} dt \exp(i\omega t) \left\{ \frac{\exp(-\beta \mathcal{H}_0)}{Z} (A - \langle A \rangle_0) \exp(-\beta \mathcal{H}_0) \right. \\ & \quad \left. \exp(\beta \mathcal{H}_0) \exp\left(\frac{i\mathcal{H}_0 t}{\hbar}\right) (B - \langle B \rangle_0) \exp\left(-\frac{i\mathcal{H}_0 t}{\hbar}\right) \right\}, \\ &= Tr \int_{-\infty}^{\infty} dt \exp(i\omega t) \frac{\exp(-\beta \mathcal{H}_0)}{Z} (B(t - i\hbar\beta) - \langle B \rangle_0) (A - \langle A \rangle_0). \end{aligned} \quad (207)$$

Now set $t' = t - i\hbar\beta$ and deform the integration path so that t' runs from $-\infty - i\hbar\beta$ to $\infty - i\hbar\beta$ along two vertical line pieces and the real axis. This then yields

$$\begin{aligned} & \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle (A - \langle A \rangle_0)(B(t) - \langle B \rangle_0) \rangle_0 \\ &= \exp(-\beta\hbar\omega) \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle (B(t) - \langle B \rangle_0)(A - \langle A \rangle_0) \rangle_0, \end{aligned} \quad (208)$$

under the following two conditions:

- i) $Tr [\exp(-\beta\mathcal{H}_0)(B(z) - \langle B \rangle_0)(A - \langle A \rangle_0)]$ is analytic on the strip $-\beta\hbar \leq Im(z) \leq 0$.
- ii) $\lim_{Re(z) \rightarrow \pm\infty} Tr [\exp(-\beta\mathcal{H}_0)(B(z) - \langle B \rangle_0)(A - \langle A \rangle_0)] = 0$. This corresponds to the Kubo-Martin-Schwinger, or KMS-condition:
 $\lim_{t \rightarrow \infty} \langle B(t)A \rangle_0 = \langle B \rangle_0 \langle A \rangle_0$.

Using this we obtain the *fluctuation dissipation theorem* through

$$\begin{aligned}
\mathbf{M}'_{BA}(\omega) &\equiv \int_{-\infty}^{\infty} dt \exp(i\omega t) \mathbf{M}_{BA}(t) \\
&= \frac{-1}{2\hbar} \int_{-\infty}^{\infty} dt \exp(i\omega t) (\langle AB(t) \rangle_0 - \langle B(t)A \rangle_0) \\
&= \frac{1 - \exp(-\beta\hbar\omega)}{2\hbar} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle (B(t) - \langle B \rangle_0)(A - \langle A \rangle_0) \rangle_0, \\
&\equiv \frac{1 - \exp(-\beta\hbar\omega)}{2\hbar} S_{BA}(\omega). \tag{209}
\end{aligned}$$

Alternatively, through (195) $\mathbf{M}'_{BA}(\omega)$ may be expressed in terms of the Kubo product as

$$\mathbf{M}'_{BA}(\omega) = \frac{\beta}{2i} \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle B^\dagger(t) | \dot{A} \rangle. \tag{210}$$

Next use

$$\begin{aligned}
\langle B^\dagger(t) | \dot{A} \rangle &= \lim_{\epsilon \rightarrow 0} \left\langle B^\dagger(t) \left| \frac{A(\epsilon) - A(0)}{\epsilon} \right. \right\rangle = \lim_{\epsilon \rightarrow 0} \left\langle \frac{B^\dagger(t - \epsilon) - B^\dagger(t)}{\epsilon} \left| A(0) \right. \right\rangle \\
&= -\frac{d}{dt} \langle B^\dagger(t) | A(0) \rangle. \tag{211}
\end{aligned}$$

Inserting this into (210) and applying a partial integration one obtains

$$\int_{-\infty}^{\infty} dt \exp(i\omega t) \langle B^\dagger(t) | A \rangle = \frac{1 - \exp(-\beta\hbar\omega)}{\beta\hbar\omega} S_{BA}(\omega). \tag{212}$$

Notice that for temperatures of $1^\circ K$ or higher $\beta\hbar \leq 10^{-11}$ s, so for practically all hydrodynamic applications the factor $(1 - \exp(-\beta\hbar\omega))/(\beta\hbar\omega)$ may be replaced by unity. But in interactions with radiation fields frequencies $\geq 10^{11}$ Hz are quite common, in which case the full expression is needed.

2.5.6 Full hydrodynamics

For the full hydrodynamic equations results similar to that for tracer diffusion may be derived again. One should be careful defining momentum and energy densities by anticommutators of \mathbf{p}_i and $\delta(\mathbf{r}_i - \mathbf{r})$ and the like, one should use Kubo products instead of correlation functions to formulate the hydrodynamic equations at first and also define the χ_{ij} of (86) in terms of Kubo products. For the latter the ratio between Kubo product and correlation function approaches unity in the limit $\mathbf{k} \rightarrow 0$. Therefore the transformations from density and energy density to chemical potential and pressure, based upon correlation expressions in the Grand canonical ensemble, can still be used. In the \mathbf{k} -dependent generalizations of these fields one should use Kubo-products to remain consistent. But, as argued in the previous subsection, in hydrodynamic applications the difference between Kubo product and correlation function usually can be ignored. However, one should notice that correlation functions between conserved densities may get more complicated due to quantum effects. E.g. in a Bose or Fermi gas the momenta of different particles may become correlated in equilibrium, due to Bose or Fermi statistics. In addition the momentum distribution at low temperatures and not too low densities is not a Maxwellian any more.

2.5.7 Dielectric response

A relatively simple application is the dielectric response to an external electric field¹⁰. In this case the Hamiltonian may be written as

$$H = H_0 - M_z E_z(t), \tag{213}$$

with $E_z(t)$ the time dependent electric field strength, which is supposed to be in the z -direction, and M_z the total electric polarization in the z -direction. This equation looks simpler than it is in reality. First of all, the electric field is the sum of the externally applied field and the internal field that is generated through the dielectric response of the medium. In analogy with the hydrodynamic equations we studied before, one might expect the response to a driving field to be separated into a direct response to the externally applied field and an indirect response to the hydrodynamic fields generated

¹⁰See [2] Ch. 21-5,6

by this field. However, this has some undesirable consequences as becomes clear especially in the case of a spatially oscillating field. Since the response to such a field has to follow the frequency of the driving field and the speed of light in the medium is different from that in vacuo, the total field has a wave length that is shorter than that of the driving field. Therefore the "response field" generated by the medium obviously has to consist of an "extinction field" that is exactly opposite to the driving field, together with the field, in this case of shorter wave length, appearing in (213). In fact it is no problem generalizing this equation to the case of an inhomogeneous field, but it becomes more obvious in that case that for E one cannot just take the external field. From (191) and (195) one finds that the average polarization at time t can be obtained as

$$\langle M_z(t) \rangle = \beta \int_0^t d\tau \langle \dot{M}_z | M_z(t - \tau) \rangle E_z(\tau). \quad (214)$$

Moving the time at which the field is turned on to $-\infty$ and requiring causal behavior (no response to fields at times $> t$) one may reexpress this as

$$\langle M_z(t) \rangle = \beta \int_{-\infty}^{\infty} d\tau \langle \dot{M}_z | M_z(\tau) \rangle \theta(\tau) E_z(t - \tau). \quad (215)$$

Taking the Fourier transform of this and dividing by V one finds that the frequency dependent polarization satisfies the relationship

$$P_z(\omega) = \chi(\omega) E_z(\omega), \quad (216)$$

with

$$\chi(\omega) = \frac{\beta}{V} \int_0^{\infty} dt \exp i\omega t \langle \dot{M}_z | M_z(t) \rangle. \quad (217)$$

This may be translated to the dielectric constant by using the relationship[13]

$$\mathbf{D} = \epsilon \mathbf{E} = \mathbf{E} + 4\pi \mathbf{P}, \quad (218)$$

yielding

$$\epsilon(\omega) = 1 + 4\pi\chi(\omega). \quad (219)$$

The interpretation of the real and imaginary part of the dielectric constant follows from the wave equation satisfied by the electric field [2, Appendix K],

$$\Delta \mathbf{E} = \frac{\epsilon\mu}{c^2} \frac{\partial^2 \mathbf{E}}{\partial t^2}, \quad (220)$$

with μ the magnetic permeability, which for most materials is very close to 1. Setting $\mu = 1$ one finds there are running wave solutions of the form

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp[i(\omega t - kx) - \kappa x]. \quad (221)$$

Now, set

$$\epsilon(\omega) = n^2(\omega). \quad (222)$$

It then follows from (221) that

$$n(\omega) = \frac{c}{\omega}(k - i\kappa). \quad (223)$$

Since ω/k is the propagation speed of electromagnetic waves of frequency ω in the medium, $Re(n(\omega))$ (or n) is the index of refraction for this frequency. Similarly the imaginary part of $n(\omega)$ is the field attenuation coefficient, describing the decay rate of the electric field per unit time. Notice that the decay rate of the radiation intensity is twice as large, as the energy density is proportional to the square of the field strength. Real and imaginary part of the dielectric constant may be expressed in terms of n and κ through

$$Re[\epsilon(\omega)] = n^2 - \left(\frac{c\kappa}{\omega}\right)^2, \quad (224)$$

$$Im[\epsilon(\omega)] = 2n\frac{c\kappa}{\omega}. \quad (225)$$

Debye developed a theory in which the correlation function $\langle M_z | M_z(t) \rangle$ decays exponentially in time with decay rate ν . In this case one obtains a Lorentzian line shape with

$$Re[\chi(\omega)] \sim \frac{\nu^2}{\nu^2 + \omega^2}, \quad (226)$$

$$Im[\chi(\omega)] \sim \frac{\omega\nu}{\nu^2 + \omega^2}. \quad (227)$$

3 Brownian Motion

The most common way of describing the motion of a Brownian particle is by means of the *Langevin equation*,

$$\begin{aligned} M\dot{\mathbf{u}} &= -\gamma\mathbf{u} + M\boldsymbol{\xi}(t) \\ \text{or} \quad \dot{\mathbf{u}} &= -\kappa\mathbf{u} + \boldsymbol{\xi}(t) \end{aligned} \quad (228)$$

$M\xi(t)$ is called *random force* and γ the *friction coefficient*. Usual assumptions on ξ are:

$$\langle \xi(t) \rangle = 0 \quad (229)$$

$$\langle \xi(t)\xi(t') \rangle = \frac{1}{d}\phi(|t-t'|)\mathbf{I}. \quad (230)$$

The most common assumption for ϕ is that it has the properties of "white noise": $\phi(|t-t'|) = \Phi\delta(t-t')$

Remark: If Φ is non-vanishing over an extended range of time one talks of "colored noise". This gives rise to memory effects in the Langevin equation, which then assumes the form:

$$\dot{\mathbf{u}} = \int d\tau \kappa(\tau)\mathbf{u}(t-\tau).$$

We will return to this later.

Eq. (228) is solved by:

$$\mathbf{u}(t) = e^{-\kappa(t-t_0)}\mathbf{u}(t_0) + \int_0^{t-t_0} d\tau e^{-\kappa\tau}\xi(t-\tau) \quad (231)$$

3.1 Classical fluctuation dissipation theorem

From (228), (229) and (231) one finds:

$$\begin{aligned} \frac{d}{dt} \langle u^2(t) \rangle &= -2\zeta \langle u^2(t) \rangle + 2 \int_0^{t-t_0} d\tau e^{-\zeta\tau} \langle \xi(t) \cdot \xi(t-\tau) \rangle \\ &= -2\zeta \langle u^2(t) \rangle + 2 \int_0^{t-t_0} d\tau e^{-\zeta\tau} \Phi \delta(t - (t-\tau)) \\ &= -2\zeta \langle u^2(t) \rangle + \Phi \end{aligned} \quad (232)$$

In the stationary state this has to vanish, so

$$\Phi = 2\zeta \langle u^2 \rangle_{\text{eq}} = 2d\zeta \frac{k_B T}{M}. \quad (233)$$

This is the classical fluctuation dissipation theorem. Let us consider in more detail this stationary process in which the Brownian particle is slowed down

by the friction force $-\gamma\mathbf{u}$ and accelerated by the random force $M\boldsymbol{\xi}(t)$ with the properties described by (229). The initial velocity decays on average as:

$$\langle \mathbf{u}(t) \rangle_{\mathbf{u}_0} = \mathbf{u}_0 e^{-\zeta(t-t_0)}.$$

Here $\langle \rangle_{\mathbf{u}_0}$ indicates an average over all realizations of the stochastic process with given initial velocity \mathbf{u}_0 at time t_0 . Next consider the behaviour of fluctuations. These are described by $\mathbf{U}(t|t_0) \equiv \mathbf{u}(t) - \langle \mathbf{u}(t) \rangle_{\mathbf{u}_0} = \int_0^{t-t_0} d\tau e^{-\zeta\tau} \boldsymbol{\xi}(t-\tau)$. They satisfy

$$\begin{aligned} \langle U_\alpha(t|t_0)U_\beta(t|t_0) \rangle &= \int_0^{t-t_0} d\tau_1 \int_0^{t-t_0} d\tau_2 e^{-\zeta\tau_1} e^{-\zeta\tau_2} \langle \xi_\alpha(t-\tau_1)\xi_\beta(t-\tau_2) \rangle \\ &= \int_0^{t-t_0} d\tau_1 e^{-2\zeta\tau_1} \frac{2\zeta k_B T}{M} \delta_{\alpha\beta} = \frac{k_B T}{M} \delta_{\alpha\beta} (1 - e^{-2\zeta(t-t_0)}), \end{aligned}$$

where (229) has been used. Next assume that the distribution of $\xi_\alpha(t)$ for each t is a gaussian and that for different times these distributions are completely uncorrelated. With this additional assumption satisfied the stochastic process is known as *Ornstein-Uhlenbeck process*. For gaussian distributions the average values of products of an even number of random variables (in this case the random force components) can be written as a sum of contributions from all different factorizations in products of pairs:

$$\langle \xi_{\alpha_1}(t_1) \dots \xi_{\alpha_n}(t_n) \rangle = \sum_{\text{choices of pairs}} \Pi \langle \xi_{\alpha_{i_1}}(t_{i_1}) \xi_{\alpha_{j_1}}(t_{j_1}) \rangle \langle \xi_{\alpha_{i_2}}(t_{i_2}) \xi_{\alpha_{j_2}}(t_{j_2}) \rangle \dots \quad (234)$$

So even moments of the distribution “factorize”, while odd moments vanish. For a proof: see Van Kampen[14] Ch. I. 6.

Now, if x_1, x_2 have a bivariate gaussian distribution, i.e.

$$P(x_1, x_2) \sim e^{-\frac{1}{2}[\alpha_{11}(x_1 - \langle x_1 \rangle)^2 + 2\alpha_{12}(x_1 - \langle x_1 \rangle)(x_2 - \langle x_2 \rangle) + \alpha_{22}(x_2 - \langle x_2 \rangle)^2]}$$

then all variables of the form $\lambda x_1 + \mu x_2$ also have gaussian distributions. E.g. introduce $\xi = \lambda x_1 + \mu x_2$; $\eta = \nu x_1 - \rho x_2$. Then x_1 and x_2 are linear combinations of ξ and η and the Jacobian of the transformation from x_1, x_2 to ξ, η , is a constant. Therefore the distribution for ξ and η is of the form

$$P(\xi, \eta) = \frac{1}{(\dots)} e^{-[(\dots)\xi^2 + 2(\dots)\xi\eta + (\dots)\eta^2]}.$$

Integration over one of the variables again leaves a gaussian distribution, e.g.

$\int d\eta P(\xi, \eta) \sim e^{-(\dots)\xi^2}$. Similarly, fixing one of the variables, e.g. η at a particular value leaves a gaussian distribution in the other one, but this may be shifted towards a different average value.

All of this generalizes to distributions of sums of arbitrary many variables with multivariate gaussian distribution. Specifically, in our case $\mathbf{U}(t | t_0)$ has a gaussian distribution.

The width of any gaussian distribution is determined by its second moment. Hence it follows from (234) that the distribution of $\mathbf{U}(t | t_0)$ is given by

$$W(\mathbf{u}, t | \mathbf{u}_0) = \left[\frac{M}{2\pi k_B T (1 - e^{-2\zeta(t-t_0)})} \right]^{d/2} \exp \frac{-M |\mathbf{u} - \mathbf{u}_0 e^{-\zeta(t-t_0)}|^2}{2k_B T (1 - e^{-2\zeta(t-t_0)})} \quad (235)$$

Similarly, the distribution of the displacement of the Brownian particle is a gaussian, since $\mathbf{r}(t) - \mathbf{r}(t_0) = \int_{t_0}^t \mathbf{u}(\tau) d\tau$.

