Equilibration of classical systems

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1 Green-Kubo formalism

See references[1, 2, 3, 4, 5, 6, 8]

1.1 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 constituing 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 **??** tracer diffusion is described at the macroscopic level by the diffusion equation

$$\frac{\partial n(\boldsymbol{r},t)}{\partial t} = D\nabla^2 n(\boldsymbol{r},t), \tag{1}$$

where, this time, I used the number density rather than the mass density. Microscopically, $n(\boldsymbol{r},t)$ 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 (1). On the other hand it should also satisfy

$$n(\boldsymbol{r},t) = \sum_i P_i(\boldsymbol{r},t), \tag{2}$$

where i runs over all tracer particles and $P_i(\boldsymbol{r},t)$ is the probability density for finding particle i at $\boldsymbol{r}$ at time t. Again, the probabilistic nature comes from averaging over macroscopically equivalent realizations of the initial state. From (2) and the linearity of the diffusion equation it follows that on macroscopic time and length scales also $P_i(\boldsymbol{r},t)$ 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

$$G_D(\boldsymbol{r},t) = \frac{1}{(4\pi Dt)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right). \tag{3}$$

Applied to $P_i(\boldsymbol{r},t)$ this describes the probability density for a tracer particle to be displaced over $\boldsymbol{r}$ 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

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

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 (4) will be valid asymptotically for $t \to \infty$. This is expressed by the famous *Einstein relation*

$$D = \lim_{t \to \infty} \frac{\langle \mid \boldsymbol{r}(t) - \boldsymbol{r}(0) \mid^2 \rangle}{2dt}. \tag{5}$$

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

$$\begin{aligned} D &= \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} \langle \mid \boldsymbol{r}(t) - \boldsymbol{r}(0) \mid^2 \rangle, \\ &\qquad \text{(provided this limit exists)} \\ &= \lim_{t \to \infty} \frac{1}{d} \langle (\boldsymbol{r}(t) - \boldsymbol{r}(0)) \cdot \boldsymbol{v}(t) \rangle, \\ &= \lim_{t \to \infty} \frac{1}{d} \int_0^t d\,\tau \langle \boldsymbol{v}(\tau) \cdot \boldsymbol{v}(t) \rangle, \\ &= \lim_{t \to \infty} \frac{1}{d} \int_0^t d\,\tau \langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t - \tau) \rangle \\ &= \frac{1}{d} \int_0^\infty d\,t \langle \boldsymbol{v}(0) \cdot \boldsymbol{v}(t) \rangle. \end{aligned} \tag{6}$$

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

$$\langle A(t_1) B(t_2) \rangle = \langle A(t_1 + \tau) B(t_2 + \tau) \rangle = \langle A(0) B(t_2 - t_1) \rangle. \tag{7}$$

This has been used in the chain of simplifications leading to (6).

1.2 Frequency and wave number dependent diffusion coefficient

Fourier and Laplace transform of the diffusion equation leads to

$$\begin{aligned}(z+Dk^2)\tilde{n}(\boldsymbol{k},z) &= n(\boldsymbol{k},t=0), && \text{or} \\ \tilde{n}(\boldsymbol{k},z) &= G_D(\boldsymbol{k},z)n(\boldsymbol{k},t=0), && \text{with} \\ G_D(\boldsymbol{k},z) &= \frac{1}{z+Dk^2}. && \end{aligned} \tag{8}$$

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

$$G(\boldsymbol{k},z) = \frac{1}{z+U(\boldsymbol{k},z)k^2}, \tag{9}$$

$$\text{with} \qquad D = \lim_{\substack{\boldsymbol{k}\to 0 \\ z\to 0^+}} U(\boldsymbol{k},z). \tag{10}$$

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

$G(\boldsymbol{k},z)$, and consequently $U(\boldsymbol{k},z)$, may be expressed in terms of time correlation functions:

$$
\begin{aligned}
G(\boldsymbol{k},z) &= \int_0^\infty d\,t\,e^{-zt}\int d\,\boldsymbol{r}\,e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\langle\delta(\boldsymbol{r}_1(t)-\boldsymbol{r}_1(0)-\boldsymbol{r})\rangle,\\
&= \int_0^\infty d\,t\,e^{-zt}\langle e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(t)-\boldsymbol{r}_1(0))}\rangle,\\
&= \left[\frac{-e^{-zt}}{z}\langle e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(t)-\boldsymbol{r}_1(0))}\rangle\right]_0^\infty+\frac{1}{z}\int_0^\infty d\,t\,e^{-zt}\langle -i\boldsymbol{k}\cdot\boldsymbol{v}_1(t)e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(t)-\boldsymbol{r}_1(0))}\rangle,\\
&= \frac{1}{z}+\int_0^\infty d\,t\frac{e^{-zt}}{z}\langle -i\boldsymbol{k}\cdot\boldsymbol{v}_1(0)e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(0)-\boldsymbol{r}_1(-t))}\rangle,\\
&= \frac{1}{z}-\left[\frac{1}{z^2}\,e^{-zt}\langle -i\boldsymbol{k}\cdot\boldsymbol{v}_1(t)e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(t)-\boldsymbol{r}_1(0))}\rangle\right]_0^\infty\\
&\quad -\frac{1}{z^2}\int_0^\infty d\,te^{-zt}\langle(\boldsymbol{k}\cdot\boldsymbol{v}_1(0))(\boldsymbol{k}\cdot\boldsymbol{v}_1(-t))e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(0)-\boldsymbol{r}_1(-t))}\rangle,\\
G(\boldsymbol{k},z) &= \frac{1}{z}-\frac{k^2}{z^2}\int_0^\infty d\,te^{-zt}\langle(\hat{\boldsymbol{k}}\cdot\boldsymbol{v}_1(0))(\hat{\boldsymbol{k}}\cdot\boldsymbol{v}_1(t))e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(t)-\boldsymbol{r}_1(0))}\rangle, \qquad (11)\\
&\equiv \frac{1}{z}-\frac{k^2}{z^2}C(\boldsymbol{k},z). \qquad (12)
\end{aligned}
$$

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

$$C(\boldsymbol{k},t)=\langle(\hat{\boldsymbol{k}}\cdot\boldsymbol{v}_1(0))(\hat{\boldsymbol{k}}\cdot\boldsymbol{v}_1(t))e^{-i\boldsymbol{k}\cdot(\boldsymbol{r}_1(t)-\boldsymbol{r}_1(0))}\rangle. \qquad (13)$$

Some algebra yields

$$
\begin{aligned}
U(\boldsymbol{k},z) &= \frac{zC(\boldsymbol{k},z)}{z-k^2C(\boldsymbol{k},z)}, \qquad (14)\\
\text{or}\quad C(\boldsymbol{k},z) &= \frac{zU(\boldsymbol{k},z)}{z+k^2U(\boldsymbol{k},z)}. \qquad (15)
\end{aligned}
$$

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

$$D=\lim_{z\to 0}\lim_{k\to 0}C(\boldsymbol{k},z). \qquad (16)$$

This is again the Green-Kubo expression (6). But note that $C(\boldsymbol{k},z)$ has a very discontinuous behavior near the origin! For example, one has