At fixed \mathbf{u}_0 it's first moment is given by

$$\langle \mathbf{r}(t) - \mathbf{r}(t_0) \rangle_{\mathbf{u}_0} = \frac{\mathbf{u}_0 (1 - e^{-\zeta(t-t_0)})}{\zeta}. \quad (236)$$

Performing an additional average over the equilibrium distribution of \mathbf{u}_0 one finds that the second moment satisfies the equation

$$\begin{aligned} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 - |\langle \mathbf{r}(t) - \mathbf{r}(0) \rangle_{\mathbf{u}_0}|^2 \rangle = \\ \frac{dk_B T}{M\zeta^2} [2\zeta(t-t_0) - 3 + 4e^{-\zeta(t-t_0)} - e^{-2\zeta(t-t_0)}]. \end{aligned}$$

From this the diffusion constant follows through the Einstein relation as

$$D = \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{2dt} = \frac{k_B T}{M\zeta}. \quad (237)$$

Alternatively it can be obtained through the Green-Kubo relation as

$$\begin{aligned} D &= \frac{1}{d} \int_0^\infty \langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle dt \\ &= \frac{1}{d} \int_0^\infty \langle u_0^2 \rangle e^{-\zeta t} dt = \frac{k_B T}{M\zeta}. \end{aligned} \quad (238)$$

Finally D and ζ may be related to the Onsager coefficient, defined through

$$\mathbf{j} = -L\nabla\mu. \quad (239)$$

For low densities of Brownian particles (no interactions between them) one has $\mu(\mathbf{r}) = \Phi(\mathbf{r}) + k_B T \log[n(\mathbf{r})\lambda_0^d]$, with $\Phi(\mathbf{r})$ the external potential of a Brownian particle at position \mathbf{r} and $\lambda_0 = h/\sqrt{Mk_B T}$ its thermal De Broglie wavelength at temperature T , assumed to be uniform. Hence one has

$$\mathbf{j} = -L \left[-F(\mathbf{r}) + \frac{k_B T}{n(\mathbf{r})} \nabla n(\mathbf{r}) \right]. \quad (240)$$

This may be identified with the phenomenological expression

$$\mathbf{j}(\mathbf{r}) = n(\mathbf{r}) \frac{F(\mathbf{r})}{M\zeta} - D\nabla n(\mathbf{r}), \quad (241)$$

leading to the identities

$$\zeta = \frac{n}{ML}; \quad D = \frac{Lk_B T}{n} \quad (242)$$

For the distribution of the position of a Brownian particle starting off with velocity \mathbf{u}_0 at \mathbf{r}_0 at time t_0 , one obtains

$$W(\mathbf{r}, t | \mathbf{u}_0 \mathbf{r}_0, t_0) = \frac{1}{(\pi(\dots))^{d/2}} \exp \frac{-d | \mathbf{r} - \mathbf{r}(t_0) - \langle \mathbf{r}(t) - \mathbf{r}(t_0) \rangle_{\mathbf{u}_0} |^2}{2 \langle | \mathbf{r}(t) - \mathbf{r}(t_0) - \langle \mathbf{r}(t) - \mathbf{r}(t_0) \rangle_{\mathbf{u}_0} |^2 \rangle}. \quad (243)$$

Notice that in the presence of a constant external force \mathbf{F} the average displacement $\langle \mathbf{r}(t) - \mathbf{r}(t_0) \rangle$ picks up an additional contribution $\mathbf{F}t/\gamma$. Finally, also $W(\mathbf{u}, \mathbf{r}, t | \mathbf{u}_0, \mathbf{r}_0, t_0)$ approaches a multivariate gaussian distribution. This rapidly approaches the product of a Maxwellian and the distribution $W(\mathbf{r}, t | \mathbf{r}_0, t_0)$.

3.2 The Fokker-Planck Equation

An alternative, but equivalent description, derives an evolution equation for the probability distribution $W(\mathbf{u}, t)$ of finding the Brownian particle with velocity \mathbf{u} at time t . The derivation of this is based on the assumption that there is a stationary transition probability per unit time, $p(\mathbf{u}, \Delta\mathbf{u})$ for

velocity changes [due to collisions with bath particles!] from velocity \mathbf{u} to $\mathbf{u} + \Delta\mathbf{u}$. These transitions are assumed to establish a Markov process which can only be justified really for a bath consisting of a very dilute gas. Under these assumptions one has:

$$W(\mathbf{u}, t + \Delta t) = W(\mathbf{u}, t) + \Delta t \int d\Delta\mathbf{u} \{ p(\mathbf{u} - \Delta\mathbf{u}, \Delta\mathbf{u}) W(\mathbf{u} - \Delta\mathbf{u}, t) - p(\mathbf{u}, \Delta\mathbf{u}) W(\mathbf{u}, t) \}$$

Next one assumes that typical jumps $\Delta\mathbf{u}$ are very small on the characteristic scale for \mathbf{u} : typical values of u are $\sim \sqrt{\frac{k_B T}{M}}$, whereas velocity changes are of order $\frac{1}{M} \Delta |\mathbf{p}| \sim \frac{1}{M} \sqrt{mk_B T}$, so smaller by an order $\sqrt{\frac{m}{M}}$.

Then $p(\mathbf{u} - \Delta\mathbf{u}, \Delta\mathbf{u}) W(\mathbf{u} - \Delta\mathbf{u}, t)$ may be Taylor expanded around $p(\mathbf{u}, \Delta\mathbf{u}) W(\mathbf{u}, t)$ [this is known as *Kramers-Moyal expansion*]. Expansion through second order gives

$$\begin{aligned} \frac{W(\mathbf{u}, t + \Delta t) - W(\mathbf{u}, t)}{\Delta t} &= \int d\Delta\mathbf{u} \left[-\Delta\mathbf{u} \cdot \nabla_{\mathbf{u}} \{ p(\mathbf{u}, \Delta\mathbf{u}) W(\mathbf{u}, t) \} \right. \\ &\quad \left. + \frac{1}{2} \Delta\mathbf{u} \Delta\mathbf{u} : \nabla_{\mathbf{u}} \nabla_{\mathbf{u}} \{ p(\mathbf{u}, \Delta\mathbf{u}) W(\mathbf{u}, t) \} \right] + (\dots) \end{aligned} \quad (244)$$

Next identify:

$$\int d\Delta\mathbf{u} \Delta\mathbf{u} p(\mathbf{u}, \Delta\mathbf{u}) = \langle \frac{\mathbf{F}(\mathbf{u})}{M} \rangle = -\zeta \mathbf{u} + \frac{\mathbf{F}^{ext}}{M} \quad (245)$$

plus, for $\Delta t \rightarrow 0$:

$$\int d\Delta\mathbf{u} \Delta\mathbf{u} \Delta\mathbf{u} p(\mathbf{u}, \Delta\mathbf{u}) = \frac{1}{\Delta t} \int_0^{\Delta t} dt_1 \int_0^{\Delta t} dt_2 \langle \boldsymbol{\xi}(t_1) \boldsymbol{\xi}(t_2) \rangle = \frac{2\zeta k_B T}{M} \mathbf{I}, \quad (246)$$

where Eqs. (229) and (233) have been used. Substituting (245) and (246) into (244) one obtains the Fokker-Planck equation.

$$\frac{\partial}{\partial t} W(\mathbf{u}, t) + \frac{\partial}{\partial \mathbf{u}} \left[\left(-\zeta \mathbf{u} + \frac{\mathbf{F}^{ext}}{M} \right) W(\mathbf{u}, t) \right] = \frac{\zeta}{\beta M} \Delta_{\mathbf{u}} W(\mathbf{u}, t) \quad (247)$$

In the absence of an external force field, the solution of this equation with $W(\mathbf{u}, t_0) = \delta(\mathbf{u} - \mathbf{u}_0)$ is

$$W(\mathbf{u}, t | \mathbf{u}_0, t_0) = \left[\frac{M}{2\pi k_B T (1 - e^{-2\zeta(t-t_0)})} \right]^{d/2} \exp \frac{-M |\mathbf{u} - \mathbf{u}_0 e^{-\zeta(t-t_0)}|^2}{2k_B T (1 - e^{-2\zeta(t-t_0)})} \quad (248)$$

So in this case the FP-equation is fully equivalent to the Langevin equation!

For a constant external force, only little changes: One obtains

$$\langle \mathbf{u}(t) \rangle = \frac{\mathbf{F}_{ext}}{m\zeta} + \left(\mathbf{u}_0 - \frac{\mathbf{F}_{ext}}{m\zeta} \right) e^{-\zeta(t-t_0)} \quad (249)$$

$W(\mathbf{u}, t | \mathbf{u}_0, t_0)$ remains the same function of $\mathbf{u} - \langle \mathbf{u}(t) \rangle$ as before.

3.3 The Chandrasekhar Equation

Chandrasekhar considered the case that the velocity distribution also depends on position:

$$\left[\frac{\partial}{\partial t} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} \right] W(\mathbf{u}, \mathbf{r}, t) + \frac{\partial}{\partial \mathbf{u}} \cdot \left[\left(-\zeta \mathbf{u} + \frac{\mathbf{F}^{ext}(\mathbf{r}, \mathbf{u})}{M} \right) W(\mathbf{u}, \mathbf{r}, t) \right] = \frac{\zeta}{\beta M} \Delta_{\mathbf{u}} W(\mathbf{u}, \mathbf{r}, t) \quad (250)$$

In case $\mathbf{F}_{ext} = -\nabla\Phi(\mathbf{r})$ the equilibrium solution of (250) is

$$\begin{aligned} W^{eq}(\mathbf{r}, \mathbf{u}) &= C \frac{e^{-\beta(\frac{1}{2}Mu^2 + \Phi(\mathbf{r}))}}{(2\pi k_B T/M)^{d/2}} \\ &\equiv n^{eq}(\mathbf{r}) \frac{e^{-\frac{\beta}{2}Mu^2}}{(2\pi k_B T/M)^{d/2}} \end{aligned} \quad (251)$$

To find the decay to equilibrium of not too large initial deviations we may employ the *Chapman-Enskog solution method* which is mostly used to construct “hydrodynamic solutions” of the Boltzmann equation and similar kinetic equations.

We rearrange the Chandrasekhar equation as

$$\left(\frac{\partial}{\partial t} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}} - \frac{\nabla\Phi(\mathbf{r})}{M} \cdot \frac{\partial}{\partial \mathbf{u}} \right) W(\mathbf{r}, \mathbf{u}, t) = \zeta \left(\frac{\partial}{\partial \mathbf{u}} \cdot \mathbf{u} + \frac{1}{\beta M} \Delta_{\mathbf{u}} \right) W(\mathbf{r}, \mathbf{u}, t) \quad (252)$$

For solutions varying on macroscopic time and length scales, the terms on the right hand side are of the order ζW versus order $\frac{1}{L} \sqrt{\frac{k_B T}{M}} W$ for the terms on the left hand side. Therefore one may apply some type of perturbation

expansion in which terms on the left hand side are always one order smaller than corresponding terms on the right side.

The zeroth order equation only keeps the right side and reads

$$\left(\frac{\partial}{\partial \mathbf{u}} \cdot \mathbf{u} + \frac{1}{\beta M} \Delta \mathbf{u} \right) W^{(0)}(\mathbf{r}, \mathbf{u}, t) = 0 \quad (253)$$

The general solution of this is of the form

$$W^{(0)}(\mathbf{r}, \mathbf{u}, t) = n(\mathbf{r}, t) \frac{e^{-\frac{\beta M \mathbf{u}^2}{2}}}{(2\pi k_B T / M)^{d/2}} \equiv n(\mathbf{r}, t) \varphi(u) \quad (254)$$

with $n(\mathbf{r}, t)$ an arbitrary function of \mathbf{r} and t . We would like to find an equation describing its time evolution, starting from an initial value $n(\mathbf{r}, 0)$. A first step towards this is taken by constructing the next order equation by equating the left hand operator acting upon $W^{(0)}$ to the right hand operator acting upon $W^{(1)}$, hence

$$\varphi(u) \left(\frac{\partial^{(1)} n}{\partial t} + \mathbf{u} \cdot (\nabla n + n \nabla \beta \Phi) \right) = \zeta \left(\frac{\partial}{\partial \mathbf{u}} \cdot \mathbf{u} + \frac{1}{\beta M} \Delta \mathbf{u} \right) W^{(1)}(\mathbf{r}, \mathbf{u}, t)$$

We find a first approximation for $\frac{\partial n}{\partial t}$ by integrating both sides over \mathbf{u} , with the result

$$\frac{\partial^{(1)} n(\mathbf{r}, t)}{\partial t} = 0 \quad (255)$$

Substituting this on the left hand side we may solve for $W^{(1)}$ with the result

$$W^{(1)}(\mathbf{r}, \mathbf{u}, t) = -\frac{1}{\zeta} \varphi(u) \mathbf{u} \cdot (\nabla n + n \nabla \beta \Phi)$$

One could add a term of form $n^{(1)}(\mathbf{r}, t) \varphi(\mathbf{u})$ to this, but the Chapman-Enskog convention is to assume that all terms of this form are accounted for in $W^{(0)}$. The next order equation becomes

$$\begin{aligned} \frac{\partial^{(2)} n(\mathbf{r}, t)}{\partial t} \varphi(u) - \frac{1}{\zeta} \varphi(u) \left\{ \mathbf{u} \cdot \left(\nabla \frac{\partial n}{\partial t} + \frac{\partial n}{\partial t} \nabla \beta \Phi \right) + \mathbf{u} \mathbf{u} : \left[\nabla (\nabla n + n \nabla \beta \Phi) \right] \right. \\ \left. - \frac{\nabla \Phi}{M} \cdot (\nabla n + n \nabla \beta \Phi) + \mathbf{u} \mathbf{u} : \left[n \nabla \beta \Phi (\nabla n + n \nabla \beta \Phi) \right] \right\} \end{aligned}$$

$$= \zeta \left(\frac{\partial}{\partial \mathbf{u}} \cdot \mathbf{u} + \frac{1}{\beta M} \Delta \mathbf{u} \right) W^{(2)}(\mathbf{r}, \mathbf{u}, t) \quad (256)$$

Integration over \mathbf{u} now gives the following contribution to $\frac{\partial n}{\partial t}$:

$$\frac{\partial^{(2)} n(\mathbf{r}, t)}{\partial t} - \frac{k_B T}{M \zeta} \left(\nabla \cdot (\nabla n + n \nabla \beta \Phi) \right) = 0 \quad (257)$$

Through second level in the Chapman-Enskog expansion this is precisely the hydrodynamic equation satisfied by the spatial density of Brownian particles. Besides as diffusion equation it is known as the *Smoluchovsky equation*. It may also be written as

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D \nabla \cdot \epsilon^{-\beta \Phi(\mathbf{r})} \nabla (n e^{\beta \Phi(\mathbf{r})}) \quad (258)$$

with $D = \frac{k_B T}{M \zeta}$.

The time scale on which the Chandrasekhar equation reduces to the Smoluchovsky equation is the relaxation time ζ^{-1} .

For a Brownian particle of radius R in a fluid ζ roughly follows from Stokes' Law as $\zeta = \frac{6\pi\eta R}{M} \sim \frac{4.5\eta}{\rho R^2}$.

A typical diffusive time is $\frac{R^2}{D} = \frac{\frac{4}{3}\rho\pi R^5\zeta}{k_B T} \approx \frac{20R^3\eta}{k_B T}$.

The two times become equal for $R \approx \frac{k_B T \rho}{100\eta^2}$. For water at room temperature this amounts to less than a nm.

3.4 Colored noise, Brownian motion with memory

The assumption that the random force is δ -correlated in time obviously is an idealization. A natural generalization is

$$\langle \boldsymbol{\xi}(t_1) \boldsymbol{\xi}(t_2) \rangle = \mathbf{I} \kappa(|t_1 - t_2|) \quad (259)$$

In this case the Langevin equation has to be extended to

$$\dot{\mathbf{u}}(t) = - \int_0^\infty d\tau \zeta(\tau) \mathbf{u}(t - \tau) + \boldsymbol{\xi}(t) \quad (260)$$

Assume further

$$\langle \boldsymbol{\xi}(t) \rangle = 0 \quad \text{.and} \quad \langle \mathbf{u}(0) \boldsymbol{\xi}(t) \rangle = 0 \quad \text{for } t > 0. \quad (261)$$

The second of these equalities in general is only an approximation. The velocity at time 0 is correlated to the random force at negative times, so is the random force at positive times, according to (259), hence there has to exist a correlation between velocity at time 0 and random force at positive times. In the limit of infinite mass ratio between Brownian particle and bath particles though, this correlation will vanish; in this limit the Brownian velocity tends to zero while the correlations between random forces at different times become independent of the mass ratio (see also the next subsection). Taking a one-sided Laplace transform of (260), one obtains

$$\mathbf{u}(\omega) \equiv \int_0^\infty dt e^{i\omega t} \mathbf{u}(t) = \frac{\mathbf{u}(0) + \boldsymbol{\xi}(\omega)}{-i\omega + \zeta(\omega)}. \quad (262)$$

From this plus (261):

$$\begin{aligned} \int_{-\infty}^\infty dt e^{i\omega t} \langle \mathbf{u}(0) \mathbf{u}(t) \rangle &= \frac{\langle \mathbf{u}(0) \mathbf{u}(0) \rangle}{-i\omega + \zeta(\omega)} + cc \\ &= \frac{k_B T (\zeta(\omega) + \zeta^*(\omega)) \mathbf{I}}{M(\omega^2 + |\zeta(\omega)|^2) - 2\omega \text{Im}(\zeta(\omega))} \end{aligned} \quad (263)$$

Next do a full Fourier transform of (260). This gives

$$(-i\omega + \zeta(\omega)) \hat{\mathbf{u}}(\omega) = \boldsymbol{\xi}(\omega) \quad (264)$$

Multiply by cc plus take thermal average \Rightarrow

$$\langle \hat{\mathbf{u}}(\omega) \hat{\mathbf{u}}(-\omega) \rangle = \frac{\langle \boldsymbol{\xi}(\omega) \boldsymbol{\xi}(-\omega) \rangle}{\omega^2 + |\zeta(\omega)|^2 - 2\omega \text{Im}(\zeta(\omega))} \quad (265)$$

Next we use the *Wiener-Khintchine theorem*:

$$\langle \hat{\mathbf{u}}(\omega) \hat{\mathbf{u}}(-\omega) \rangle = \lim_{t_0 \rightarrow \infty} \int_{-t_0}^{t_0} dt_1 \int_{-t_0}^{t_0} dt_2 \langle \mathbf{u}(t_1) \mathbf{u}(t_2) \rangle e^{i\omega(t_1 - t_2)}$$

Introduce $\tau = t_1 - t_2$ and $t = \frac{t_1 + t_2}{2}$. Use

$$\begin{aligned}
\langle \mathbf{u}(t_1)\mathbf{u}(t_2) \rangle &= \langle \mathbf{u}(0)\mathbf{u}(\tau) \rangle \Rightarrow \\
\langle \hat{\mathbf{u}}(\omega)\hat{\mathbf{u}}(-\omega) \rangle &= \lim_{t_0 \rightarrow \infty} \int_{-2t_0}^{2t_0} d\tau (2t_0 - \tau) \langle \mathbf{u}(0)\mathbf{u}(\tau) \rangle e^{i\omega\tau} \\
&\approx \lim_{t_0 \rightarrow \infty} \frac{2t_0(\zeta(\omega) + \zeta^*(\omega))}{\omega^2 + |\zeta(\omega)|^2 - 2\omega \operatorname{Im}(\zeta(\omega))} \frac{k_B T}{M} \mathbf{I} \quad (266)
\end{aligned}$$

In a similar way

$$\langle \boldsymbol{\xi}(\omega)\boldsymbol{\xi}(-\omega) \rangle \approx \lim_{t_0 \rightarrow \infty} \int_{-2t_0}^{2t_0} d\tau (2t_0 - \tau) \langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(\tau) \rangle e^{i\omega\tau} \quad (267)$$

Combining (267), (266) and (265) one may conclude that

$$\langle \boldsymbol{\xi}(t_1)\boldsymbol{\xi}(t_2) \rangle = \frac{k_B T}{M} \zeta(|t_1 - t_2|) \mathbf{I}, \quad (268)$$

or $\kappa(t) = k_B T/M \zeta(t)$. It is not known how to construct a corresponding Fokker-Planck equation in this case. On the other hand, if the distribution of $\boldsymbol{\xi}(t)$ is a multivariate gaussian, the distribution of \mathbf{u} is a gaussian again, determined by $\langle \mathbf{u}(t) \rangle$ and $\langle (\mathbf{u}(t) - \langle \mathbf{u}(t) \rangle)(\mathbf{u}(t) - \langle \mathbf{u}(t) \rangle) \rangle$.

Interpretation of ζ :

$$\zeta(|t_1 - t_2|) = \frac{1}{dMk_B T} \langle (\mathbf{F}(t_1) - \langle \mathbf{F}(t_1) \rangle) \cdot (\mathbf{F}(t_2) - \langle \mathbf{F}(t_2) \rangle) \rangle \quad (269)$$

Since $\langle \mathbf{F}(t) \rangle = \int d\tau M\zeta(\tau) \langle \mathbf{u}(t - \tau) \rangle$, it vanishes in the limit of $M \rightarrow \infty$ (in this limit the initial velocity vanishes always). So, $\zeta(|t_1 - t_2|)$ is proportional to the force-force correlation function of a particle of infinite mass, suspended in the fluid. In the case of finite mass, the subtraction of the average force is crucial: otherwise one would have

$$\begin{aligned}
\text{“}\zeta\text{”} &= \int_0^\infty dt \langle \mathbf{F}(0) \cdot \mathbf{F}(t) \rangle = \int_0^\infty dt \langle \mathbf{F}(0) \cdot \frac{d}{dt} M\mathbf{u}(t) \rangle \\
&= \langle \mathbf{F}(0) \cdot M\mathbf{u}(t) \rangle \Big|_0^\infty \\
&= 0
\end{aligned}$$

because at $t = 0$ force and momentum in equilibrium are uncorrelated and in the limit $t \rightarrow \infty$ the velocity of the Brownian particle becomes uncorrelated from the initial force again.

3.5 Formal derivation with the aid of projection operator formalism

As projection operator we choose

$$\mathcal{P} = \frac{|\mathbf{P}_B\rangle \cdot \langle \mathbf{P}_B|}{Mk_B T} = \frac{|M\mathbf{u}\rangle \cdot \langle M\mathbf{u}|}{Mk_B T}. \quad (270)$$

For a Brownian particle this is sensible because the time scale on which P_B varies typically is $\frac{M}{6\pi\eta R} = \frac{2\rho R^2}{9\eta}$, which is very slow compared to (almost) all time scales in the surrounding fluid. According to eq.(69) of the script, the derivation of a distribution function from equilibrium, characterized through $\rho(t) = \rho_0(1 + \Delta(t))$, satisfies

$$\frac{\partial}{\partial t} \mathcal{P} \Delta(t) = \int_0^\infty d\tau \mathcal{P} \mathcal{L} e^{-\hat{\mathcal{L}}\tau} \mathcal{L} \mathcal{P} \Delta(t - \tau) \quad (271)$$

where I used $\mathcal{P} \mathcal{L} \mathcal{P} = 0$. Now take the inner product $\langle \mathbf{u} |$ and use $\mathcal{L} \mathbf{P}_B = \mathbf{F}_B(\mathbf{R}, \mathbf{r}_1 \dots \mathbf{r}_N)$ to obtain

$$\frac{\partial}{\partial t} \langle \mathbf{u}(t) \rangle = \frac{-1}{Mk_B T} \int_0^\infty d\tau \langle \mathbf{F}_B e^{-\hat{\mathcal{L}}\tau} \mathbf{F}_B \rangle \langle \mathbf{u}(t - \tau) \rangle \quad (272)$$

Next use:

$$\begin{aligned} \hat{\mathcal{L}} \mathbf{F}_B &= (1 - \mathcal{P}) \mathcal{L} (1 - \mathcal{P}) \mathbf{F}_B \\ &= (1 - \mathcal{P}) \left(\frac{\mathbf{P}_B}{M} \cdot \frac{\partial}{\partial \mathbf{R}_B} + \mathbf{F}_B \cdot \frac{\partial}{\partial \mathbf{P}_B} + \mathcal{L}_{(M=\infty)} \right) \mathbf{F}_B \\ &= (\mathcal{L}_{(M=\infty)}) \mathbf{F}_B \end{aligned} \quad (273)$$

because \mathbf{F}_B does not depend on \mathbf{P}_B and $(1 - \mathcal{P}) \frac{\mathbf{P}_B}{M} \cdot \frac{\partial}{\partial \mathbf{R}_B} = 0$. By induction, $(\hat{\mathcal{L}}^n) \mathbf{F}_B = (\mathcal{L}_{M=\infty}^n) \mathbf{F}_B$ and so $e^{-\hat{\mathcal{L}}\tau} \mathbf{F}_B = e^{-\hat{\mathcal{L}}_{(M=\infty)}\tau} \mathbf{F}_B$. Hence, comparing

with (261) averaged over the random force distribution, one recovers (269) with the interpretation of $\langle(\mathbf{F} - \langle\mathbf{F}(t_1)\rangle)(\mathbf{F} - \langle\mathbf{F}(t_2)\rangle)\rangle$ as the infinite mass limit of the force autocorrelation function. And for large M , $e^{+\hat{\mathcal{L}}\tau}\mathbf{F}_B$ may be identified with the actual force minus its average, conditioned on the initial force \mathbf{F}_B ; for not too long times the actual dynamics will be virtually the same as the infinite mass dynamics.

The memory kernel

The memory kernel may be obtained by solving linearized hydrodynamic equations for the flow field around a sphere moving through a fluid with a time dependent velocity.

For small ω the result for stick boundary conditions is[15]:

$$\zeta(\omega) = \frac{6\pi\eta R}{M} \left[1 + R \left(\frac{-i\omega}{\nu} \right)^{\frac{1}{2}} - \frac{i\omega R^2}{9\nu} \right]$$

with $\nu = \eta/\rho$. This implies a long-time decay $\sim t^{-3/2}$. For the velocity correlation function (263) implies, with $C(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle$,

$$C(\omega) = \frac{3k_B T}{M} \frac{1}{-i\omega + \frac{6\pi\eta R}{M} \left[1 + R \left(\frac{-i\omega}{\nu} \right)^{\frac{1}{2}} - \frac{i\omega R^2}{9\nu} \right]} + cc.$$

When is the white-noise approximation good? This would amount to $\zeta(\omega) = \frac{6\pi\eta R}{M}$ and would give rise to a pole at $i\omega = \frac{6\pi\eta R}{M}$.

For this value of ω the neglected terms in the memory kernel are

$$\left(\frac{-6\pi\eta R^3}{M\eta/\rho} \right)^{\frac{1}{2}} = \left(-\frac{6\pi R^3 \rho}{\frac{4}{3}\pi R^3 \rho_B} \right)^{\frac{1}{2}} = \left(\frac{-9\rho}{2\rho_B} \right)^{\frac{1}{2}}$$

and $\frac{\rho}{-2\rho_B}$. These have to be $\ll 1$, requiring $\rho_B \gg \rho$. But under such conditions, the Brownian particle will sediment to the bottom. This has first been noted by Lorentz[16] and been rediscovered by Hauge and Martin-Löf[17]. The effect of the $i\omega$ -term in this kernel obviously is to replace the Brownian mass by an effective mass $M^{eff} = M + \frac{2}{3}\pi R^3 \rho$. The $(-i\omega)^{\frac{1}{2}}$ -term

indicates the existence of a long-time-tail in the Brownian-particle velocity autocorrelation function:

$$\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle \sim \frac{2k_B T}{(4\pi\nu t)^{3/2} \rho}$$

As we will see, this may be interpreted as the effect of the left-over from the initial momentum of the Brownian particle, diffusing slowly away from its initial position. If the self-diffusion of the Brownian particle is taken into account as well, this results in a replacement of ν by $\nu + D$, but for Brownian particles always $D \ll \nu$. We may conclude that unless $\rho_B \gg \rho$, the Fokker-Planck equation is never adequate for Brownian motion. But the correctness of the Smoluchowsky equation on time scales $\gg \zeta^{-1}$ remains valid.

4 Long time tails

4.1 Velocity autocorrelation function

Look at $\langle \mathbf{v}_1(0) \cdot \mathbf{v}_1(t) \rangle$ for a molecular liquid. Suppose particle 1 is at the origin at $t = 0$ with velocity \mathbf{v}_0 in a system in equilibrium. On average this has no influence on the velocity distribution of the rest of the system. This means, on average this corresponds to an initial momentum density $m\mathbf{v}_0\delta(\mathbf{r})$. Similarly, there is an initial tagged particle density $\delta(\mathbf{r})$. After a long time t , the average velocity of the tagged particle will be given by

$$\int d\mathbf{r} n_t(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t).$$

If normal diffusive behavior holds one has:

$$n_t(\mathbf{r}, t) = \frac{\exp(-\frac{r^2}{4Dt})}{(4\pi Dt)^{d/2}} \quad (274)$$

Or, for the Fourier components, which satisfy $\hat{n}_t(\mathbf{k}, 0) = \int d\mathbf{r} e^{-i\mathbf{k}\cdot\mathbf{r}} \delta(\mathbf{r}) = 1$,

$$\hat{n}_t(\mathbf{k}, t) = e^{-Dk^2 t} \quad (275)$$

For the velocity field, the Fourier components normal to $\hat{\mathbf{k}}$ satisfy

$$\frac{\partial}{\partial t} \hat{\mathbf{u}}_{\perp}(\mathbf{k}, t) = -\nu k^2 \hat{\mathbf{u}}_{\perp}(\mathbf{k}, t) \quad (276)$$

with $\mathbf{u}_{\perp} = (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \cdot \mathbf{u}$ and $\nu = \eta/\rho$ the so-called kinematic viscosity. This is solved by

$$\hat{\mathbf{u}}_{\perp}(\mathbf{k}, t) = \frac{m_t \mathbf{v}_0}{\rho} \cdot (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) e^{-\nu k^2 t} \quad (277)$$

The irrotational velocity field behaves as

$$\hat{\mathbf{u}}(\mathbf{k}, t) \cdot \hat{\mathbf{k}}\hat{\mathbf{k}} = \sum_{\sigma=\pm 1} \frac{1}{2} \frac{m_t \mathbf{v}_0}{\rho} \cdot \hat{\mathbf{k}}\hat{\mathbf{k}} e^{\sigma i \mathbf{k} \cdot \mathbf{r} - \frac{1}{2} \Gamma k^2 t} \quad (278)$$

For the average velocity of the tagged particle at time t this leads to the estimate

$$\begin{aligned} \mathbf{u}(t) &\approx \int d\mathbf{r} n_t(\mathbf{r}, t) \mathbf{u}_{\perp}(\mathbf{r}, t) \\ &\approx \frac{1}{(2\pi)^{2d}} \int d\mathbf{r} \int d\mathbf{k} \int d\mathbf{k}' e^{i\mathbf{k} \cdot \mathbf{r}} e^{i\mathbf{k}' \cdot \mathbf{r}} \hat{n}_t(\mathbf{k}, t) \hat{\mathbf{u}}_{\perp}(\mathbf{k}', t) \\ &= \frac{1}{(2\pi)^d} \int d\mathbf{k} \int d\mathbf{k}' \delta(\mathbf{k} + \mathbf{k}') \hat{n}_t(\mathbf{k}, t) \hat{\mathbf{u}}_{\perp}(\mathbf{k}', t) \\ &= \frac{1}{(2\pi)^d} \int d\mathbf{k} \hat{n}_t(\mathbf{k}, t) \hat{\mathbf{u}}_{\perp}(-\mathbf{k}, t) \\ &= \frac{1}{(2\pi)^d} \int d\mathbf{k} e^{-Dk^2 t} \frac{m_t \mathbf{v}_0}{\rho} \cdot (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) e^{-\nu k^2 t} \\ &= \frac{(d-1)m_t \mathbf{v}_0}{2^d d \rho [\pi(D + \nu)t]^{d/2}} \end{aligned} \quad (279)$$

Taking an inner product with \mathbf{v}_0 and averaging over the distribution of the initial velocity one arrives at

$$\langle \mathbf{v}_0 \cdot \mathbf{v}(t) \rangle = \frac{(d-1)k_B T}{\rho [4\pi(D + \nu)t]^{d/2}} \quad (280)$$

Note that this result is independent of the mass of the tracer particle!