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

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 $U(\boldsymbol{k}, z)$ 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 $U(\boldsymbol{k}, z)$. 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 $U(\boldsymbol{k}, z)$ 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 $U(\boldsymbol{k}, z)$. The form of this equation is

$$\frac{\partial n(\boldsymbol{r}, t)}{\partial t} = \nabla^2 \int d\,\boldsymbol{r}' \int_0^t d\,t' u(\boldsymbol{r}', t') n(\boldsymbol{r} - \boldsymbol{r}', t - t'). \tag{17}$$

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

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

$$\widehat{f}(\omega) = \int_{-\infty}^{\infty} d\,t\, e^{i\omega t} f(t).$$

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

1.3 Projection operator formalism

The projection operator method has been introduced in Green-Kubo theory by Zwanzig[9] and Mori[10]. 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

$$\langle f \mid g \rangle = \sum_N \int d\,\Gamma \rho_G(\Gamma)(f(\Gamma) - \langle f(\Gamma)\rangle)^*(g(\Gamma) - \langle g(\Gamma)\rangle). \tag{18}$$

Here $\Gamma \equiv (\boldsymbol{r}_1 \cdots \boldsymbol{r}_N, \boldsymbol{p}_1 \cdots \boldsymbol{p}_N)$ 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.

$$\begin{aligned} \frac{df(\Gamma)}{dt} &= \mathcal{L}f(\Gamma) = \sum_{i=1}^{N} \left\{ \frac{\boldsymbol{p}_i}{m} \cdot \frac{\partial}{\partial \boldsymbol{r}_i} - \frac{\partial V(\boldsymbol{r}_1 \cdots \boldsymbol{r}_N)}{\partial \boldsymbol{r}_i} \cdot \frac{\partial}{\boldsymbol{p}_i} \right\} f(\Gamma), \qquad (19) \\ f(\Gamma(t)) &= e^{\mathcal{L}t} f(\Gamma). \qquad (20) \end{aligned}$$

In addition the time evolution of an ensemble in phase space is described by[1]

$$\begin{aligned} \frac{\partial \rho(\Gamma)}{\partial t} &= -\mathcal{L}\rho(\Gamma), \qquad (21) \\ \rho(\Gamma, t) &= e^{-\mathcal{L}t}\rho(\Gamma, 0) = \rho(e^{-\mathcal{L}t}\Gamma, 0). \qquad (22) \end{aligned}$$

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

$$T(\boldsymbol{a}) f(\boldsymbol{r}_1 \cdots \boldsymbol{r}_N, \boldsymbol{p}_1 \cdots \boldsymbol{p}_N) = f(\boldsymbol{r}_1 + \boldsymbol{a} \cdots \boldsymbol{r}_N + \boldsymbol{a}, \boldsymbol{p}_1 \cdots \boldsymbol{p}_N). \tag{23}$$

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[1] Here Γ denotes an arbitrary point in phase space and *not* the set of coordinates of all particles, as in (19).

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

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

with $\boldsymbol{R}$ the center of mass and $\boldsymbol{\rho}_i = \boldsymbol{r}_i - \boldsymbol{R}$. The operator $e^{\mathcal{L}t}$ maps each Fourier component onto itself[2]

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 (18) of its coordinates, $\boldsymbol{r}_1, \boldsymbol{p}_1$ and their equilibrium averages $\langle f(\boldsymbol{r}_1, \boldsymbol{p}_1)\rangle$. They can be decomposed into functions of the form $\exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_1)P_n(\boldsymbol{p}_1)$, with P_n a complete set of orthogonal polynomials under the inner product (18). Note that the equilibrium averages vanish for all non-zero $\boldsymbol{k}$. One may investigate how the averages of all these functions over a *non-equilibrium ensemble* evolve in time. For $k \to 0$ one should expect this decay is very slow for the averages $\langle \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_1)\rangle$, 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 $\exp -i\boldsymbol{k}\cdot\boldsymbol{r}_1$. But these slow decays are not independent of the decay of $\langle \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_1)\rangle$ 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 $\langle \exp(-i\boldsymbol{k}\cdot\boldsymbol{r}_1)\rangle$.

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[2] One 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[3] [4] with the idea that the average time evolution of the set of functions $n_t(\boldsymbol{k})$ will determine the slowly decaying part of an arbitrary function $f(\boldsymbol{r}_1, \boldsymbol{p}_1)$. In addition we define

$$\mathcal{P}_\perp = 1 - \mathcal{P} \tag{24}$$

and

$$\widehat{\mathcal{L}} = \mathcal{P}_\perp \mathcal{L} \mathcal{P}_\perp. \tag{25}$$

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

$$\rho(t) = \rho_0(1 + \Delta(t)) = \rho_0 \left(1 + \mathcal{P}\Delta(t) + \mathcal{P}_\perp \Delta(t)\right), \tag{26}$$

with ρ_0 the Grand canonical distribution. The time evolution of this is described by Liouville's equation (21)

$$\frac{\partial \rho(t)}{\partial t} = -\mathcal{L}\rho(t) = -\rho_0 \mathcal{L}\Delta(t), \tag{27}$$

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

$$\begin{aligned} \frac{\partial \mathcal{P}\Delta(t)}{\partial t} &= -\mathcal{P}\mathcal{L}\mathcal{P}_\perp \Delta(t), & (28) \\ \frac{\partial \mathcal{P}_\perp \Delta(t)}{\partial t} &= -\mathcal{P}_\perp \mathcal{L} \mathcal{P}_\perp \Delta(t) - \mathcal{P}_\perp \mathcal{L} \mathcal{P} \Delta(t). & (29) \end{aligned}$$

In deriving (28) we used $\mathcal{P}\mathcal{L}\mathcal{P} = 0$, following from $\langle n_t(\boldsymbol{k}) \mid \mathcal{L} \mid n_t(\boldsymbol{k})\rangle = 0$. Eq. (29) can be solved for $\mathcal{P}_\perp \mathcal{L} \mathcal{P} \Delta(t)$, as

$$\mathcal{P}_\perp \Delta(t) = -\int_0^t d\,\tau\, e^{-\widehat{\mathcal{L}}(t-\tau)} \mathcal{P}_\perp \mathcal{L} \mathcal{P} \Delta(\tau) + e^{-\widehat{\mathcal{L}}t} \mathcal{P}_\perp \Delta(0). \tag{30}$$

Substitution into (28) results into

$$\frac{\partial \mathcal{P}\Delta(t)}{\partial t} = \int_0^t d\,\tau \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\widehat{\mathcal{L}}\tau} \mathcal{P}_\perp \mathcal{L}\mathcal{P}\Delta(t-\tau) - \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\widehat{\mathcal{L}}t} \mathcal{P}_\perp \Delta(0). \tag{31}$$

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[3] There is no need here to subtract the averages of phase space functions, as is done in (18). For $\boldsymbol{k} \neq 0$ the averages all vanish. For $\boldsymbol{k} = 0$ $n_t(\boldsymbol{k})$ reduces to a constant, so it's time evolution is trivial.

[4] In 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 $\boldsymbol{k}$ this does not really matter. For any value of $\boldsymbol{k}$ the projection operator projects onto a single function within the corresponding set.