4.2 Problems in low-dimensional systems

For $d \leq 2$ $\int_0^\infty \frac{dt}{t^{d/2}}$ diverges, so D and ν do not exist. This means $\langle r^2(t) \rangle$ grows faster than linearly with t . Its actual behavior may be estimated in the following way: assume the distribution of the tracer particle's position is still gaussian, and so is the position dependence of the divergence free part of the average velocity field, hence

$$p(\mathbf{r}, t) = \frac{\exp\left(-\frac{r^2}{2\langle x_D^2(t) \rangle}\right)}{(2\pi \langle x_D^2(t) \rangle)^{d/2}} \text{ etc.} \quad (281)$$

One then obtains

$$\begin{aligned} C(t) &= (d-1) \frac{k_B T}{\rho} \frac{\int d\mathbf{r} \exp\left(\frac{-r^2}{2\langle x_D^2(t) \rangle}\right) \exp\left(\frac{-r^2}{2\langle x_{sh}^2(t) \rangle}\right)}{((2\pi)^2 \langle x_D^2(t) \rangle \langle x_{sh}^2(t) \rangle)^{\frac{d}{2}}} \\ &= (d-1) \frac{k_B T}{\rho} \frac{1}{(2\pi \langle x_D^2(t) + x_{sh}^2(t) \rangle)^{\frac{d}{2}}} \end{aligned} \quad (282)$$

If $\langle x_D^2(t) \rangle = f(t)$ and $\langle x_{sh}^2(t) \rangle$ is proportional to this, then for $d = 2$

$$\frac{d^2 f(t)}{dt^2} = \frac{C}{f(t)}, \quad (283)$$

which is solved by $f(t) \sim t\sqrt{\log t}$.

For $d = 1$ there are no shear modes. But longitudinal stress-stress correlation functions may couple to pairs of opposite sound modes. The same self-consistency argument then leads to

$$\left(\frac{d^2 f(t)}{dt^2} = \frac{C}{\sqrt{f(t)}} \right) \Rightarrow f(t) \sim t^{4/3}.$$

This indeed is the correct result!

4.3 Mode-coupling analysis

A possible starting point for the analysis of tracer diffusion are the fluctuating hydrodynamic equations:

$$\frac{\partial}{\partial t} n_t(\mathbf{r}, t) = -\nabla \cdot [n_t(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) - D(n(\mathbf{r}, t), T(\mathbf{r}, t))\nabla n_t(\mathbf{r}, t) + \mathbf{j}_t^r(\mathbf{r}, t)] \quad (284)$$

$$\begin{aligned} \frac{\partial}{\partial t} \mathbf{G}(\mathbf{r}, t) + \nabla \cdot [\mathbf{u}(\mathbf{r}, t)\mathbf{G}(\mathbf{r}, t)] = & -\nabla p(\mathbf{r}, t) + \nabla \cdot \{\eta(n(\mathbf{r}, t), T(\mathbf{r}, t))\nabla \mathbf{u}(\mathbf{r}, t)\} \\ & + \nabla \cdot \left\{ \zeta(n(\mathbf{r}, t), T(\mathbf{r}, t)) + \frac{d-1}{d} \eta(n(\mathbf{r}, t), T(\mathbf{r}, t)) \nabla \cdot \mathbf{u}(\mathbf{r}, t) \right\} + \nabla \cdot \boldsymbol{\sigma}^r(\mathbf{r}, t) \end{aligned} \quad (285)$$

Plus an equation for the energy density plus the continuity equation for the bulk density.

In these expressions $\mathbf{j}_t^r(\mathbf{r}, t)$ and $\boldsymbol{\sigma}^r(\mathbf{r}, t)$ respectively are the *random tagged particle current* and the *random stress tensor*. Both of them are usually represented by gaussian white noise, with zero mean and variances dictated by the fluctuation dissipation theorem. Next, expand variables like D, p, η around equilibrium $D(n(\mathbf{r}, t), T(\mathbf{r}, t)) = D_0 + \frac{\partial D}{\partial n} \delta n + \frac{\partial D}{\partial T} \delta T + \dots$ etc. Fourier transforms of products become convolutions, e.g.

$$n_t(\mathbf{r}, t)\mathbf{u}(\mathbf{r}, t) = \frac{1}{V} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}} \sum_{\mathbf{q}} \hat{n}_t(\mathbf{q}, t) \hat{\mathbf{u}}(\mathbf{k} - \mathbf{q}, t)$$

Consider the equations for the Fourier components and keep only the most important non-linear terms. Restrict the equation for the velocity field to the divergence free components. This leads to

$$\frac{\partial}{\partial t} \hat{n}_t(\mathbf{k}, t) = -D_0 k^2 \hat{n}_t(\mathbf{k}, t) - i\mathbf{k} \cdot \frac{1}{V} \sum_{\mathbf{q}} \hat{n}_t(\mathbf{k} - \mathbf{q}, t) \hat{\mathbf{u}}(\mathbf{q}, t) - i\mathbf{k} \cdot \mathbf{j}_t^r(\mathbf{k}, t) \quad (286)$$

$$\begin{aligned} \frac{\partial}{\partial t} \hat{\mathbf{u}}_{\perp}(\mathbf{k}, t) = & -\nu_0 k^2 \hat{\mathbf{u}}_{\perp}(\mathbf{k}, t) - i\mathbf{k} \cdot \frac{1}{V} \sum_{\mathbf{q}} \hat{\mathbf{u}}(\mathbf{k} - \mathbf{q}, t) \hat{\mathbf{u}}(\mathbf{q}, t) \cdot (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \\ & - i\mathbf{k} \cdot \boldsymbol{\sigma}^r(\mathbf{k}, t) \cdot (\mathbf{I} - \hat{\mathbf{k}}\hat{\mathbf{k}}) \end{aligned} \quad (287)$$

The first equation may be iterated twice:

$$\begin{aligned}
\hat{n}_t(\mathbf{k}, t) &= e^{-D_0 k^2 t} \hat{n}_t(\mathbf{k}, 0) - \int_0^t d\tau e^{-D_0 k^2 (t-\tau)} \left\{ \frac{i\mathbf{k}}{V} \cdot \left[\sum_{\mathbf{q}} \hat{n}_t(\mathbf{k} - \mathbf{q}, \tau) \hat{\mathbf{u}}(\mathbf{q}, \tau) + \mathbf{j}_t^r(\mathbf{k}, \tau) \right] \right\} \\
&= e^{-D_0 k^2 t} \hat{n}_t(\mathbf{k}, 0) - \int_0^t d\tau e^{-D_0 k^2 (t-\tau)} \left\{ \frac{i\mathbf{k}}{V} \cdot \left[\mathbf{j}_t^r(\mathbf{k}, \tau) + \sum_{\mathbf{q}} \hat{\mathbf{u}}(\mathbf{q}, \tau) \right. \right. \\
&\quad \left. \left. \left\{ e^{-D_0 |\mathbf{k}-\mathbf{q}|^2 \tau} \hat{n}_t(\mathbf{k} - \mathbf{q}, 0) - \int_0^\tau d\tau_1 e^{-D_0 |\mathbf{k}-\mathbf{q}|^2 (\tau-\tau_1)} \right. \right. \right. \\
&\quad \left. \left. \left. \left\{ \frac{i(\mathbf{k} - \mathbf{q})}{V} \cdot \left[\sum_{\mathbf{q}_1} \hat{n}_t(\mathbf{k} - \mathbf{q} - \mathbf{q}_1, \tau_1) \hat{\mathbf{u}}(\mathbf{q}_1, \tau_1) + \mathbf{j}_t^r(\mathbf{k} - \mathbf{q}, \tau_1) \right] \right\} \right\} \right\} \right\} \quad (288)
\end{aligned}$$

Consider now $\langle \hat{n}_t(-\mathbf{k}, 0) \hat{n}_t(\mathbf{k}, t) \rangle$ averaged over gaussian distribution of initial fields plus random currents. Dominant contribution comes from $\mathbf{q}_1 = -\mathbf{q}$, because $\langle n(\mathbf{q}_1, 0) n(\mathbf{q}_2, 0) \rangle \sim \delta(\mathbf{q}_1 + \mathbf{q}_2) \Rightarrow$

$$\begin{aligned}
\frac{\partial}{\partial t} \langle \hat{n}_t(-\mathbf{k}, 0) \hat{n}_t(\mathbf{k}, t) \rangle &= -k^2 \int_0^t d\tau (D_0 \delta(\tau) + \frac{1}{V} \sum_{\mathbf{q}} e^{-D_0 |\mathbf{k}-\mathbf{q}|^2 \tau} \\
\hat{\mathbf{k}}\hat{\mathbf{k}}: \langle \hat{\mathbf{u}}(-\mathbf{q}, 0) \cdot \hat{\mathbf{u}}(\mathbf{q}, \tau) \rangle &\langle \hat{n}_t(-\mathbf{k}, 0) \hat{n}_t(\mathbf{k}, t - \tau) \rangle \quad (289)
\end{aligned}$$

Here I used that the velocity correlation function is independent of the tracer density plus time translation invariance of this function. In fact the latter follows from the fluctuation dissipation relations between random currents and the decay rates of the correlation functions. Now by using

$$\begin{aligned}
\langle \hat{\mathbf{u}}(-\mathbf{q}, 0) \hat{\mathbf{u}}(\mathbf{q}, \tau) \rangle &= (\mathbf{I} - \hat{\mathbf{q}}\hat{\mathbf{q}}) \frac{\langle \hat{\mathbf{u}}(-\mathbf{q}, 0) \cdot \hat{\mathbf{u}}(\mathbf{q}, 0) \rangle}{d} e^{-\nu q^2 \tau} \\
&+ \hat{\mathbf{q}}\hat{\mathbf{q}} \frac{\langle \hat{\mathbf{u}}(-\mathbf{q}, 0) \cdot \hat{\mathbf{u}}(\mathbf{q}, 0) \rangle}{2d} \sum_{\sigma=\pm 1} e^{(\sigma i c q - \frac{1}{2} \Gamma q^2) \tau}
\end{aligned}$$

one reproduces the intuitive result for $C(\mathbf{k}, \tau)$.

4.4 Mode-coupling for full hydrodynamics

(See e.g. Ernst, Hauge, Van Leeuwen, Ref.[18])

Instead of using fluctuating hydrodynamics I will base this on the projection operator formalism.

Basic idea: if $\hat{n}_\alpha(\mathbf{k}, t)$ is, on average, a slowly decaying function of time, the same must be true for products like $\hat{n}_\alpha(\mathbf{k}, t)\hat{n}_\beta(\mathbf{k}_2, t)$ and $\hat{n}_\alpha(\mathbf{k}, t)\hat{n}_\beta(\mathbf{k}_2, t)\hat{n}_\gamma(\mathbf{k}_3, t)$. For $e^{\mathcal{L}t}[\hat{n}_\alpha(\mathbf{k}, 0)\hat{n}_\beta(\mathbf{k}, 0)] = [e^{\mathcal{L}t}\hat{n}_\alpha(\mathbf{k}, 0)][e^{\mathcal{L}t}\hat{n}_\beta(\mathbf{k}, 0)]$. Hence, a more complete set of slow variables is spanned by the hydrodynamic densities $\hat{n}_\alpha(\mathbf{k}, t)$ plus all possible products of these. The form of the projection operator \mathcal{P} upon this extended hydrodynamic space becomes somewhat complicated by the fact that products of densities are not orthogonal to each other, e.g.

$$\begin{aligned}
\frac{1}{V} \langle \hat{\mathbf{u}}(\mathbf{k}) \cdot |\hat{n}(-\mathbf{q} + \mathbf{k})\hat{\mathbf{u}}(\mathbf{q}) \rangle &= \frac{1}{V} \langle \sum_i \mathbf{v}_i e^{i\mathbf{k}\cdot\mathbf{r}_i} \cdot \sum_j e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j} \sum_\ell e^{-i\mathbf{q}\cdot\mathbf{r}_\ell} \mathbf{v}_\ell \rangle \\
&= \frac{1}{V} \langle \sum_i \frac{k_B T d}{m} e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_i} \sum_j e^{-i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_j} \rangle \\
&= \frac{k_B T d}{Vm} \langle \hat{n}(\mathbf{k} - \mathbf{q}) | \hat{n}(\mathbf{k} - \mathbf{q}) \rangle
\end{aligned} \tag{290}$$

For inner products of pairs of modes one has an approximate factorization property.

$$\begin{aligned}
\langle \hat{n}_\alpha(\mathbf{k}_1)\hat{n}_\beta(\mathbf{k}_2) | \hat{n}_\gamma(\mathbf{k}_3)\hat{n}_\delta(\mathbf{k}_4) \rangle &= \delta_{\mathbf{k}_1\mathbf{k}_3} \delta_{\mathbf{k}_2\mathbf{k}_4} \langle \hat{n}_\alpha(\mathbf{k}_1) | \hat{n}_\gamma(\mathbf{k}_3) \rangle \langle \hat{n}_\beta(\mathbf{k}_2) | \hat{n}_\delta(\mathbf{k}_4) \rangle \\
&+ \delta_{\mathbf{k}_1\mathbf{k}_4} \delta_{\mathbf{k}_2\mathbf{k}_3} \langle \hat{n}_\alpha(\mathbf{k}_1) | \hat{n}_\gamma(\mathbf{k}_4) \rangle \langle \hat{n}_\beta(\mathbf{k}_2) | \hat{n}_\delta(\mathbf{k}_3) \rangle \\
&+ \delta_{\mathbf{k}_1+\mathbf{k}_2, \mathbf{k}_3+\mathbf{k}_4} \left[\langle \hat{n}_\alpha(-\mathbf{k}_1)\hat{n}_\beta(-\mathbf{k}_2)\hat{n}_\gamma(\mathbf{k}_3)\hat{n}_\delta(\mathbf{k}_4) \rangle \right. \\
&- \delta_{\mathbf{k}_1\mathbf{k}_3} \delta_{\mathbf{k}_2\mathbf{k}_4} \langle \hat{n}_\alpha(\mathbf{k}_1) | \hat{n}_\gamma(\mathbf{k}_3) \rangle \langle \hat{n}_\beta(\mathbf{k}_2) | \hat{n}_\delta(\mathbf{k}_4) \rangle \\
&\left. - \delta_{\mathbf{k}_1\mathbf{k}_4} \delta_{\mathbf{k}_2\mathbf{k}_3} \langle \hat{n}_\alpha(\mathbf{k}_1) | \hat{n}_\delta(\mathbf{k}_4) \rangle \langle \hat{n}_\beta(\mathbf{k}_2) | \hat{n}_\gamma(\mathbf{k}_3) \rangle \right],
\end{aligned} \tag{291}$$

where it was assumed that $\mathbf{k}_1 \neq -\mathbf{k}_2$. The first two terms are of the order V^2 , the last one of order V . So it looks like the last one may be skipped right away. This is too simple: for each pair $\mathbf{k}_1, \mathbf{k}_2$ there are only two pairs $\mathbf{k}_3, \mathbf{k}_4$ for which the first two terms are non-zero but the number of $\mathbf{k}_3, \mathbf{k}_4$ pairs for which the last term vanishes, increases as V . Nevertheless, for large t the range of relevant k -values decreases, typically as $\frac{1}{\sqrt{t}}$. Therefore the last terms may still be ignored for large enough t .

Let us restrict ourselves, for simplicity, to a space spanned by single densities and products of two densities.

For single modes, one component, we had (89),

$$\begin{aligned}\mathcal{P}^{(s)} &= \frac{1}{V} \sum_{\mathbf{k}} \left[|\hat{\mathbf{n}}(\mathbf{k}) \rangle \langle \hat{\nu}(\mathbf{k})| + \frac{\beta_0}{mn_0} |\hat{\mathbf{G}}(\mathbf{k}) \rangle \cdot \langle \hat{\mathbf{G}}(\mathbf{k})| - |\hat{\varepsilon}(\mathbf{k}) \rangle \langle \hat{\beta}(\mathbf{k})| \right] \\ &\equiv \frac{1}{V} |\Psi(\mathbf{k}) \rangle \circ \langle \Phi(\mathbf{k})| \end{aligned} \quad (292)$$

For single plus product modes this extends to:

$$\begin{aligned}\mathcal{P}^{(f)} &= \frac{1}{V} \sum_{\mathbf{k}} |\Psi(\mathbf{k}) \rangle \circ \langle \Phi(\mathbf{k})| + \frac{1}{2V^2} \sum_{\mathbf{k}_1 \mathbf{k}_2} |\Psi(\mathbf{k}_1) \Psi(\mathbf{k}_2) \rangle \circ \langle \Phi(\mathbf{k}_2) \Phi(\mathbf{k}_1)| \\ &\quad - \frac{1}{2V^3} \sum_{\mathbf{k} \mathbf{k}_1 \mathbf{k}_2} \left\{ |\Psi(\mathbf{k}) \rangle \circ \langle \Phi(\mathbf{k})| |\Psi(\mathbf{k}_1) \Psi(\mathbf{k}_2) \rangle \circ \langle \Phi(\mathbf{k}_2) \Phi(\mathbf{k}_1)| \right. \\ &\quad \left. + |\Psi(\mathbf{k}_1) \Psi(\mathbf{k}_2) \rangle \circ \langle \Phi(\mathbf{k}_2) \Phi(\mathbf{k}_1)| |\Psi(\mathbf{k}) \rangle \circ \langle \Phi(\mathbf{k})| \right\} \end{aligned} \quad (293)$$

plus higher order terms.

Note that the action of $\mathcal{P}^{(f)}$ on $|\Psi(\mathbf{k}) \rangle$ respectively $|\Psi(\mathbf{k}_1) \Psi(\mathbf{k}_2) \rangle$ reproduces these entities, up to corrections of the type

$$\frac{1}{2V^3} \sum_{\mathbf{k}_1} |\Psi(\mathbf{k}) \rangle \circ \langle \Phi(\mathbf{k})| |\Psi(\mathbf{k}_1) \Psi(\mathbf{k} - \mathbf{k}_1) \rangle \langle \Phi(\mathbf{k}_1) \Phi(\mathbf{k} - \mathbf{k}_1)| |\Psi(\mathbf{k}) \rangle$$

which are small due to the restriction of \mathbf{k}_1 to small \mathbf{k} -values. $\mathcal{P}^{(f)}$ may be split up in two ways as

$$\mathcal{P}^{(f)} = \mathcal{P}_r^{(1)} + \mathcal{P}_r^{(2)}, \quad (294)$$

$$\mathcal{P}^{(f)} = \mathcal{P}_\ell^{(1)} + \mathcal{P}_\ell^{(2)}. \quad (295)$$

$\mathcal{P}_{r,\ell}^{(n)}$ acting to the right respectively left, projects on the space of products of n densities. $\mathcal{P}_r^{(1)}$ consists of the first plus the third term of equation (293); $\mathcal{P}_r^{(2)}$ of the second plus the fourth one, $\mathcal{P}_\ell^{(1)}$ of the first plus the fourth one and $\mathcal{P}_\ell^{(2)}$ of the second plus the third one.

Now return to equation (97) of the script:

$$\frac{\partial \mathcal{P} \Delta(t)}{\partial t} = -\mathcal{P} \mathcal{L} \mathcal{P} \Delta(t) + \int_0^t d\tau \mathcal{P} \mathcal{L} \mathcal{P}_\perp e^{-\hat{\mathcal{L}}\tau} \mathcal{P}_\perp \mathcal{L} \mathcal{P} \Delta(t-\tau) - \mathcal{P} \mathcal{L} \mathcal{P}_\perp e^{-\hat{\mathcal{L}}t} \mathcal{P}_\perp \Delta(0) \quad (296)$$

As usual, we drop the last term and replace the initial time by $-\infty$. Standard mode-coupling theory is obtained by replacing in the integral expression in (296) the first \mathcal{P} by \mathcal{P}_ℓ^1 and the second \mathcal{P} by \mathcal{P}_r^1 . This is not entirely justified. I will discuss briefly later how to improve on this.

If we restrict to first approximation, $\mathcal{P}\mathcal{L}\mathcal{P}$ to $\mathcal{P}^{(s)}\mathcal{L}\mathcal{P}^{(s)}$ we are back to the equations we solved before in the framework of Green-Kubo theory, except that $e^{\hat{\mathcal{L}}t}$ now really will induce a rapid decay. So we recover the hydrodynamic equations

$$\frac{\partial\Psi(\mathbf{k}, t)}{\partial t} = V[-i\mathbf{k}\Phi(\mathbf{k}, t) \circ \Omega(\mathbf{k}) - k^2\Phi(\mathbf{k}, t) \circ U(\mathbf{k})] \quad (297)$$

$$\text{with } U(\mathbf{k}) = \frac{1}{V} \int_0^\infty \langle J(k) | e^{\hat{\mathcal{L}}t} J(\mathbf{k}) \rangle dt \quad (298)$$

$$\text{and } \Phi(\mathbf{k}, t) = V \langle \Psi(\mathbf{k}) | \Psi(k) \rangle^{-1} \circ \Psi(\mathbf{k}, t) \quad (299)$$

For the long time tail analysis it is important to identify the eigenfunctions of this equation, which are, first of all, $d-1$ *shear modes*

$$\Psi_i^s(\mathbf{k}) = \hat{\ell}_i \cdot \hat{\mathbf{G}}(\mathbf{k}) = \sum_j (\hat{\ell}_i \cdot m\mathbf{v}_j) e^{-i\mathbf{k}\cdot\mathbf{r}_j} \quad (300)$$

with $\hat{\ell}_i$ a unit vector normal to \mathbf{k} . These have eigenvalues $-\nu k^2 = -\frac{\eta}{\rho} k^2$.

The corresponding $\Phi_i(\mathbf{k})$ are the same, up to a different normalization. Then there are the *sound modes*:

$$\Psi^\pm(\mathbf{k}) = \sum_j \pm(\hat{\mathbf{k}} \cdot m\mathbf{v}_j) e^{-i\mathbf{k}\cdot\mathbf{r}_j} + \frac{1}{c_0} \hat{p}(\mathbf{k}) = \pm(\hat{\mathbf{k}} \cdot \hat{\mathbf{G}}(\mathbf{k})) + \frac{1}{c_0} \hat{p}(\mathbf{k}), \quad (301)$$

with c_0 the speed of sound and $\hat{p}(\mathbf{k}) = \left(\frac{\partial p}{\partial e}\right)_n \hat{\varepsilon}(\mathbf{k}) + \left(\frac{\partial p}{\partial n}\right)_e \hat{n}(\mathbf{k})$. From (92), i.e.

$$\mathcal{P}^{(s)} = \frac{\beta_0}{2n_0V} \sum_{\mathbf{k}} |\hat{n}(\mathbf{k}) \rangle \langle \hat{p}(\mathbf{k})| + \frac{1}{m} |\hat{\mathbf{G}}(\mathbf{k}) \rangle \cdot \langle \mathbf{G}(\mathbf{k})| + n_0^2 |\hat{\sigma}(\mathbf{k}) \rangle \langle \hat{T}(\mathbf{k})|$$

it follows that the corresponding left eigenvectors may be cast into the form

$$\Phi^\pm(\mathbf{k}) = \frac{mn_0}{2\beta_0} [\pm(\hat{\mathbf{k}} \cdot \hat{\mathbf{G}}(\mathbf{k}) + mc_0\hat{n}(k))]. \quad (302)$$

These modes have eigenvalues $\pm ic_0 k - \frac{1}{2}\Gamma k^2$.

Finally there are the heat modes

$$\Psi^h(\mathbf{k}) = \hat{\sigma}(\mathbf{k}) = \frac{1}{nT}(\hat{\varepsilon}(\mathbf{k}) - h\hat{n}(\mathbf{k})) \quad (303)$$

with $h = \frac{e+p}{n}$. The eigenvalues are $-D_T k^2$. The adjoint follows from (92) as: $\Phi^h(\mathbf{k}) = \frac{1}{n_0\beta_0}\hat{T}(\mathbf{k})$.

Next include in (296) the contributions $\mathcal{P}_r^{(2)}\mathcal{L}\mathcal{P}_r^{(1)}$ and $\mathcal{P}_\ell^{(1)}\mathcal{L}\mathcal{P}_\ell^{(2)}$ (plus whatever else is needed from $\mathcal{P} - \mathcal{P}^{(1)}$).

First iteration gives

$$\delta^{(1)}(\mathcal{P}\Delta t) \approx - \int_0^\infty d\tau e^{-\mathcal{P}(\mathcal{L}+\mathcal{U})\mathcal{P}\tau} \mathcal{P}_r^{(2)}\mathcal{L}\mathcal{P}\Delta(t-\tau), \quad (304)$$

$$\text{with } \mathcal{U} = \int_0^\infty d\tau \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{\hat{\mathcal{L}}t} \mathcal{P}_\perp \mathcal{L}\mathcal{P}. \quad (305)$$

By decomposing the action of $\mathcal{P}_r^{(2)}$ into components of products of hydrodynamic modes one may replace $\mathcal{P}(\mathcal{L} + \mathcal{U})\mathcal{P}$ by the sum of two hydrodynamic decay rates. One obtains

$$\begin{aligned} \delta^{(1)}(\mathcal{P}\Delta t) &= \sum_{\mathbf{k}\mathbf{q}\alpha\beta} \frac{-1}{2V^2} \int_0^\infty d\tau e^{-[\nu_\alpha(\mathbf{q})+\nu_\beta(\mathbf{k}-\mathbf{q})]\tau} |\Psi_\alpha(\mathbf{q})\Psi_\beta(\mathbf{k}-\mathbf{q})\rangle \quad (306) \\ &\langle \Phi_\alpha(\mathbf{q})\Phi_\beta(\mathbf{k}-\mathbf{q}) | \left(1 - \frac{1}{V} \sum_\gamma |\Psi_\gamma(\mathbf{k})\rangle \langle \Phi_\gamma(\mathbf{k})| \right) \mathcal{L}\mathcal{P}\Delta(t-\tau) \end{aligned} \quad (307)$$

Applying $-\mathcal{P}_\ell^{(1)}\mathcal{L}\mathcal{P}_\ell^{(2)}$ to this, we see from (296) that the leading mode-coupling contribution is

$$\begin{aligned} \frac{\partial}{\partial t}(\delta\mathcal{P}\Delta(t))^{(2)} &= -\mathcal{P}_\ell^{(1)}\mathcal{L}\delta^{(1)}(\mathcal{P}\Delta(t)), \\ &= \frac{1}{2} \int_0^\infty d\tau \sum_{\mathbf{k}\mathbf{q}\alpha\beta\gamma} |\Psi_\gamma(\mathbf{k})\rangle \langle \Phi_\gamma(\mathbf{k})| \mathcal{L} \left(1 - \frac{1}{V} \sum_\delta |\Psi_\delta(\mathbf{k})\rangle \langle \Phi_\delta(\mathbf{k})| \right) \\ &\quad |\Psi_\alpha(\mathbf{q})\Psi_\beta(\mathbf{k}-\mathbf{q})\rangle e^{-[\nu_\alpha(\mathbf{q})+\nu_\beta(\mathbf{k}-\mathbf{q})]\tau} \langle \Phi_\alpha(\mathbf{q})\Phi_\beta(\mathbf{k}-\mathbf{q})| \quad (308) \\ &\quad \left(1 - \frac{1}{V} \sum_{\delta'} |\Psi_{\delta'}(\mathbf{k})\rangle \langle \Phi_{\delta'}(\mathbf{k})| \right) \mathcal{L}\Psi_\gamma(\mathbf{k}) \langle \Phi_\gamma(\mathbf{k}) | \Delta(\mathbf{k}, t-\tau) \rangle \end{aligned}$$

Remarks:

1. Because the $\Psi_\gamma(\mathbf{k})$ already are eigenfunctions of $\mathcal{P}^{(1)}\mathcal{L}\mathcal{P}^{(1)} + \mathcal{P}^{(1)}\mathcal{U}\mathcal{P}^{(1)}$, the leading mode-coupling corrections are diagonal between the Ψ_γ .
2. One may define the mode coupling corrections such that their full time integrals vanish. Amounts to adding constants to $\mathcal{U}_{\alpha\beta}$. In this way, the transport coefficients appearing in the hydrodynamic frequencies are full transport coefficients.
3. Long time tails come from combinations of two diffusive modes ($\nu_\alpha(\mathbf{q}) \sim q^2$) or two opposite sound modes ($\nu_\pm(\mathbf{q}) = \pm icq - \frac{1}{2}\Gamma k^2$). Both give rise to tails of type $\int d\mathbf{q} e^{-\alpha q^2 t} \sim t^{-d/2}$, for $d > 2$.
4. It is not hard to see which couplings of type $\langle \Phi_\alpha(\mathbf{q})\Phi_\beta(\mathbf{k}-\mathbf{q}) | \mathcal{L}\Psi_j(\mathbf{k}) \rangle$ give rise to $t^{-d/2}$ contributions. For shear modes,

$$\begin{aligned} \mathcal{L}\Psi_i(\mathbf{k}) &= \frac{d}{dt} \sum_j e^{-i\mathbf{k}\cdot\mathbf{r}_j} (\hat{\ell}_i \cdot \mathbf{v}_j) \\ &= -ik \sum_j e^{-i\mathbf{k}\cdot\mathbf{r}_j} (\hat{\ell}_i \cdot \mathbf{v}_j) (\hat{\mathbf{k}} \cdot \mathbf{v}_j) + \frac{1}{2} \sum_{jj'} (e^{-i\mathbf{k}\cdot\mathbf{r}_j} - e^{-i\mathbf{k}\cdot\mathbf{r}_{j'}}) \left(\hat{\ell}_j \cdot \frac{\mathbf{F}_{jj'}}{m} \right) \end{aligned} \quad (309)$$

To leading order only the first term contributes. The second one leads to $\hat{\mathbf{k}} \cdot \hat{\ell} = 0$.

The time derivative of a heat mode to leading order is odd in \mathbf{v} , therefore couples to shear and heat mode or opposite sound modes. Finally the time derivative of a sound mode couples to opposite sound modes, pairs of shear modes, shear plus heat mode and pairs of heat modes.

5. Terms in (296) with $\int d\tau P_r^{(2)} \mathcal{L}P_\perp e^{-\hat{\mathcal{L}}\tau} \mathcal{P}\mathcal{L}\mathcal{P}_r^{(1)}$ sum up to terms like $\nabla \cdot \frac{\partial \eta}{\partial n} (\delta n \nabla \mathbf{u}_\perp)$ etc. These may become important in cases where “convective contributions” to the currents are absent.

5 Mode coupling and exact results in one dimension

As remarked above the mode coupling contributions to the current-current time correlation functions lead to divergent Green-Kubo integrals in one and two dimensions. As a result the time correlation functions between hydrodynamic modes satisfy highly intricate nonlinear equations, which in principle have to be solved self-consistently. However, it turns out that for the long time and large distance behavior of these correlation functions in one dimension, this solution scheme may be circumvented by using an exact solution obtained by Prähofer and Spohn for a one-dimensional growth model. For doing so one still needs a mode coupling analysis, but only to show that the dominant terms in the mode coupling expansions for heat mode and sound mode correlation functions can be mapped one to one to the terms in a mode coupling expansion for the model solved by Prähofer and Spohn. In the present section I will describe this scheme in some detail, starting with the fluctuating Burgers equation in one dimension. This equation describes the time evolution of a density field without couplings to momentum and/or energy density under the influence of some driving force. It is nonlinear and therefore allows for a mode coupling expansion. By a simple integration it can be transformed into a growth model, belonging to the Kardar-Parisi-Zhang (KPZ) universality class. Therefore its long time and large distance behavior is the same as that of the Polynuclear growth model, the model solved exactly by Prähofer and Spohn, which belongs to this universality class. Next I will argue how these results translate to one-dimensional hydrodynamics and lead to exact expressions for the long time behavior of current-current correlation functions and the asymptotic size dependence of transport coefficients.

5.1 Fluctuating Burgers equation

Consider driven diffusive systems, described by

$$\frac{\partial c(\mathbf{r}, t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r}, t) = 0 \quad [\text{continuity equation}]$$

with

$$\mathbf{j}(\mathbf{r}, t) = -D(c)\nabla c(\mathbf{r}, t) + c(\mathbf{r}, t)\mathbf{u}(c(\mathbf{r}, t)) + \tilde{\mathbf{j}}_L(\mathbf{r}, t).$$

Here $\tilde{\mathbf{j}}_L(\mathbf{r}, t)$ is a Langevin noise term. It is supposed to behave as gaussian noise, with average $\langle \tilde{\mathbf{j}}_L(\mathbf{r}, t) \rangle = 0$ and variance

$$\langle \tilde{\mathbf{j}}_L(\mathbf{r}, t) \tilde{\mathbf{j}}_L(\mathbf{r}', t') \rangle = N(\mathbf{r} - \mathbf{r}') \delta(t - t') \mathbf{1} \quad (310)$$

The brackets indicate an average over all realizations of the stochastic time evolution and the noise strenght N will be specified a little below. Expand the convective current, with $c(\mathbf{r}, t) = \bar{c} + \tilde{\phi}(\mathbf{r}, t)$, as

$$c(\mathbf{r}, t) \mathbf{u}(c(\mathbf{r}, t)) = \bar{c} \mathbf{u}(\bar{c}) + \mathbf{v} \tilde{\phi}(\mathbf{r}, t) + \frac{\mathbf{w}}{2} \tilde{\phi}^2(\mathbf{r}, t)$$

with

$$\mathbf{v} = \frac{\partial}{\partial c} (c \mathbf{u}(c))_{c=\bar{c}} = \mathbf{u}(\bar{c}) + \bar{c} \left(\frac{\partial \mathbf{u}}{\partial c} \right)_{c=\bar{c}} \quad (311)$$

$$\mathbf{w} = \frac{\partial^2}{\partial c^2} (c \mathbf{u}(c)) = \frac{\partial \mathbf{v}}{\partial c} \quad (312)$$

both evaluated at $c = \bar{c}$.