Next use:

$$\mathcal{L}n_t(\boldsymbol{k}) = \mathcal{L}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_1} = -i\boldsymbol{k}\cdot\frac{\boldsymbol{p}_1}{m_1}e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_1} \equiv -ikj_t(\boldsymbol{k}). \tag{32}$$

Insert this into (31) letting the first $\mathcal{L}$ act to the left. This yields

$$\frac{\partial\mathcal{P}\Delta(t)}{\partial t} = -\sum_{\boldsymbol{k}} k^2 \int_0^t d\tau \big\langle j_t(\boldsymbol{k}) | e^{-\widehat{\mathcal{L}}\tau} j_t(\boldsymbol{k})\big\rangle \mathcal{P}\Delta(t-\tau) - \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\widehat{\mathcal{L}}t}\mathcal{P}_\perp\Delta(0). \tag{33}$$

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

$$\begin{aligned}\overline{n}_t(\boldsymbol{k}, t) &= \sum_N \int d\Gamma\,\rho_0[1+\Delta(t)]n_t(\boldsymbol{k}) \\ &= \delta_{\boldsymbol{k}0} + \langle\Delta(t)\mid n_t(\boldsymbol{k})\rangle \end{aligned} \tag{34}$$

With this notation we may rewrite the adjoint of (33) as

$$\frac{\partial\overline{n}_t(\boldsymbol{k}, t)}{\partial t} = -k^2 \int_0^t d\tau \big\langle j_t(\boldsymbol{k}) \mid e^{\widehat{\mathcal{L}}\tau} j_t(\boldsymbol{k})\big\rangle \overline{n}_t(\boldsymbol{k}, t-\tau) + \big\langle \Delta(0) \mid \mathcal{P}_\perp e^{\widehat{\mathcal{L}}t}\mathcal{P}_\perp\mathcal{L}n_t(\boldsymbol{k})\big\rangle, \tag{35}$$

where we used that $-\widehat{\mathcal{L}}$ is the adjoint of $\widehat{\mathcal{L}}$. We expect that for the perturbations under consideration (only particle 1 out of equilibrium) the propagator $e^{\widehat{\mathcal{L}}t}$ induces a rapid decay to zero[5]. Then the second term on the rhs. of (35) may be neglected and we recover the generalized diffusion equation

$$\frac{\partial\overline{n}_t(\boldsymbol{k}, t)}{\partial t} = -k^2 \int_0^t d\tau\, u(\boldsymbol{k}, \tau)\bar{n}_t(\boldsymbol{k}, t-\tau). \tag{36}$$

with now

$$u(\boldsymbol{k}, t) = \big\langle j_t(\boldsymbol{k}) \mid e^{\widehat{\mathcal{L}}t} j_t(\boldsymbol{k})\big\rangle. \tag{37}$$

From (36) we see that $\big\langle j_t(\boldsymbol{k}) \mid e^{\widehat{\mathcal{L}}\tau} j_t(\boldsymbol{k})\big\rangle$ describes the response of $\partial n_t(\boldsymbol{k}, t)/\partial t$ to $n_t(\boldsymbol{k}, t-\tau)$. The orthogonal projection in $e^{\widehat{\mathcal{L}}\tau}$ prevents double counting of

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[5] The assumption underlying this is that it is true for $\boldsymbol{k} = 0$, where all functions depend on $\boldsymbol{p}_1$ only. The function $n_t(0)$ is just unity and does not decay. The averages of all functions of $\boldsymbol{p}_1$ orthogonal to this under the inner product (18) 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 $\widehat{\mathcal{L}}$ depends smoothly on $\boldsymbol{k}$.

the response to $n_t(\boldsymbol{k},\tau')$, with $t-\tau<\tau'<t$. In the limit $k\to 0$ $n_t(\boldsymbol{k},\tau')$ is not excited and $e^{\widehat{\mathcal{L}}\tau}$ becomes identical to $e^{\mathcal{L}\tau}$, as follows from (15).

We may also use the projection operator technique for deriving (15) in an alternative way. First note the identity

$$C(\boldsymbol{k},z)=\left\langle j_t(\boldsymbol{k})\,|\,(z-\mathcal{L})^{-1}j_t(\boldsymbol{k})\right\rangle . \tag{38}$$

Next we need a chain of algebraic operator identities:

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

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

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

The same identity has been used again for $(z-\mathcal{L})^{-1}$, plus $\mathcal{P}(z-\widehat{\mathcal{L}}\,)^{-1}\mathcal{P}_\perp=0$. Using this once more leads to

$$\mathcal{P}_\perp(z-\mathcal{L})^{-1}\mathcal{P}_\perp=\mathcal{P}_\perp(z-\widehat{\mathcal{L}}\,)^{-1}\left[1-|\,ikj_t(\boldsymbol{k})\rangle\langle n_t(\boldsymbol{k})\,|\,(z-\widehat{\mathcal{L}})^{-1}n_t(\boldsymbol{k})\rangle ikj_t(\boldsymbol{k})\,|\,(z-\mathcal{L})^{-1}\right]\mathcal{P}_\perp. \tag{39}$$

Next use $(z-\widehat{\mathcal{L}}\,)^{-1}n_t(\boldsymbol{k})=n_t(\boldsymbol{k})/z$ and take the inner product $\langle j_t(\boldsymbol{k})\,|\cdots j_t(\boldsymbol{k})\rangle$ on both sides. This reproduces eq. (14);

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

An important remark to be made here is that the tagged particle density-density time correlation function satisfies exactly the same generalized diffusion equation (35) as the tagged particle density itself. This follows from the identities

$$\begin{array}{rrcl} & \langle n_t(\boldsymbol{k})\,|\,n_t(\boldsymbol{k},t)\rangle &=& \left\langle n_t(\boldsymbol{k})\,|\,e^{\mathcal{L}t}n_t(\boldsymbol{k})\right\rangle ,\\ \text{and} & \langle\Delta(t)\,|\,n_t(\boldsymbol{k})\rangle &=& \left\langle e^{-\mathcal{L}t}\Delta(0)\,|\,n_t(\boldsymbol{k})\right\rangle=\left\langle\Delta(0)\,|\,e^{\mathcal{L}t}n_t(\boldsymbol{k})\right\rangle . \end{array}$$

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 $P(\boldsymbol{r},t)$ for the position of a tagged particle according to the (generalized) diffusion equation is just one example of this.

1.4 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

$$\widehat{n}(\boldsymbol{k}) = \sum_{i=1}^{N} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i}, \tag{40}$$

$$\widehat{\boldsymbol{G}}(\boldsymbol{k}) = \sum_{i=1}^{N} \boldsymbol{p}_i e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i}, \tag{41}$$

$$\widehat{\epsilon}(\boldsymbol{k}) = \sum_{i=1}^{N} \epsilon_i e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i}, \tag{42}$$

with

$$\epsilon_i = \frac{p_i^2}{2m} + \frac{1}{2}\sum_{j\neq i}\phi(r_{ij}). \tag{43}$$

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

$$T(\boldsymbol{r},t) = T_0(\boldsymbol{r},t) + \left(\frac{\partial T}{\partial n}\right)_\epsilon \delta n(\boldsymbol{r},t) + \left(\frac{\partial T}{\partial \epsilon}\right)_n \delta\epsilon(\boldsymbol{r},t), \tag{44}$$

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

$$\widehat{T}(\boldsymbol{k},t) = \left(\frac{\partial T}{\partial n}\right)_\epsilon \widehat{n}(\boldsymbol{k},t) + \left(\frac{\partial T}{\partial \epsilon}\right)_n \widehat{\epsilon}(\boldsymbol{k},t). \tag{45}$$