D may be approximated by $D(\bar{c})$.

$$\longrightarrow \left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \tilde{\phi}(\mathbf{r}, t) = +D \nabla^2 \tilde{\phi}(\mathbf{r}, t) - \frac{\mathbf{w}}{2} \cdot \nabla \tilde{\phi}^2(\mathbf{r}, t) - \nabla \cdot \tilde{\mathbf{j}}_L(\mathbf{r}, t)$$

Next make Galilei transformation:

$$\begin{aligned} \phi(\mathbf{r}, t) &= \tilde{\phi}(\mathbf{r} + \mathbf{v}t, t) && \text{[notice sign!]} \\ \Rightarrow \frac{\partial \phi(\mathbf{r}, t)}{\partial t} &= -\frac{\mathbf{w}}{2} \cdot \nabla \phi^2(\mathbf{r}, t) + D \nabla^2 \phi(\mathbf{r}, t) - \nabla \cdot \mathbf{j}_L(\mathbf{r}, t) && (313) \\ &\text{with } \mathbf{j}_L(\mathbf{r}, t) = \tilde{\mathbf{j}}_L(\mathbf{r} + \mathbf{v}t, t) \end{aligned}$$

For Fourier components:

$$\frac{\partial}{\partial t} \hat{\phi}(\mathbf{k}, t) = -\frac{i\mathbf{k} \cdot \mathbf{w}}{2V} \sum_{\mathbf{q}} \hat{\phi}(\mathbf{q}, t) \hat{\phi}(\mathbf{k} - \mathbf{q}, t) - Dk^2 \hat{\phi}(\mathbf{k}, t) - i\mathbf{k} \cdot \hat{\mathbf{j}}_L(\mathbf{k}, t) \quad (314)$$

Can be transformed to

$$\begin{aligned} \hat{\phi}(\mathbf{k}, t) &= e^{-Dk^2(t-t_0)} \hat{\phi}(\mathbf{k}, t_0) - \int_{t_0}^t d\tau e^{-Dk^2(t-\tau)} i\mathbf{k} \cdot \hat{\mathbf{j}}_L(\mathbf{k}, \tau) \\ &\quad - \int_{t_0}^t d\tau e^{-Dk^2(t-\tau)} \frac{i\mathbf{k} \cdot \mathbf{w}}{2V} \sum_{\mathbf{q}} \hat{\phi}(\mathbf{q}, \tau) \hat{\phi}(\mathbf{k} - \mathbf{q}, \tau) \end{aligned} \quad (315)$$

One can iterate this equation and make a diagrammatic expansion for the time correlation function $\hat{S}(\mathbf{k}, t - t_0) = \frac{1}{V} \langle \hat{\phi}(-\mathbf{k}, t_0) \hat{\phi}(\mathbf{k}, t) \rangle$. Each diagram represents a term in the iteration series and consists of line pieces

$\underline{\mathbf{q}}$ representing factors $e^{-Dq^2(\tau_j - \tau_{j-1})}$ and vertices $\mathbf{k} \begin{array}{c} \curvearrowright \\ \mathbf{k} - \mathbf{q} \end{array}$

representing factors $\frac{i\mathbf{k} \cdot \boldsymbol{\omega}}{2V} \int_{\tau_{j-1}}^t d\tau_j \sum \mathbf{q}$. In addition factors $\hat{\phi}(\mathbf{q}, t_0)$ will be denoted by dots and factors $\int d\tau - i\mathbf{q} \cdot \hat{\mathbf{j}}_L(\mathbf{q}, \tau)$ by asterisks.

In the first iteration of Eq. (314) one approximates the functions $\hat{\phi}(\mathbf{q}, \tau)$ and $\hat{\phi}(\mathbf{k} - \mathbf{q}, \tau)$ by the first two terms in this equation. In diagrammatic representation this leads to

$$\begin{aligned} \langle \hat{\phi}(-\mathbf{k}, t_0) \hat{\phi}(\mathbf{k}, t) \rangle = & \bullet \text{---} \mathbf{k} \text{---} \bullet + \bullet \text{---} \mathbf{k} \text{---} * + \bullet \text{---} \mathbf{k} \text{---} \bullet \begin{array}{c} \mathbf{q} \\ \curvearrowright \\ \mathbf{k} - \mathbf{q} \end{array} \\ & + \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ * \\ \curvearrowright \\ \mathbf{k} - \mathbf{q} \end{array} \bullet + \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \curvearrowright \\ \mathbf{k} - \mathbf{q} \\ * \end{array} \bullet + \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ * \\ \curvearrowright \\ \mathbf{k} - \mathbf{q} \end{array} \bullet \\ & + \dots \end{aligned} \quad (316)$$

For the fluctuating current correlation function in Fourier representation we now postulate the form

$$\frac{1}{V} \langle \hat{\mathbf{j}}_L(\mathbf{q}, t) \hat{\mathbf{j}}_L(\mathbf{q}', t') \rangle = 2D \hat{S}(\mathbf{q}) \delta(\mathbf{q} + \mathbf{q}') \delta(t - t') \mathbf{1}, \quad (317)$$

with $\hat{S}(\mathbf{q}) \equiv \hat{S}(\mathbf{q}, t = 0)$. This fixes the function $N(\mathbf{r} - \mathbf{r}')$ in Eq. (310) as $2D$ times the equal-time pair correlation function. With this choice, the density-density time correlation function $\langle \hat{\phi}(-\mathbf{k}, t_0) \hat{\phi}(\mathbf{k}, t) \rangle$ will turn out to depend on the time difference $t - t_0$ only, as it should be the case in a stationary state:

$$\begin{aligned} \hat{S}(\mathbf{k}, t - t_0) &= \frac{1}{V} \langle \hat{\phi}(-\mathbf{k}, t_0) \hat{\phi}(\mathbf{k}, t) \rangle \\ &= \frac{1}{V} \langle \hat{\phi}(-\mathbf{k}, t_0 + \tau) \hat{\phi}(\mathbf{k}, t + \tau) \rangle \end{aligned}$$

As a result of Eq. (317) and the assumption that the fluctuating current behaves as Gaussian noise with vanishing average, only the first and third of the diagrams shown in Eq. (316) may give nonvanishing contributions. A second iteration yields:

$$\begin{aligned}
\langle \hat{\phi}(-\mathbf{k}, t_0) \hat{\phi}(\mathbf{k}, t) \rangle = & \bullet \text{---} \mathbf{k} \text{---} \bullet + \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \bullet \\
+ & \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \begin{array}{c} \mathbf{q}_1 \\ \text{---} \\ \mathbf{q} - \mathbf{q}_1 \end{array} \bullet \\
+ & \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \begin{array}{c} \mathbf{q}_1 \\ \text{---} \\ \mathbf{q} - \mathbf{q}_1 \end{array} \bullet \\
+ & \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \begin{array}{c} \mathbf{q}_1 \\ \text{---} \\ \mathbf{q} - \mathbf{q}_1 \end{array} \bullet \\
+ & \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \begin{array}{c} \mathbf{q}_1 \\ \text{---} \\ \mathbf{q} - \mathbf{q}_1 \end{array} \bullet \\
+ & \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \begin{array}{c} \mathbf{q}_1 \\ \text{---} \\ \mathbf{q} - \mathbf{q}_1 \end{array} \bullet \\
+ & \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \begin{array}{c} \mathbf{q}_1 \\ \text{---} \\ \mathbf{q} - \mathbf{q}_1 \end{array} \bullet \\
+ & \bullet \text{---} \mathbf{k} \text{---} \begin{array}{c} \mathbf{q} \\ \text{---} \\ \mathbf{k} - \mathbf{q} \end{array} \begin{array}{c} \mathbf{q}_1 \\ \text{---} \\ \mathbf{q} - \mathbf{q}_1 \end{array} \bullet \\
+ & \dots
\end{aligned} \tag{318}$$

In this equation a number of two-vertex diagrams have been left out that give vanishing contributions: that is, all diagrams with an odd number of fluctuating currents and also diagrams with two fluctuating currents at wave numbers that cannot be each others opposites. A first simplification of this equation can be reached by making the common approximation that $2n$ -point equal time density correlation functions can be factorized into products of pair correlation functions (and correlation functions of an odd number of densities vanish). Specifically, for four-point correlation functions this implies

$$\begin{aligned}
\langle \phi(\mathbf{k}_1) \phi(\mathbf{k}_2) \phi(\mathbf{k}_3) \phi(\mathbf{k}_4) \rangle = & \langle \phi(\mathbf{k}_1) \phi(\mathbf{k}_2) \rangle \langle \phi(\mathbf{k}_3) \phi(\mathbf{k}_4) \rangle \delta(\mathbf{k}_1 + \mathbf{k}_2) \delta(\mathbf{k}_3 + \mathbf{k}_4) + \\
& + \langle \phi(\mathbf{k}_1) \phi(\mathbf{k}_3) \rangle \langle \phi(\mathbf{k}_2) \phi(\mathbf{k}_4) \rangle \delta(\mathbf{k}_1 + \mathbf{k}_3) \delta(\mathbf{k}_2 + \mathbf{k}_4) + \\
& + \langle \phi(\mathbf{k}_1) \phi(\mathbf{k}_4) \rangle \langle \phi(\mathbf{k}_2) \phi(\mathbf{k}_3) \rangle \delta(\mathbf{k}_1 + \mathbf{k}_4) \delta(\mathbf{k}_2 + \mathbf{k}_3).
\end{aligned} \tag{319}$$

For Eq. (318) this implies that \mathbf{q}_1 must be equal to \mathbf{k} (third, 5th, 6th and 8th diagram), to $\mathbf{k} - \mathbf{q}$ (third and 4th diagram) or to $-\mathbf{q}$ (6th and 7th diagram).

Next, a further simplification can be reached by using the identity

$$e^{-2Dk^2t} \hat{S}(\mathbf{k}) + \frac{1}{V} \int_0^t d\tau_1 \int_0^t d\tau_2 e^{-Dk^2(\tau_1+\tau_2)} \langle \hat{\mathbf{j}}_L(\mathbf{k}, \tau_1) \hat{\mathbf{j}}_L(-\mathbf{k}, \tau_2) \rangle = \hat{S}(\mathbf{k}) \mathbf{1}, \quad (320)$$


which follows directly from Eq. (317). Apply this to the third plus the fifth diagram, and to the 6th and the 8th diagram, both with $\mathbf{q}_1 = \mathbf{k}$, to the third and 4th diagram, with $\mathbf{q}_1 = \mathbf{k} - \mathbf{q}$ and to the 6th and 7th diagram, with $\mathbf{q}_1 = -\mathbf{q}$, in all cases for the time argument $\tau_2 - t_0$, with τ_2 the time argument of the second vertex. The sum of all these terms may be represented by a

vertex, $\mathbf{k} \overbrace{\quad \mathbf{q}}^{\mathbf{q}} \mathbf{k}$ corresponding to $i\mathbf{k} \cdot \mathbf{w} \hat{S}(0) \int_0^{\tau_1} d\tau_2$, where

$\hat{S}(\mathbf{q}) + \hat{S}(\mathbf{k} - \mathbf{q})$ has been approximated by $2\hat{S}(0)$.

Applying the same reductions to the full diagrammatic expansion of $\hat{S}(\mathbf{k}, t)$ one obtains

$$\begin{aligned} \hat{S}(\mathbf{k}, t) = & \text{---} + \text{---} \text{---} + \\ & + \text{---} \text{---} \text{---} + \dots \\ \equiv & \text{---} \end{aligned} \quad (321)$$

Here the self-energy operator represented by  is given by the sum of all *irreducible diagrams*, that is, all diagrams, beginning and ending with a vertex that cannot be divided into two disconnected pieces by cutting one line. The wave numbers have been left out, since it is obvious now how these have to be chosen. A next reduction step is a *skeleton renormalization*. In this step the self-energy operator is reexpressed in terms of so-called skeleton diagrams consisting of vertices and bold lines, which have such a structure that no diagrams contributing to the self-energy can be extracted from them by cutting two lines. The simplest mode coupling approximation for the self-energy, the so-called one-loop approximation is

(322)

Under this approximation the density-density time correlation function satisfies the equation

$$\frac{\partial \hat{S}(\mathbf{k}, t)}{\partial t} = -Dk^2 \delta(t) - \frac{(\mathbf{w} \cdot \mathbf{k})^2}{2\hat{S}(\mathbf{0})V} \int_0^{t-t_0} d\tau \sum_{\mathbf{q}} \hat{S}(\mathbf{q}, \tau) \hat{S}(\mathbf{k} - \mathbf{q}, \tau) \hat{S}(\mathbf{k}, t - \tau), \quad (323)$$

where again all equal-time correlation functions have been approximated by $\hat{S}(0)$. Notice that in the limit $V \rightarrow \infty$, $\frac{1}{V} \sum_{\mathbf{q}}$ approaches $\frac{1}{(2\pi)^d} \int d\mathbf{q}$.

The Green-Kubo formalism relates the time derivative of $\hat{S}(\mathbf{k}, t)$ to a current-current time correlation function (see e.g.[18]) through

$$\frac{\partial}{\partial t} \hat{S}(\mathbf{k}, t) = -k^2 \int_0^\infty d\tau \hat{M}(\mathbf{k}, \tau) \hat{S}(\mathbf{k}, t - \tau) \quad (324)$$

with

$$\lim_{k \rightarrow 0} \hat{M}(\mathbf{k}, \tau) = \frac{\hat{\mathbf{k}}\hat{\mathbf{k}}}{V} : \left\langle \left(\mathbf{J}(0) - \langle \mathbf{J}(0) \rangle - \frac{\partial J(\bar{c})}{\partial \bar{c}} (N(0) - \langle N \rangle) \right) \cdot \left(\mathbf{J}(t) - \langle \mathbf{J} \rangle - \frac{\partial J(\bar{c})}{\partial \bar{c}} (N(t) - \langle N \rangle) \right) \right\rangle. \quad (325)$$

The subtracted terms are important if the average is taken over a grand ensemble, in which the number of particles is not fixed.

On the other hand one-loop mode coupling identifies the memory kernel, according to Eq. (323) as

$$M(\mathbf{k}, t) = -Dk^2 \delta(t) - \frac{(\mathbf{w} \cdot \hat{\mathbf{k}})^2}{2\hat{S}(\mathbf{0})V} \sum_{\mathbf{q}} \hat{S}(\mathbf{q}, t) \hat{S}(\mathbf{k} - \mathbf{q}, t). \quad (326)$$

For dimension $d > 2$, $\hat{S}(\mathbf{k}, t)$ may be approximated to leading order by $\hat{S}(0)e^{-Dk^2t}$. In this case one obtains from (326)

$$\hat{M}(\hat{\mathbf{k}}, t) = \frac{(\mathbf{w} \cdot \hat{\mathbf{k}})^2 \hat{S}(0)}{2(8\pi Dt)^{d/2}}$$

For $d = 1, 2$ the mode coupling terms dominate the diffusion equation. To analyze this for $d = 1$, first introduce dimensionless variables: $\tau = \alpha t$; $\kappa = \beta k$; $\Sigma(\kappa, \tau) = \frac{\hat{S}(\frac{\kappa}{\beta}, \frac{\tau}{\alpha})}{\hat{S}(0)}$ with $\alpha = \frac{w^4 S^2(0)}{128 D^3}$ $\beta = \frac{16 D^2}{w^2 \hat{S}(0)} \Rightarrow$

$$\frac{\partial \Sigma(\kappa, \tau)}{\partial \tau} = -\frac{1}{2} \kappa^2 \left[\Sigma(\kappa, \tau) + \frac{2}{\pi} \int_0^\tau d\sigma \int_{-\infty}^\infty d\lambda \Sigma(\lambda, \sigma) \Sigma(\kappa - \lambda, \tau - \sigma) \Sigma(\kappa, \tau - \sigma) \right] \quad (327)$$