This has to be generalized slightly as $\boldsymbol{k}$ 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 $\boldsymbol{k}$ 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

$$\boldsymbol{\psi}(\boldsymbol{k}) \quad = \quad \begin{matrix} \widehat{n}(\boldsymbol{k}) \\ \widehat{\boldsymbol{G}}(\boldsymbol{k}) \\ \widehat{\epsilon}(\boldsymbol{k}) \end{matrix} \tag{46}$$

plus the adjoint vector

$$\boldsymbol{\phi}(\boldsymbol{k}) \quad = \quad \boldsymbol{\psi}(\boldsymbol{k}) \circ \boldsymbol{\chi}^{-1}(\boldsymbol{k}). \tag{47}$$

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

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

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

$$\chi_{ij}(\boldsymbol{k}) = \langle \psi_i(\boldsymbol{k}) \mid \psi_j(\boldsymbol{k}) \rangle \,, \tag{48}$$

from which one immediately obtains the identities

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

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

$$\begin{aligned} \mathcal{P} \quad &= \quad \sum_{\boldsymbol{k}} |\boldsymbol{\psi}(\boldsymbol{k})\big\rangle \circ \big\langle \boldsymbol{\phi}(\boldsymbol{k})|, &(49) \\ &= \quad \sum_{\boldsymbol{k}} |\boldsymbol{\phi}(\boldsymbol{k})\big\rangle \circ \big\langle \boldsymbol{\psi}(\boldsymbol{k})|. &(50) \end{aligned}$$

This may be rewritten in a physically more appealing form as

$$\mathcal{P} = \frac{1}{V} \sum_{\boldsymbol{k}} \left[|\widehat{n}(\boldsymbol{k})\big\rangle\big\langle\widehat{\nu}(\boldsymbol{k})| + \frac{\beta_0}{m n_0} |\widehat{\boldsymbol{G}}(\boldsymbol{k})\big\rangle \cdot \big\langle \widehat{\boldsymbol{G}}(\boldsymbol{k})| - |\widehat{\epsilon}(\boldsymbol{k})\big\rangle\big\langle\widehat{\beta}(\boldsymbol{k})| \right]. \tag{51}$$

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

$$\begin{aligned} \beta(\boldsymbol{r}, t) \quad &= \quad \frac{1}{k_B T(\boldsymbol{r}, t)}, &(52) \\ \nu(\boldsymbol{r}, t) \quad &= \quad \beta(\boldsymbol{r}, t)\mu(\boldsymbol{r}, t), &(53) \end{aligned}$$

with μ the chemical potential. Precise definitions and a derivation of (51) are given in Appendix A. An alternative for (51) may be obtained by replacing the energy density $\widehat{\epsilon}(\boldsymbol{k})$ and the variable $\widehat{\nu}(\boldsymbol{k})$ by $\boldsymbol{k}$-dependent generalizations of the entropy per unit mass, $\widehat{\sigma}(\boldsymbol{k})$ and the pressure, $\widehat{p}(\boldsymbol{k})$ (Appendix A). This yields

$$\mathcal{P} = \frac{\beta_0}{V n_0} \sum_{\boldsymbol{k}} \left[\mid \widehat{n}(\boldsymbol{k}) \rangle \langle \widehat{p}(\boldsymbol{k}) \mid + \frac{1}{m} \mid \widehat{\boldsymbol{G}}(\boldsymbol{k}) \rangle \cdot \langle \widehat{\boldsymbol{G}}(\boldsymbol{k}) \mid + n_0^2 \mid \widehat{\sigma}(\boldsymbol{k}) \rangle \langle \widehat{T}(\boldsymbol{k}) \mid \right]. \tag{54}$$

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

$$\rho(t) = \rho_0[1 + \mathcal{P}\Delta(t) + \mathcal{P}_\perp \Delta(t)]. \tag{55}$$

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

$$\begin{aligned} \frac{\partial \mathcal{P}\Delta(t)}{\partial t} &= -\mathcal{P}\mathcal{L}\mathcal{P}\Delta(t) - \mathcal{P}\mathcal{L}\mathcal{P}_\perp\Delta(t), && (56) \\ \frac{\partial \mathcal{P}_\perp\Delta(t)}{\partial t} &= -\mathcal{P}_\perp\mathcal{L}\mathcal{P}_\perp\Delta(t) - \mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(t), && (57) \end{aligned}$$

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

$$\mathcal{P}_\perp\Delta(t) = -\int_0^t d\tau\, e^{-\widehat{\mathcal{L}}(t-\tau)}\mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(\tau) + e^{-\widehat{\mathcal{L}}t}\mathcal{P}_\perp\Delta(0). \tag{58}$$

Now substitution into (56) gives

$$\begin{aligned} \frac{\partial \mathcal{P}\Delta(t)}{\partial t} &= -\mathcal{P}\mathcal{L}\mathcal{P}\Delta(t) + \int_0^t d\tau \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\widehat{\mathcal{L}}\tau}\mathcal{P}_\perp\mathcal{L}\mathcal{P}\Delta(t-\tau) \\ &\quad -\mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{-\widehat{\mathcal{L}}t}\mathcal{P}_\perp\Delta(0). \end{aligned} \tag{59}$$

Set $\overline{\boldsymbol{\psi}}(\boldsymbol{k},t) = \langle \Delta(t) \mid \boldsymbol{\psi}(\boldsymbol{k}) \rangle = \langle \psi(-\boldsymbol{k}) \mid \Delta(t) \rangle$. Using (50) and neglecting the last term in (59) one obtains

$$\begin{aligned} \frac{\partial \overline{\boldsymbol{\psi}}(\boldsymbol{k},t)}{\partial t} &= \overline{\boldsymbol{\phi}}(\boldsymbol{k},t) \circ \langle \boldsymbol{\psi}(\boldsymbol{k}) \mid \mathcal{L}\boldsymbol{\psi}(\boldsymbol{k}) \rangle \\ &\quad + \int_0^t d\tau \overline{\boldsymbol{\phi}}(\boldsymbol{k},t-\tau) \circ \langle \boldsymbol{\psi}(\boldsymbol{k}) \mid \mathcal{P}\mathcal{L}\mathcal{P}_\perp e^{\widehat{\mathcal{L}}\tau}\mathcal{P}_\perp\mathcal{L}\mathcal{P}\boldsymbol{\psi}(\boldsymbol{k}) \rangle. \end{aligned} \tag{60}$$

Next we have to introduce some further notation:

$$\Omega(\boldsymbol{k}) = \frac{-1}{ikV}\big\langle \boldsymbol{\psi}(\boldsymbol{k}) \,|\, \mathcal{L}\boldsymbol{\psi}(\boldsymbol{k})\big\rangle, \tag{61}$$

$$\mathcal{U}(\boldsymbol{k},t) = \frac{-1}{k^2V}\big\langle \boldsymbol{\psi}(\boldsymbol{k}) \,|\, \mathcal{L}\mathcal{P}_\perp e^{\widehat{\mathcal{L}}t}\mathcal{P}_\perp\mathcal{L}\boldsymbol{\psi}(\boldsymbol{k})\big\rangle. \tag{62}$$

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

$$\mathrm{J}(\boldsymbol{k}) = \frac{\mathcal{L}\boldsymbol{\psi}(\boldsymbol{k})}{-ik}, \tag{63}$$

which are called this way in view of the conservation laws[6]

$$\frac{d\psi_i(\boldsymbol{k})}{dt} = -i\boldsymbol{k}\cdot\boldsymbol{J}_i(\boldsymbol{k}). \tag{64}$$

In terms of these we have

$$\Omega(\boldsymbol{k}) = \frac{1}{V}\big\langle \boldsymbol{\psi}(\boldsymbol{k}) \,|\, \mathrm{J}(\boldsymbol{k})\big\rangle, \tag{65}$$

$$\mathcal{U}(\boldsymbol{k},t) = \frac{1}{V}\big\langle \mathrm{J}(\boldsymbol{k}) \,|\, e^{\widehat{\mathcal{L}}t}\mathrm{J}(\boldsymbol{k})\big\rangle. \tag{66}$$

We can now rewrite (60) in terms of the generalized hydrodynamic equations

$$\frac{\partial\overline{\boldsymbol{\psi}}(\boldsymbol{k},t)}{\partial t} = V\left[-ik\overline{\boldsymbol{\phi}}(\boldsymbol{k},t)\circ\Omega(\boldsymbol{k}) - k^2\int_0^t d\tau\,\overline{\boldsymbol{\phi}}(\boldsymbol{k},t-\tau)\circ\mathcal{U}(\boldsymbol{k},\tau)\right]. \tag{67}$$

The Laplace transform of this equation reads

$$z\tilde{\boldsymbol{\psi}}(\boldsymbol{k},z) = V\tilde{\boldsymbol{\phi}}(\boldsymbol{k},z)\circ\Omega\left[-ik\Omega(\boldsymbol{k}) - k^2\mathcal{U}(\boldsymbol{k},z)\right] + \overline{\boldsymbol{\psi}}(\boldsymbol{k},t=0). \tag{68}$$

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 $\lim_{\substack{\boldsymbol{k}\to 0\\ z\to 0^+}}\mathcal{U}(\boldsymbol{k},z)$ has to exist (and be positive definite!), just like in the case of the diffusion equation.

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[6] for the interpretation of (64) as a set of conservation laws it is crucial that the limit of $\mathrm{J}(\boldsymbol{k})$ for $\boldsymbol{k}\to 0$ exists, implying $d\boldsymbol{\psi}(0)/dt = 0$.

1.4.1 Specific form of the hydrodynamic equations

To appreciate that indeed (67,68) 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:

$$\begin{aligned}\mathcal{L} m\widehat{n}(\boldsymbol{k}) &= -i\boldsymbol{k}\cdot\widehat{\boldsymbol{G}}(\boldsymbol{k}), &(69)\\ \mathcal{L}\widehat{\boldsymbol{G}}(\boldsymbol{k}) &= -i\boldsymbol{k}\cdot\widehat{\mathsf{P}}(\boldsymbol{k}), &(70)\\ T_0\mathcal{L}\widehat{\sigma}(\boldsymbol{k}) &= -i\boldsymbol{k}\cdot\widehat{\boldsymbol{J}}_q(\boldsymbol{k}). &(71)\end{aligned}$$

Here $\widehat{\boldsymbol{G}}(\boldsymbol{k})$ was defined in (41). The Fourier components of the microscopic pressure tensor $\widehat{\mathsf{P}}(\boldsymbol{k})$ are defined as

$$\widehat{\mathsf{P}}(\boldsymbol{k}) = \sum_i \frac{\boldsymbol{p}_i\boldsymbol{p}_i}{m} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i} - \sum_{i<j} \frac{e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_i} - e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_j}}{i\boldsymbol{k}\cdot\boldsymbol{r}_{ij}} \boldsymbol{r}_{ij}\boldsymbol{F}_{ij}. \tag{72}$$

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

$$\widehat{p}(\boldsymbol{k}) = \mathcal{P}\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k}). \tag{73}$$

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

$$\langle \widehat{\sigma}(\boldsymbol{k}) \,|\, \widehat{p}(\boldsymbol{k})\rangle = 0 \tag{74}$$

plus

$$\lim_{k\to 0} \widehat{\sigma}(\boldsymbol{k}) = \frac{1}{n_0 T_0}\left[\widehat{\epsilon}(\boldsymbol{k}) - \frac{p_0+\epsilon_0}{n_0}\widehat{n}(\boldsymbol{k})\right]. \tag{75}$$

As shown in Appendix A this leads to

$$\widehat{\sigma}(\boldsymbol{k}) = \frac{1}{n_0 T_0}[\widehat{\epsilon}(\boldsymbol{k}) - h_0(\boldsymbol{k})\widehat{n}(\boldsymbol{k})], \tag{76}$$

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

$$\widehat{\boldsymbol{J}}_q(\boldsymbol{k}) = \frac{-T_0}{ik}\mathcal{L}\widehat{\sigma}(\boldsymbol{k}). \tag{77}$$

Notice that, thanks to (74), $\mathcal{P}\widehat{\boldsymbol{J}}_q = 0$. The matrix elements of $\mathcal{L}$ may now be worked out as

$$\begin{aligned}
\left\langle \widehat{n}(\boldsymbol{k}) \mid \mathcal{L}\widehat{n}(\boldsymbol{k}) \right\rangle &= \left\langle \widehat{n}(\boldsymbol{k}) \mid \mathcal{L}\widehat{\epsilon}(\boldsymbol{k}) \right\rangle = \left\langle \widehat{\epsilon}(\boldsymbol{k}) \mid \mathcal{L}\widehat{\epsilon}(\boldsymbol{k}) \right\rangle \\
&= \left\langle \widehat{\epsilon}(\boldsymbol{k}) \mid \mathcal{L}\widehat{n}(\boldsymbol{k}) \right\rangle = 0, && (78) \\
\left\langle \widehat{\boldsymbol{G}}(\boldsymbol{k}) \mid \mathcal{L}\widehat{\boldsymbol{G}}(\boldsymbol{k}) \right\rangle &= \boldsymbol{0}, && (79) \\
\left\langle \widehat{n}(\boldsymbol{k}) \mid \mathcal{L}\widehat{\boldsymbol{G}}(\boldsymbol{k}) \right\rangle &= \left\langle \widehat{\boldsymbol{G}}(\boldsymbol{k}) \mid \mathcal{L}\widehat{n}(\boldsymbol{k}) \right\rangle = -\frac{1}{m}\left\langle \widehat{\boldsymbol{G}}(\boldsymbol{k}) \mid i\boldsymbol{k}\cdot\widehat{\boldsymbol{G}}(\boldsymbol{k}) \right\rangle \\
&= \frac{-i\boldsymbol{k}Vn_0}{\beta_0}, && (80) \\
\left\langle \widehat{\boldsymbol{G}}(\boldsymbol{k}) \mid \mathcal{L}\widehat{\sigma}(\boldsymbol{k}) \right\rangle &= \left\langle \widehat{\sigma}(\boldsymbol{k}) \mid \mathcal{L}\widehat{\boldsymbol{G}}(\boldsymbol{k}) \right\rangle = i\boldsymbol{k}\left\langle \widehat{\sigma}(\boldsymbol{k}) \mid \widehat{p}(\boldsymbol{k}) \right\rangle = 0. && (81)
\end{aligned}$$

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

$$\frac{\partial\overline{n}(\boldsymbol{k},t)}{\partial t} = -\frac{i\boldsymbol{k}}{m}\cdot\overline{\boldsymbol{G}}(\boldsymbol{k},t) = -i\boldsymbol{k}\cdot n_0\boldsymbol{u}(\boldsymbol{k},t), \qquad (82)$$