In the limit $\kappa \rightarrow 0$ $\tau \rightarrow \infty$ one may look for a solution of the form $\Sigma(\kappa, \tau) = h(\kappa\tau^{2/3})$ because the mode-coupling term scales as $\kappa^3\tau^2\Sigma^2$ in comparison to $\partial\Sigma/\partial\tau$. The diffusive term scales as $\kappa^2\tau$, which is $\sim \tau^{-1/3}$ under scaling of h . So it becomes small for large τ indeed. Inserting the scaling form into (327) one may rewrite this as

$$\frac{dh(x)}{dx} = -\frac{9}{4\pi} x \int_0^1 ds s^{-1/2} \int_{-\infty}^\infty dy h(y) h(sx - y) h(x(1 - s^{3/2})^{2/3}),$$

by substituting $x = \kappa\tau^{2/3}$, $y = \lambda\sigma^{2/3}$ and $s = (\sigma/\tau)^{2/3}$. From this scaling it follows that

$$\frac{\partial^2}{\partial k^2} \log \hat{S}(k, t)_{k \rightarrow 0} = \frac{\partial^2}{\partial k^2} \log[h(kt^{2/3})] = \frac{t^{4/3} h''(0)}{h(0)}, \quad (328)$$

where $h'(0) = 0$ has been used. On the other hand,

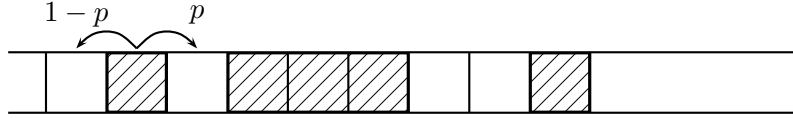
$$\begin{aligned} \hat{S}(\mathbf{k}, t) &= \frac{1}{V} \left\langle \sum_{j\ell} e^{i\mathbf{k} \cdot \mathbf{r}_j(t)} e^{-i\mathbf{k} \cdot \mathbf{r}_\ell(0)} \right\rangle & (329) \\ &= \frac{1}{V} \left\langle \sum_{j\ell} (1 + i\mathbf{k} \cdot (\mathbf{r}_j(t) - \mathbf{r}_\ell(0))) - \frac{1}{2} \mathbf{k}\mathbf{k} : (\mathbf{r}_j(t) - \mathbf{r}_\ell(0))(\mathbf{r}_j(t) - \mathbf{r}_\ell(0)) + \dots \right\rangle \\ &= \frac{1}{V} \left\langle \sum_{j\ell} (1 + i\mathbf{k} \cdot (\mathbf{r}_j(t) - \mathbf{r}_\ell(0))) \right. \\ &\quad \left. - \frac{1}{2} \mathbf{k}\mathbf{k} : (\mathbf{r}_j(t) - \mathbf{R}(t) - (\mathbf{r}_\ell(0) - \mathbf{R}(0)) + \mathbf{R}(t) - \mathbf{R}(0)) \right. \\ &\quad \left. (\mathbf{r}_j(t) - \mathbf{R}(t) - (\mathbf{r}_\ell(0) - \mathbf{R}(0)) + \mathbf{R}(t) - \mathbf{R}(0)) \right\rangle + \dots \end{aligned}$$

$$\Rightarrow \frac{\partial^2}{\partial k^2} \log \hat{S}(k, t) = - \langle \left[(\mathbf{R}(t) - \mathbf{R}(0)) \cdot \hat{\mathbf{k}} \right]^2 + 2 \left[(\mathbf{r}_j - \mathbf{R}) \cdot \hat{\mathbf{k}} \right]^2 \rangle$$

The $t^{4/3}$ long time behavior found in Eq. (328) is entirely due to the first term on the right hand side, since the second term is time independent. So the mean square displacement of the center of mass increases as $t^{4/3}$ in the comoving frame. Its second time derivative is the current-current time correlation function in the comoving frame, behaving as $t^{-2/3}$.

5.2 Asymmetric Simple Exclusion Process

This analysis may be tested on the Asymmetric Simple Exclusion Process [ASEP]. This model consists of a lattice, mostly considered in one dimension, each site of which may either be empty or occupied by a single particle. The particles may jump to unoccupied neighboring sites with jump rates defined, for $d=1$ as follows:



$$\begin{aligned} \text{Jump rate to unoccupied site} &= p\Gamma && \text{to right} \\ &= (1-p)\Gamma && \text{to left} \end{aligned}$$

This is called asymmetric for $p \neq 1/2$. The stationary distribution of particle configurations gives equal weight to all allowed configurations (then both the gain and the loss rate for a configuration equals $\Gamma n_{clusters}$). On macroscopic time and length scales this model is well-described by the fluctuating Burgers equation. The average current in the stationary state equals

$$c(1-c)(2p-1)\Gamma$$

The contributions to this from jumps to the right and to the left are $c(1-c)\Gamma p$ and $(1-c)c\Gamma(1-p)$ respectively. From this one obtains

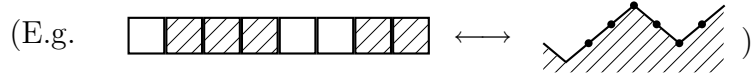
$$v = (2p-1)\Gamma(1-2c) \quad (330)$$

$$w = -\frac{(2p-1)}{2}\Gamma \quad (331)$$

Simulations on this model confirm the $t^{4/3}$ -behavior of the mean-square displacement of the center of mass[19].

5.3 The Kardar-Parisi-Zhang equations[20]

As an introduction let us consider again the ASEP. It may be considered as a $1d$ interface model by identifying a particle with a surface element \nearrow and an empty space as a surface element \searrow



The dynamics correspond to a growth process where units of mass are removed $\left[\begin{array}{c} \text{shaded square} \rightarrow \text{empty square} \\ \text{empty square} \rightarrow \text{shaded square} \end{array} \right] \iff \begin{array}{c} \text{shaded square} \rightarrow \text{shaded square} \\ \text{empty square} \rightarrow \text{empty square} \end{array} \rightarrow \begin{array}{c} \text{shaded square} \rightarrow \text{empty square} \\ \text{empty square} \rightarrow \text{shaded square} \end{array}$

or added $\left[\begin{array}{c} \text{empty square} \rightarrow \text{shaded square} \\ \text{shaded square} \rightarrow \text{empty square} \end{array} \right] \iff \begin{array}{c} \text{empty square} \rightarrow \text{empty square} \\ \text{shaded square} \rightarrow \text{shaded square} \end{array} \rightarrow \begin{array}{c} \text{empty square} \rightarrow \text{shaded square} \\ \text{shaded square} \rightarrow \text{empty square} \end{array}$ at corners.

The height variable is obtained from the density of the ASEP by a discrete integration over x , so one has $h(x) \approx \int_0^x dx' [2\rho(x') - 1]$.

The $1d$ KPZ-equation equally follows from the $1d$ fluctuating Burgers equation by integration over x . It has the form

$$\frac{\partial h(x, t)}{\partial t} = D \frac{\partial^2 h(x, t)}{\partial x^2} - w \left(\frac{\partial h(x, t)}{\partial x} \right)^2 + \eta_L(x, t) \quad (332)$$

A first remark is that in a situation of steady growth (or evaporation/solution) one should add a constant term v_0 equal to the average growth speed, on the right hand side. Mathematically this makes no difference. One may describe the process in a comoving frame through $\tilde{h}(x, t) = h(x, t) - v_0 t$. This satisfies (332) again.

A second remark is that (332) generalizes in d dimensions (especially $d = 2$ is physically relevant) to

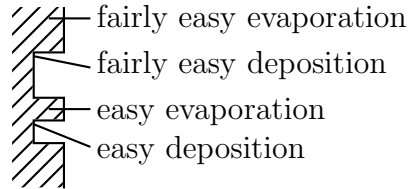
$$\frac{\partial h(\mathbf{r}, t)}{\partial t} = +D \nabla^2 h(\mathbf{r}, t) - \frac{w}{2} |\nabla h(\mathbf{r}, t)|^2 + \eta_L(\mathbf{r}, t). \quad (333)$$

Notice that for $d > 1$ this is not equivalent to the Burgers equation.

A third remark is about the physical interpretation of the various terms. The noise term η_L describes random fluctuations in the deposition and evaporation process. The term $-D \nabla^2 h$ describes the effects of diffusion of adatoms

and vacancies along the surface. Finally the non-linear term $\frac{w}{2} |\nabla h|^2$ describes the effect of the surface slope on the average evaporation or growth rate. There are two causes for this:

1. On rough surfaces both evaporation and deposition proceeds more easily, because fewer bonds have to be broken respectively more can be saturated.



2. Particles (or holes) left on a flat surface diffuse easily until they reach some step edge (so the dynamics tends to enhance their smoothness). Notice that for the ASEP horizontal surfaces are rough and sloped ones are smooth. This implies that the constant w is negative. For the model properties this makes no difference: on transforming from h to $-h$ the relative signs of w and the other constants are changed.

5.4 The polynuclear growth model. Exact results

Prähofer and Spohn[23] managed to solve exactly a specific one-dimensional growth model within the KPZ universality class; the polynuclear growth model. This model consists of line pieces stacked on top of each other. Growth nuclei are created at a constant rate at completely random positions. After creation a nucleus grows with constant speed v in both directions, thus creating a new line piece just above an existing one. When two growth fronts collide they stop moving. For this model density-density and current-current time correlations can be solved exactly and expressed in terms of scaling functions, which have been tabulated with great precision by the authors. Since the long time behavior within a universality class is the same for all members, provided parameters are identified correctly, the long time behavior of time correlation functions for the fluctuating Burgers equation can be expressed in terms of the Prähofer-Spohn scaling functions[25]. The

most striking results are first of all a prediction for the decay of the current-current time correlation function as

$$\frac{1}{L} \langle \tilde{J}(t) \tilde{J}(0) \rangle = \frac{2.1056}{\sqrt{3}\Gamma_E(1/3)} \left(\frac{\hat{S}(0)w^2}{4t} \right)^{2/3}, \quad (334)$$

with $\tilde{J}(t) = \hat{J}(0, t) - \langle \hat{J}(0, t) \rangle - \frac{\partial \hat{J}(\bar{c})}{\partial \bar{c}} (N(0, t) - \langle N \rangle)$ and Γ_E denoting Euler's gamma function. Secondly, for the wave number dependent diffusion coefficient, characterizing the decay rate of a sine-wave of wavelength k in a periodic system, as $D(k)k^2$ one finds

$$D(k) = \int_0^\infty dt M(k, t) = \frac{8}{19.444} \sqrt{\frac{2\hat{S}(0)w^2}{|k|}}. \quad (335)$$

One can obtain more detailed results from the Prähofer-Spohn scaling functions, which are discussed in Ref.[23].

5.5 Hydrodynamics in one dimension

Hamiltonian systems in one dimension have three global conservation laws, for mass (or number), momentum and energy. Therefore one has three hydrodynamic equations, which on adding fluctuating terms are of the form

$$\begin{aligned} \frac{\partial \rho(x, t)}{\partial t} &= -\frac{\partial}{\partial x} [\rho(x, t)u(x, t)] \\ \rho \left(\frac{\partial}{\partial t} + u(x, t) \frac{\partial}{\partial x} \right) u(x, t) &= -\frac{\partial p(x, t)}{\partial x} + \frac{\partial}{\partial x} \left\{ \kappa(n(x, t), T(x, t)) \frac{\partial u(x, t)}{\partial x} \right\} + \frac{\partial \sigma^r(x, t)}{\partial x}. \\ \rho(x, t)T(x, t) \left(\frac{\partial}{\partial t} + u(x, t) \frac{\partial}{\partial x} \right) s(x, t) &= \kappa(n(x, t), T(x, t)) \left(\frac{\partial u(x, t)}{\partial x} \right)^2 + \\ + \sigma^r(x, t) \frac{\partial u(x, t)}{\partial x} + \frac{\partial}{\partial x} \left(\lambda(x, t) \frac{\partial T(x, t)}{\partial x} \right) - \frac{\partial q^r(x, t)}{\partial x}. \end{aligned} \quad (336)$$

In these expressions $\rho(x, t)$ is the mass density. The pressure $p(x, t)$ may be expressed as

$$p(x, t) = \left(\frac{\partial p}{\partial n} \right)_e n(x, t) + \left(\frac{\partial p}{\partial e} \right)_n e(x, t),$$

with $e(x, t)$ the local energy density and the entropy per unit mass; $s(x, t)$ is defined in similar way. Furthermore, κ is the bulk viscosity, $\sigma^r(x, t)$ is the random stress tensor and $q^r(x, t)$ the random heat current. For both of these random currents it is usually assumed they are distributed as gaussian white noise, with zero mean and variances dictated by fluctuation dissipation theorems. As starting point of a mode coupling expansion one has to linearize these equations, like we did with the fluctuating Burgers equation. Taking a spatial Fourier transform one obtains the equations discussed already in section [1],

$$\frac{\partial \hat{n}(k, t)}{\partial t} = -ikn_0 \hat{u}(k, t), \quad (337)$$

$$\rho_0 \frac{\partial \hat{u}(k, t)}{\partial t} = -ik\hat{p}(k, t) + ik [ik\kappa_0 \hat{u}(k, t) + \hat{\sigma}^r(k, t)], \quad (338)$$

$$T_0 \frac{\partial \hat{s}(k, t)}{\partial t} = -\frac{\lambda_0}{\rho_0} k^2 \hat{T}(k, t) - \frac{ik}{\rho_0} q^r(k, t). \quad (339)$$

Here the subscript 0 denotes equilibrium values. These equations can be diagonalized. One then finds three eigenmodes, called hydrodynamic modes. These are two sound modes¹¹ $a_1(k, t)$ and $a_{-1}(k, t)$ and a heat mode $a_H(k, t)$, given respectively, to leading order in k by

$$a_\sigma(k, t) = \left(\frac{\beta}{2\rho_0} \right)^{1/2} (c_0^{-1} p(k, t) + \sigma g(k, t)), \quad (340)$$

$$a_H(k, t) = \left(\frac{\beta}{n_0 T_0 C_p} \right)^{1/2} (e(k, t) - h_0 n(k, t)). \quad (341)$$

Here, $\sigma = \pm 1$, T_0 is the equilibrium temperature, $\beta = (k_B T_0)^{-1}$; $C_p = T(\partial s / \partial T)_p$ is the specific heat per unit mass at constant pressure p ; $c_0 = (\partial p / \partial \rho)_s^{1/2}$ is the adiabatic sound velocity in the limit of zero wave number and h_0 is the equilibrium enthalpy per particle. The allowed values of k are of the form $k = \frac{2\pi n}{L}$. To leading order in k the hydrodynamic modes are normalized under the inner product $(f, g) = \frac{1}{L} \langle f^* g \rangle$, with $\langle \rangle$ a grand canonical equilibrium average.

The time correlation functions of the hydrodynamic modes satisfy linear

¹¹I use $\sigma = \pm 1$ for right respectively left moving sound modes, rather than positive respectively negative frequency, as is conventional.

equations involving memory kernels, of similar form as Eq. (324), viz.

$$\frac{\partial \hat{S}_\sigma(k, t)}{\partial t} = -i\sigma c_0 k \hat{S}_\sigma(k, t) - k^2 \int_0^t d\tau \hat{M}_\sigma(k, \tau) \hat{S}_\sigma(k, t - \tau), \quad (342)$$

$$\frac{\partial \hat{S}_H(k, t)}{\partial t} = -k^2 \int_0^t d\tau \hat{M}_H(k, \tau) \hat{S}_H(k, t - \tau). \quad (343)$$

Here $\hat{S}_\sigma(k, t) = (a_\sigma(k, 0), a_\sigma(k, t))$ etc. Like for the fluctuating Burgers equation the memory kernels may be expressed through a diagrammatic mode coupling expansion as a sum of irreducible skeleton diagrams[26]. These consist of propagators, representing density density correlation functions $\hat{S}_\zeta(\ell, t_\alpha)$, and vertices representing the coupling of one propagator $\hat{S}_\zeta(\ell, t_\alpha)$ to two propagators $\hat{S}_\mu(q, t_{\alpha'})$ and $\hat{S}_\nu(\ell - q, t_{\alpha''})$, with coupling strength $\ell W_\zeta^{\mu\nu}$. For the long time dynamics only a few of these 27 couplings are important; only couplings to two sound modes of the same sign or to two heat modes may give rise to long-lived perturbations, all other combinations of pairs of modes rapidly die out through oscillations. From EHvL[18] the relevant non-vanishing coupling strengths to leading order in k can be obtained as¹²

$$W_\sigma^{\sigma'\sigma'} = \frac{\sigma}{(2\rho\beta)^{1/2}c_0} \left(\frac{\partial c_0 n}{\partial n} \right)_s \quad (344)$$

$$W_\sigma^{HH} = \frac{-\sigma(\gamma - 1)n}{(2\rho\beta)^{1/2}C_p} \left(\frac{\partial C_p}{\partial n} \right)_p \quad (345)$$

$$W_H^{\sigma\sigma} = \frac{\sigma k_B^{1/2} c_0}{(nC_p)^{1/2}}. \quad (346)$$

Notice that $W_\sigma^{\sigma'\sigma'}$ does not depend on the value of σ' .

Now a central observation is the following: due to the first term on the right-hand side of Eq. (342) the sound-sound correlation functions will have their weights centered around the positions $x(t) = x(0) \pm c_0 t$, in other words, these functions will assume the forms $\hat{S}_\sigma(k, t) = \exp(-i\sigma c_0 k t) \hat{\Sigma}_\sigma(k, t)$, with $\hat{\Sigma}_\sigma(k, t)$ to a first approximation real non-oscillating functions. As a consequence the mode coupling contributions to \hat{M}_σ are dominated by those diagrams in which all vertices are of the type $V_\sigma^{\sigma\sigma}$. All other contributions for at least some time will oscillate out of phase with the angular frequency

¹²For obtaining Eq. (345) from the EHvL expression some thermodynamics is required.