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

$$\begin{aligned}
&\frac{\partial\overline{\boldsymbol{G}}(\boldsymbol{k},t)}{\partial t} = -i\boldsymbol{k}\overline{p}(\boldsymbol{k},t) \\
&-\frac{k^2}{n_0 m}\int_0^t d\tau \left[\eta(\boldsymbol{k},\tau)\overline{\boldsymbol{G}}(\boldsymbol{k},t-\tau) + \{\kappa(\boldsymbol{k},\tau) + \frac{1}{3}\eta(\boldsymbol{k},\tau)\}\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\cdot\overline{\boldsymbol{G}}(\boldsymbol{k},t-\tau)\right] \\
&-\frac{k^2 n_0\beta_0^2\hat{\boldsymbol{k}}}{V}\int_0^t d\tau \left\langle \mathcal{P}_\perp(\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k}) \mid e^{\widehat{\mathcal{L}}\tau}\mathcal{P}_\perp\hat{\boldsymbol{k}}\cdot\widehat{\boldsymbol{J}}_q(\boldsymbol{k}) \right\rangle k_B\overline{T}(\boldsymbol{k},t-\tau). \qquad (83)
\end{aligned}$$

Here the transport kernels η and κ are defined as

$$\begin{aligned}
\eta(\boldsymbol{k},t) &= \frac{\beta_0}{V}\left\langle \hat{\boldsymbol{k}}\hat{\boldsymbol{l}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k}) \mid e^{\widehat{\mathcal{L}}t}\hat{\boldsymbol{k}}\hat{\boldsymbol{l}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k}) \right\rangle, && (84) \\
\kappa(\boldsymbol{k},t) + \frac{2(d-1)}{d}\eta(\boldsymbol{k},t) &= \frac{\beta_0}{V}\left\langle \mathcal{P}_\perp\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k}) \mid e^{\widehat{\mathcal{L}}t}\mathcal{P}_\perp\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k}) \right\rangle, && (85)
\end{aligned}$$

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

$$\begin{aligned}
\frac{\partial\overline{\sigma}(\boldsymbol{k},t)}{\partial t} &= -\frac{k^2}{n_0 T_0}\int_0^t d\tau\, \lambda(\boldsymbol{k},\tau)\overline{T}(\boldsymbol{k},t-\tau) && (86) \\
&\quad -\frac{k_B\beta_0^2 k^2}{mn_0 V}\int_0^t d\tau \left\langle \mathcal{P}_\perp\hat{\boldsymbol{k}}\cdot\widehat{\boldsymbol{J}}_q(\boldsymbol{k}) \mid e^{\widehat{\mathcal{L}}\tau}\mathcal{P}_\perp\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k}) \right\rangle \hat{\boldsymbol{k}}\cdot\overline{\boldsymbol{G}}(\boldsymbol{k},t-\tau),
\end{aligned}$$

with

$$\lambda(\boldsymbol{k},t) \;=\; \frac{n_0^2 k_B \beta_0^2}{V}\left\langle \mathcal{P}_\perp \hat{\boldsymbol{k}}\cdot\widehat{\boldsymbol{J}}_q(\boldsymbol{k}) \,|\, e^{\widehat{\mathcal{L}}t}\mathcal{P}_\perp \hat{\boldsymbol{k}}\cdot\widehat{\boldsymbol{J}}_q(\boldsymbol{k})\right\rangle . \tag{87}$$

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

$$\boldsymbol{\mathcal{U}}(\boldsymbol{k},z) \;=\; \frac{1}{V}\left\langle \mathcal{P}_\perp \mathsf{J}(\boldsymbol{k}) \,|\, (z-\widehat{\mathcal{L}})^{-1}\mathcal{P}_\perp \mathsf{J}(\boldsymbol{k})\right\rangle \tag{88}$$

$$\mathcal{C}(\boldsymbol{k},z) \;=\; \frac{1}{V}\left\langle \mathcal{P}_\perp \mathsf{J}(\boldsymbol{k}) \,|\, (z-\mathcal{L})^{-1}\mathcal{P}_\perp \mathsf{J}(\boldsymbol{k})\right\rangle \tag{89}$$

one has the relationship

$$\boldsymbol{\mathcal{U}}(\boldsymbol{k},z) = \mathcal{C}(\boldsymbol{k},z)\left[\boldsymbol{I} + k^2\left\{\frac{\langle \boldsymbol{\psi}(\boldsymbol{k}) \mid \boldsymbol{\psi}(\boldsymbol{k})\rangle}{V} z + ik\Omega - k^2\mathcal{C}(\boldsymbol{k},z)\right\}^{-1}\mathcal{C}(\boldsymbol{k},z)\right] . \tag{90}$$

In the limit $\boldsymbol{k}\to 0$ $\boldsymbol{\mathcal{U}}$ 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,

$$\eta = \frac{\beta_0}{V}\int_0^\infty d\,t\left\langle \hat{\boldsymbol{k}}\hat{\boldsymbol{l}}{:}\mathsf{P}(0)\hat{\boldsymbol{k}}\hat{\boldsymbol{l}}{:}\mathsf{P}(t)\right\rangle , \tag{91}$$

$$\kappa = \frac{\beta_0}{V}\int_{-\infty}^\infty d\,t\,\langle\, \frac{1}{d}Tr[\mathsf{P}(0)] - \left(\frac{\partial p}{\partial e}\right)_n (H-\langle H\rangle) - \left(\frac{\partial p}{\partial n}\right)_e (N-\langle N\rangle) - pV\,| \tag{92}$$

$$\frac{1}{d}Tr[\mathsf{P}(t)] - \left(\frac{\partial p}{\partial e}\right)_n (H-\langle H\rangle) - \left(\frac{\partial p}{\partial n}\right)_e (N-\langle N\rangle) - pV\,\rangle\,. \tag{93}$$

Here $\mathsf{P}(t)$ is $\frac{1}{d}Tr\widehat{\mathsf{P}}(\boldsymbol{k}=0)$ evaluated as function of the particle coordinates at time t. In (93) we have used (73) and subtracted $pV = \langle\widehat{p}(\boldsymbol{k}=0)\rangle$. By combining Eqs. (87), (77), (74) and (69) one finds that the heat conduction coefficient becomes

$$\lambda \;=\; \frac{\beta_0}{dVT_0}\int_0^\infty d\,t\left\langle \boldsymbol{J}_e(0) - \frac{h_0}{m}\boldsymbol{G}| \cdot \boldsymbol{J}_e(t) - \frac{h_0}{m}\boldsymbol{G}\right\rangle . \tag{94}$$

Here the energy current is

$$\boldsymbol{J}_e(\Gamma) \;=\; \sum_i \epsilon_i \frac{\boldsymbol{p}_i}{m} + \frac{1}{2}\sum_{i<j}\left(\frac{\boldsymbol{p}_i}{m}\cdot\boldsymbol{F}_{ij}\right)\boldsymbol{r}_{ij} \tag{95}$$

and $\boldsymbol{G}$ is the total momentum.

1.4.2 Positivity of transport coefficients

For Re$(z) > 0$ the real parts of $\eta(\boldsymbol{k}, z)$, $\lambda(\boldsymbol{k}, z)$ and $\kappa(\boldsymbol{k}, z)+2(d-1)\eta(\boldsymbol{k}, z)/d$ 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[2] gives the following, more subtle argument: one has

$$I \equiv \langle \int_{-T}^{T} d\,t_1\, e^{\hat{\mathcal{L}} t_1} J(\boldsymbol{k}) e^{-i\omega t_1} \mid \int_{-T}^{T} d\,t_2\, e^{\hat{\mathcal{L}} t_2} J(\boldsymbol{k}) e^{-i\omega t_2} \,\rangle \geq 0. \tag{96}$$

Time translation invariance allows rewriting I as

$$I \;=\; T \int_0^{2T} d\,\tau \,\left(1 - \frac{\tau}{2T}\right) \left[\left\langle J(\boldsymbol{k}) \mid e^{\hat{\mathcal{L}}\tau} J(\boldsymbol{k}) \right\rangle e^{-i\omega\tau} + cc\right]. \tag{97}$$

Here $\tau = t_2 - t_1$ and an integration has been performed over $(t_1 + t_2)/2$. If $\left\langle J(\boldsymbol{k}) \mid e^{\hat{\mathcal{L}}\tau} J(\boldsymbol{k}) \right\rangle = o(1/\tau)$ for $\tau \to \infty$ the contribution of the term with $\tau/(2T)$ will vanish in the limit $T \to \infty$. In this case the remaining term approaches combinations such as $[\eta(k, i\omega) + \eta(k, -i\omega)]$. From (96) it follows that this is ≥ 0. The possibility that transport coefficients are 0 or infinite remains open! For both possibilities there exist ample examples.

1.4.3 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

$$\widehat{\rho}_l(\boldsymbol{k}) \equiv m_l \sum_{j=1}^{N_l} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_j}, \tag{98}$$

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

$$\chi_{ln}(\boldsymbol{k}) = \langle \widehat{\rho}_l(\boldsymbol{k}) \mid \widehat{\rho}_n(\boldsymbol{k}) \rangle \,; \qquad \chi_{le}(\boldsymbol{k}) = \langle \widehat{\rho}_l(\boldsymbol{k}) \mid \epsilon(\boldsymbol{k}) \rangle \tag{99}$$

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

$$\Omega_{lG} = \Omega_{Gl} = \rho_{l_0} k_B T_0, \tag{100}$$

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

$$\begin{aligned}
\frac{\partial \overline{\rho}_l(\boldsymbol{k},t)}{\partial t} &= -\frac{\rho_{l_0}}{\rho_0} i\boldsymbol{k} \cdot \overline{\boldsymbol{G}}(\boldsymbol{k},t) - k^2 \left[\sum_n L_{ln} \overline{\tilde{\nu}}_n(\boldsymbol{k},t) - L_{le} \overline{\beta}(\boldsymbol{k},t) \right] &(101)\\
\frac{\partial \overline{\epsilon}(\boldsymbol{k},t)}{\partial t} &= -\frac{p_0}{\rho_0} i\boldsymbol{k} \cdot \overline{\boldsymbol{G}}(\boldsymbol{k},t) - k^2 \left[\frac{1}{n_0} \lambda \overline{T}(\boldsymbol{k},t) + \sum_n L_{en} \overline{\tilde{\nu}}_n(\boldsymbol{k},t) \right] &(102)\\
\frac{\partial \overline{\boldsymbol{G}}(\boldsymbol{k},t)}{\partial t} &= -ik\overline{p}(\boldsymbol{k},t) - k^2 \left[\eta \overline{\boldsymbol{G}}(\boldsymbol{k},t) + (\kappa + \frac{d-2}{d}\eta) \hat{\boldsymbol{k}}\hat{\boldsymbol{k}} \boldsymbol{:} \overline{\boldsymbol{G}}(\boldsymbol{k},t) \right] &(103)
\end{aligned}$$

Here the *Onsager coefficients* were introduced, defined as

$$\begin{aligned}
L_{ln} &= \lim_{\boldsymbol{k}\to 0} \frac{-1}{k^2} \int_0^\infty dt \, \left\langle \mathcal{P}_\perp \mathcal{L} \rho_l(\boldsymbol{k}) \,|\, e^{\mathcal{L}t} \mathcal{P}_\perp \mathcal{L} \rho_n(\boldsymbol{k}) \right\rangle , \\
&= \frac{1}{d} \int_0^\infty dt \, \langle \boldsymbol{J}_l(0) \cdot \boldsymbol{J}_n(t) \rangle , &(104)\\
L_{le} &= \frac{1}{d} \int_0^\infty dt \, \langle \boldsymbol{J}_l(0) \cdot \boldsymbol{J}_q(t) \rangle , &(105)\\
L_{el} &= \frac{1}{d} \int_0^\infty dt \, \langle \boldsymbol{J}_q(0) \cdot \boldsymbol{J}_l(t) \rangle . &(106)
\end{aligned}$$

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

$$\boldsymbol{J}_l = \sum_{j=1}^{N_l} \boldsymbol{p}_j - \frac{\rho_{l_0}}{\rho_0} \boldsymbol{G}. \tag{107}$$

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. (104-106) and (107) one obtains the relationships

$$\sum_l L_{ln} = \sum_n L_{ln} = 0, \tag{108}$$

$$\sum_l L_{le} = \sum_l L_{el} = 0. \tag{109}$$

1.4.4 Onsager relations

Onsager was the first one to note the symmetry relations

$$L_{ln} = L_{nl}, \tag{110}$$

$$L_{le} = L_{el}. \tag{111}$$

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;

$$\mathcal{T} f(\boldsymbol{r}_1 \cdots \boldsymbol{r}_N, \boldsymbol{p}_1 \cdots \boldsymbol{p}_N) = f(\boldsymbol{r}_1 \cdots \boldsymbol{r}_N, -\boldsymbol{p}_1 \cdots - \boldsymbol{p}_N). \tag{112}$$

Obviously $\mathcal{T}^2 = 1$ and for a Hamiltonian that is even in the momenta[7] one has

$$\mathcal{T}\mathcal{L}\mathcal{T} = -\mathcal{L}, \tag{113}$$

$$\mathcal{T} e^{\mathcal{L}t}\mathcal{T} = e^{-\mathcal{L}t}. \tag{114}$$

On the basis of this, one obtains

$$\begin{aligned} \left\langle J_1 \,|\, e^{\mathcal{L}t} J_2 \right\rangle &= \left\langle \mathcal{T} J_1 \,|\, \mathcal{T} e^{\mathcal{L}t} \mathcal{T}\mathcal{T} J_2 \right\rangle, \\ &= \left\langle \mathcal{T} J_1 \,|\, e^{-\mathcal{L}t} \mathcal{T} J_2 \right\rangle, \\ &= \left\langle \mathcal{T} J_2 \,|\, e^{\mathcal{L}t} \mathcal{T} J_1 \right\rangle. \end{aligned} \tag{115}$$

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 $\boldsymbol{p}_i$ by $-\boldsymbol{p}_i$ in the equilibrium average $\langle\rangle$. This is the basis of all the Onsager symmetries contained in (104-105).

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[7] This 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.

1.5 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.