$\sigma c_0 k$ of the sound mode under consideration. The remaining contributions, especially so if described in a coordinate frame comoving at the speed of sound have exactly the same structure as the terms in the mode coupling expansion for the fluctuating Burgers equation[27]; all propagators correspond to the same type of correlation function and all vertex pairs carry the same weight factor W , in the case of the Burgers equation given by $W_B = \frac{w^2}{2} \hat{S}(0)$. Therefore, to leading order in time this memory kernel may be expressed in terms of the Prähler-Spohn scaling functions, like the memory kernel for the fluctuating Burgers equation.

Let us consider the wave number dependent sound damping constant $\Gamma(k) = 2\tilde{M}_\sigma(k, 0)$ and the sound currents, defined as

$\hat{J}_\sigma(k, t) = \left(\frac{\beta}{2\rho}\right)^{1/2} \sigma \hat{J}_l(k, t) + \frac{1}{c_0} \hat{J}_H(k, t) - \sigma \left(\frac{\partial p}{\partial n}\right)_e$, where $\hat{J}_l(k, t)$ and $\hat{J}_H(k, t)$ are the longitudinal current and the heat current[18], denoted by EHvL as J_l and J_λ respectively. Eq. (5.28) of Ref.[23] can now be used to obtain the leading small- k behavior of $\Gamma(k)$ and long time behavior of $\langle \hat{J}_\sigma(0, 0) \hat{J}_\sigma(0, t) \rangle$ as

$$\Gamma(k) = \frac{16}{19.444} \sqrt{\frac{W_s}{|k|}} \quad (347)$$

$$\frac{1}{L} \langle \hat{J}_\sigma(0, t) \hat{J}_\sigma(0, 0) \rangle = \frac{2.1056}{2\sqrt{3}\Gamma_E(1/3)} \left(\frac{W_s}{t}\right)^{2/3}. \quad (348)$$

The leading higher order corrections are obtained by replacing in the diagrammatic expansion of the memory kernel just one pair of vertices of type $V_\sigma^{\sigma\sigma}$ by vertices of type $V_\sigma^{-\sigma-\sigma}$ or V_σ^{HH} . Note this can only be done by having the new vertices connected by the same pair of propagators. One easily shows that all these terms add contributions proportional to $|k|^{-1/3}$ to $\Gamma(k)$ and contributions proportional to $t^{-7/9}$ to the current-current correlation function. Since there are infinitely many such contributions, there seems to be no straightforward way of determining the coefficients exactly. However, estimates based on the simplest contributing diagrams can be made[24]. Further corrections obtain from terms with 4, 6, \dots vertices of type $V_\sigma^{-\sigma-\sigma}$ or V_σ^{HH} . Each of these appears to be of the form $Ck^{-\mu}$ for $\Gamma(k)$ and $Dt^{-\nu}$ for the current correlation function, with C and D constants and μ and ν of the form $\mu = 1/3 - \sum_{j=2}^{\infty} m_j (2/3)^j$ and $\nu = 2/3 + \sum_{j=2}^{\infty} 2n_j (2/3)^j$ respectively, with m_j and n_j natural numbers. Again, for each exponent there is an infinity of contributing terms.

The leading long time behavior of $\hat{S}_H(k, t)$ is determined in similar way by the sum of all contributions to $\hat{M}^H(k, t)$ where the first and last vertex are of type $V_H^{\sigma\sigma}$ and all other vertices are of type $V_\sigma^{\sigma\sigma}$, all with the same value of σ . These terms do contain an oscillating factor $\exp(-i\sigma c_0 kt)$, but these oscillations are much slower than the oscillations in any of the other terms. Since we have to include the contributions to \hat{M}^H of either sign of σ , we cannot express \hat{S}_H directly in terms of the Prähofer-Spohn scaling functions, but we can do so immediately for the memory kernel. A simple analysis yields to leading order

$$\hat{M}_H(k, t) = 2 \frac{W_H}{W_s} \cos(\sigma c_0 kt) \hat{M}_\sigma(k, t), \quad (349)$$

with $W_H = |W_H^{\sigma\sigma}|$. For the k -dependent heat conduction coefficient and the heat current time correlation function this leads to the expressions

$$\lambda(k) = nC_p D_T(k) = 2nC_p \left(\frac{W_H}{W_s} \right) W_s^{2/3} \frac{2.1056}{4\sqrt{3}(c_0 |k|)^{1/3}}, \quad (350)$$

$$\frac{1}{L} \langle \hat{J}_H(0, t) \hat{J}_H(0, 0) \rangle = 2nC_p \left(\frac{W_H}{W_s} \right) \frac{2.1056}{\Gamma_E(1/3)} \left(\frac{W_s^2}{t} \right)^{2/3}. \quad (351)$$

Higher order corrections may be obtained in similar way as for the sound modes.

The analysis presented here clearly shows that for long times the dynamics of 1d hydrodynamic systems to leading order belongs to the KPZ universality class and can be described exactly by means of the Prähofer-Spohn scaling functions. However, the correction terms decay only slightly faster with time and in most cases will not be negligible.

6 Appendix A

Starting point for the formulation of the "hydrodynamic projection operator" as (89) are the following observations: from the Grand-canonical distribution

$$\rho(\Gamma) = \frac{1}{\Xi} e^{\nu N - \beta H}$$

one obtains the identities

$$\begin{aligned}\lim_{\mathbf{k} \rightarrow 0} \langle \hat{n}(\mathbf{k}) | \hat{a}(\mathbf{k}) \rangle &= \langle N - \langle N \rangle | \hat{a}(0) \rangle, \\ &= \left(\frac{\partial \hat{a}(0)}{\partial \nu} \right)_\beta.\end{aligned}\quad (352)$$

$$\begin{aligned}\lim_{\mathbf{k} \rightarrow 0} \langle \hat{\epsilon}(\mathbf{k}) | \hat{a}(\mathbf{k}) \rangle &= \langle H - \langle H \rangle | \hat{a}(0) \rangle, \\ &= - \left(\frac{\partial \hat{a}(0)}{\partial \beta} \right)_\nu.\end{aligned}\quad (353)$$

$$(354)$$

Next introduce $\tilde{\chi}$ as the restriction of the matrix χ to the two-dimensional subspace (for each \mathbf{k}) spanned by the matrix elements between $\hat{n}(\mathbf{k})$ and $\hat{\epsilon}(\mathbf{k})$. From 353 one finds in the limit $\mathbf{k} \rightarrow 0$,

$$\lim_{\mathbf{k} \rightarrow 0} \tilde{\chi}(\mathbf{k}) = \lim_{\mathbf{k} \rightarrow 0} \begin{pmatrix} \langle \hat{n}(\mathbf{k}) | \hat{n}(\mathbf{k}) \rangle & \langle \hat{n}(\mathbf{k}) | \hat{\epsilon}(\mathbf{k}) \rangle \\ \langle \hat{\epsilon}(\mathbf{k}) | \hat{n}(\mathbf{k}) \rangle & \langle \hat{\epsilon}(\mathbf{k}) | \hat{\epsilon}(\mathbf{k}) \rangle \end{pmatrix} = V \begin{pmatrix} \left(\frac{\partial n}{\partial \nu} \right)_\beta & \left(\frac{\partial e}{\partial \nu} \right)_\beta \\ - \left(\frac{\partial n}{\partial \beta} \right)_\nu & - \left(\frac{\partial e}{\partial \beta} \right)_\nu \end{pmatrix}.\quad (355)$$

The inverse of this is

$$\frac{1}{V} \begin{pmatrix} \left(\frac{\partial \nu}{\partial n} \right)_e & - \left(\frac{\partial \beta}{\partial n} \right)_e \\ \left(\frac{\partial \nu}{\partial e} \right)_n & - \left(\frac{\partial \beta}{\partial e} \right)_n \end{pmatrix},\quad (356)$$

which, acting to the left on $(\delta n, \delta e)$ produces, to linear order, the fluctuations $(\delta \nu, -\delta \beta)/V$. This is generalized to *define* the \mathbf{k} -dependent fluctuations $\hat{\nu}(\mathbf{k})$ and $\hat{\beta}(\mathbf{k})$ through

$$\begin{vmatrix} \hat{\nu}(\mathbf{k}) \\ -\hat{\beta}(\mathbf{k}) \end{vmatrix} = V \begin{vmatrix} \hat{n}(\mathbf{k}) \\ \hat{\epsilon}(\mathbf{k}) \end{vmatrix} \circ \tilde{\chi}^{-1}(\mathbf{k}).\quad (357)$$

Inserting this equation (or its adjoint) into (87) one obtains (89). To rewrite this further one may introduce the \mathbf{k} -dependent pressure $\hat{p}(\mathbf{k})$ through

$$\hat{p}(\mathbf{k}) = \mathcal{P} \left[\hat{\mathbf{k}} \hat{\mathbf{k}} : \hat{\mathbf{P}}(\mathbf{k}) \right],\quad (358)$$

$$= \mathcal{P} \left[\frac{-1}{ik} \mathcal{L} \hat{\mathbf{G}}(\mathbf{k}) \cdot \hat{\mathbf{k}} \right].\quad (359)$$

The form of this can be made more explicit through

$$\begin{aligned}
\hat{p}(\mathbf{k}) &= \frac{-1}{ikV} \left[\langle \hat{n}(\mathbf{k}) | \mathcal{L}\hat{\mathbf{G}}(\mathbf{k}) \cdot \hat{\mathbf{k}} \rangle \hat{v}(\mathbf{k}) - \langle \hat{\epsilon}(\mathbf{k}) | \mathcal{L}\hat{\mathbf{G}}(\mathbf{k}) \cdot \hat{\mathbf{k}} \rangle \hat{\beta}(\mathbf{k}) \right], \\
&= \frac{-1}{ikV} \left[\langle \mathcal{L}\hat{n}(\mathbf{k}) | \hat{\mathbf{G}}(\mathbf{k}) \cdot \hat{\mathbf{k}} \rangle \hat{v}(\mathbf{k}) - \langle \mathcal{L}\hat{\epsilon}(\mathbf{k}) | \hat{\mathbf{G}}(\mathbf{k}) \cdot \hat{\mathbf{k}} \rangle \hat{\beta}(\mathbf{k}) \right], \\
&= n_0 k_B T_0 [\hat{v}(\mathbf{k}) - h_0(\mathbf{k})\hat{\beta}(\mathbf{k})].
\end{aligned} \tag{360}$$

An alternative is

$$\hat{p}(\mathbf{k}) = \frac{-1}{ikV} \left[\langle \hat{v}(\mathbf{k}) | \hat{\mathbf{k}}\hat{\mathbf{k}}:\hat{\mathbf{P}}(\mathbf{k}) \rangle \hat{n}(\mathbf{k}) - \langle \hat{\beta}(\mathbf{k}) | \hat{\mathbf{k}}\hat{\mathbf{k}}:\hat{\mathbf{P}}(\mathbf{k}) \rangle \hat{\epsilon}(\mathbf{k}) \right], \tag{361}$$

which, in the limit $\mathbf{k} \rightarrow 0$ reduces to

$$\hat{p}(\mathbf{k}) = \left(\frac{\partial p}{\partial n} \right)_e \hat{n}(\mathbf{k}) + \left(\frac{\partial p}{\partial e} \right)_n \hat{\epsilon}(\mathbf{k}). \tag{362}$$

Here the notation $h_0(\mathbf{k})$ was introduced for the \mathbf{k} -dependent *enthalpy density*. This equation may be used to express $\hat{v}(\mathbf{k})$ as

$$\hat{v}(\mathbf{k}) = \frac{1}{n_0 k_B T_0} [\hat{p}(\mathbf{k}) + h_0(\mathbf{k})\hat{\beta}(\mathbf{k})], \tag{363}$$

with

$$h_0(\mathbf{k}) = \frac{1}{n_0 k_B T_0} \langle \hat{\epsilon}(\mathbf{k}) | \hat{p}(\mathbf{k}) \rangle. \tag{364}$$

Notice that one indeed has $\lim_{\mathbf{k} \rightarrow 0} h_0(\mathbf{k}) = p_0 + \epsilon_0$. Introducing finally the \mathbf{k} -dependent entropy per particle

$$\hat{\sigma}(\mathbf{k}) = \frac{1}{n_0 k_B T_0} [\hat{\epsilon}(\mathbf{k}) - h_0(\mathbf{k})\hat{n}(\mathbf{k})], \tag{365}$$

plus the notation

$$\hat{T}(\mathbf{k}) = -k_B T_0^2 \hat{\beta}(\mathbf{k}), \tag{366}$$

one finds that substitution of (363) into (89) leads to (92).

References

- [1] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, (Pergamon, London 1959)

- [2] D. A. McQuarrie, *Statistical Mechanics* Ch. 21-8, (Harper and Row, New York 1976, see <http://www.abebooks.com/> for an inexpensive Indian edition)
- [3] D. Forster, *Hydrodynamic fluctuations, broken symmetry, and correlation functions*, (W. A. Benjamin, Reading, Mass.)
- [4] P. Résibois and M. De Leener, *Classical kinetic theory of fluids*, (Wiley, New York 1977)
- [5] J. R. Dorfman, *Kinetic and hydrodynamic theory of time correlation functions*, in "Fundamental Problems in Statistical Mechanics", E. G. D. Cohen ed. (North Holland, Amsterdam 1975)
- [6] R. J. Zwanzig, *Ann. Rev. Phys. Chem.* **16** (1965) 67
- [7] I. M. de Schepper and M. H. Ernst, *Physica* **98 A** (1979) 189
- [8] J. A. McLennan, *Introduction to Non Equilibrium Statistical Mechanics* (Prentice Hall, 1988)
- [9] W. A. Steele in *Transport Phenomena in Fluids*, H. J. M. Hanley ed. (Dekker, New York 1969)
- [10] R. J. Zwanzig, *Phys. Rev.* **124** (1961) 963
- [11] H. Mori, *Prog. Theor. Phys.* **33** (1964) 423
- [12] see e.g. R. Evans, *Adv. Phys.* **28** (1979) 143
- [13] J. D. Jackson, *Classical Electrodynamics* (Academic, New York)
- [14] N. G. van Kampen, *Stochastic processes in physics and chemistry*, (North Holland; 3d edition, Amsterdam 2007)
- [15] H. van Beijeren and J. R. Dorfman, *Kinetic theory of hydrodynamic flow, I. The generalized normal solution method and its application to the drag on a sphere*, *J. Stat. Phys.* **23** (1980) 335; *Kinetic theory of hydrodynamic flow, II. The drag on a sphere and on a cylinder*, *J. Stat. Phys.* **23** (1980) 443.
- [16] H. Lorentz *Lessen over Theor. Natuurkunde, Vol. V, Kinetische problemen*, (Brill, Leiden 1921)

- [17] E. H. Hauge and A. Martin Löf, *J. Stat. Phys.* **7** (1973) 259
- [18] M. H. Ernst, E. H. Hauge, J. M. Van Leeuwen, *Phys. Lett.* **34A** (1971) 419
- [19] H. van Beijeren, R. Kutner and H. Spohn, *Phys. Rev. Lett.* **54** (1981) 2026
- [20] J. Krug and H. Spohn in *Solids far from equilibrium*, C. Godrèche ed. (Cambridge University Press, Cambridge, 1992).
- [21] J. R. Dorfman and E. G. D. Cohen, *Velocity Correlation Functions in Two and Three Dimensions*, *Phys. Rev. Lett.* **25**, 1257 (1970); *Velocity-Correlation Functions in Two and Three Dimensions: Low Density*, *Phys. Rev. A* **6**, 776 (1972); *Velocity-correlation functions in two and three dimensions. II. Higher density*, *ibid.* **12**, 292 (1975).
- [22] D. Bedeaux, P. Mazur, *Physica* **73**, 431 (1974); D. Bedeaux, P. Mazur, *Physica* **75**, 79 (1974)
- [23] M. Prähofer, H. Spohn, *J. Stat. Phys.* **115**, 255 (2004)
- [24] H. van Beijeren, to be published (Cambridge University Press, Cambridge, 1992).
- [25] H. van Beijeren, *Exact results for anomalous transport in one dimensional Hamiltonian systems* arXiv:1106.3298v2 [cond-mat.stat-mech]
- [26] A. Khuranat, *J. Phys. A: Math. Gen.* **18**, 2415 (1985); H. van Beijeren, M. H. Ernst, *J. Stat. Phys.* **21**, 125 (1979) sec. 7
- [27] H. van Beijeren, R. Kutner, H. Spohn, *Phys. Rev. Lett.* **54**, 2026 (1985); E. Frey, U. C. Täuber, T. Hwa, *Phys. Rev. E* **53**, 4424 (1996)