1.5.1 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

$$\begin{aligned} \boldsymbol{j}_{el} &= -\sigma\nabla\Phi, \quad (116)\\ \boldsymbol{j}_{diff} &= -De_t\nabla n_t, \quad (117) \end{aligned}$$

with Φ the Coulomb potential, e_t the charge of a tracer particle and $n_t(\boldsymbol{r}, t)$ 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

$$Z(T, V, N_i, \phi_i) = \exp(-\sum_i N_i\beta\phi_i)Z(T, V, N_i), \quad (118)$$

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

$$\mu_i(T, V, N_i, \phi_i) = \frac{\partial(-k_BT\ln Z)}{\partial N_i} = \phi_i + \tilde{\mu}_i(T, V, N_i), \quad (119)$$

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 relationship[8]

$$\mu_i(T(\boldsymbol{r}), n_i(\boldsymbol{r}), \phi_i(\boldsymbol{r})) = \phi_i(\boldsymbol{r}) + \tilde{\mu}_i(T, n_i(\boldsymbol{r})). \tag{120}$$

In an equilibrium system μ_i should be uniform, hence

$$\nabla\tilde{\mu}_i(T, n_i(\boldsymbol{r})) = -\nabla\phi_i(\boldsymbol{r}). \tag{121}$$

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

$$\nabla\tilde{\mu}_t = \frac{\partial\mu_t}{\partial n_t}\nabla n_t. \tag{122}$$

Substitution of (120-121) into (116-117), using $\phi_t = e_t\Phi$, and requiring the vanishing of the sum of these currents leads to the Einstein relation

$$\frac{\sigma}{e_t^2} = D\left(\frac{\partial n_t}{\partial\mu_t}\right)_{T,n_b}. \tag{123}$$

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

$$\begin{aligned}\Xi(\mu_t, \mu_b, T, V) &= \Xi_0(\mu_b, T, V)\left[1 + \sum_{n_t=1}^{\infty}\exp n_t\beta\mu_t\frac{\Delta(\mu_b, T, V)^{n_t}}{n_t!}\right] \\ &= \Xi_0\exp\{\exp[\beta\mu_t]\Delta(\mu_b, T, V)\},\end{aligned} \tag{124}$$

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

$$n_t = \frac{1}{V}\frac{(\partial k_B T\log\Xi)}{\partial\mu_t} = \exp[\beta\mu_t]\Delta(\mu_b, T, V), \tag{125}$$

leading to the identity

$$\left(\frac{\partial n_t}{\partial\mu_t}\right)_{T,n_b} = \beta n_t, \tag{126}$$

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[8] Adequate generalizations are also known in the case of strong gradients[11].

solved by $n_t = C \exp \beta\mu_t$. Substituting this into the Einstein relation (123) one obtains

$$\sigma = \frac{n_t e_t^2 D}{k_B T}. \tag{127}$$

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

$$H = H_0 + \Delta H(t) \tag{128}$$

with $\Delta H(t) = e_t \sum_{j=1}^{\langle N_t \rangle} \Phi(\boldsymbol{r}_j, t) = \frac{e_t}{V} \sum_{\boldsymbol{k}} \Phi(\boldsymbol{k}, t) n_t(-\boldsymbol{k}, t)$ 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

$$\mathcal{L} = \mathcal{L}_0 + \Delta\mathcal{L}(t), \tag{129}$$

$$\rho = \rho_0(1 + \Delta(t)), \tag{130}$$

$$\frac{\partial \rho}{\partial t} = -(\mathcal{L}_0 + \Delta\mathcal{L}(t))\rho. \tag{131}$$

Linearization of the Liouville equation yields

$$\frac{\partial \Delta(t)}{\partial t} = -\mathcal{L}_0 \Delta(t) - \Delta\mathcal{L}(t) \log \rho_0. \tag{132}$$

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

$$\Delta(t) = \mathcal{P}\Delta(t) + \mathcal{P}_\perp \Delta(t) \tag{133}$$

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

$$\mathcal{P}_\perp \Delta(t) = -\int_0^t d\tau\, e^{-\hat{\mathcal{L}}_0(t-\tau)} \left[\mathcal{P}_\perp \mathcal{L}_0 \mathcal{P}\Delta(\tau) + \mathcal{P}_\perp \Delta\mathcal{L}(\tau) \log \rho_0\right], \tag{134}$$

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

$$\begin{aligned} \frac{\partial \mathcal{P}\Delta(t)}{\partial t} &= -\mathcal{P}\mathcal{L}_0 \mathcal{P}\Delta(t) - \mathcal{P}\Delta\mathcal{L} \log \rho_0 \\ &\quad + \int_0^t d\tau\, \mathcal{P}\mathcal{L}_0 \mathcal{P}_\perp \exp(-\hat{\mathcal{L}}_0 \tau) \left[\mathcal{P}_\perp \mathcal{L}_0 \mathcal{P}\Delta(t-\tau) + \mathcal{P}_\perp \Delta\mathcal{L}(t-\tau) \log \rho_0\right]. \end{aligned} \tag{135}$$

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

$$\begin{aligned} \mathcal{P} &= \frac{1}{\langle\langle N_t\rangle\rangle}\sum_{\boldsymbol{k}} \mid n_t(\boldsymbol{k})\ \rangle\ \langle\ n_t(\boldsymbol{k}) \mid, && (136)\\ \Delta\mathcal{L}(t) &= \sum_j e_t\boldsymbol{E}(\boldsymbol{r}_j,t)\cdot\frac{\partial}{\partial\boldsymbol{p}_j}, && (137)\end{aligned}$$

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

$$\begin{aligned} \Delta\mathcal{L}(t)\log\rho_0 &= -\sum_{j=1}^{N_t}\frac{\beta\boldsymbol{p}_j}{m}\cdot e_t\boldsymbol{E}(\boldsymbol{r}_j,t),\\ &= -\beta\int d\boldsymbol{r}\,\boldsymbol{j}_t(\boldsymbol{r})\cdot e_t\boldsymbol{E}(\boldsymbol{r},t),\\ &= -\frac{\beta}{V}\sum_{\boldsymbol{k}}\boldsymbol{j}_t(\boldsymbol{k})\cdot e_t\boldsymbol{E}(-\boldsymbol{k},t), && (138)\end{aligned}$$

with $\boldsymbol{j}_t(\boldsymbol{r}) = \sum_{i=1}^{N_t}(\boldsymbol{p}_i/m_t)\delta(\boldsymbol{r}-\boldsymbol{r}_i)$. In the case of tracer diffusion $\mathcal{P}\Delta\mathcal{L}\log\rho_0$ vanishes. Inserting (136) and (138) into (136) we obtain

$$\begin{aligned} \frac{\partial\mathcal{P}\Delta(t)}{\partial t} &= \sum_{\boldsymbol{k}}\int_0^t d\tau\,\frac{\mid n_t(\boldsymbol{k})\ \rangle}{\langle N_t\rangle}\ \frac{\langle\ \hat{\boldsymbol{k}}\cdot\boldsymbol{j}_t(\boldsymbol{k}) \mid \exp(-\hat{\mathcal{L}}_0\tau)\hat{\boldsymbol{k}}\cdot\boldsymbol{j}_t(\boldsymbol{k})\ \rangle}{\langle N_t\rangle}\\ &\qquad\left[-k^2\left\langle n_t(\boldsymbol{k})\mid\Delta(t-\tau)\right\rangle - \frac{\beta\langle N_t\rangle}{V}e_t i\boldsymbol{k}\cdot\boldsymbol{E}(-\boldsymbol{k},t-\tau)\right] && (139)\end{aligned}$$

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

$$\begin{aligned} \frac{\partial\overline{n}_t(\boldsymbol{k},t)}{\partial t} &= \left\langle\frac{\partial\mathcal{P}\Delta(t)}{\partial t}\middle| n_t(\boldsymbol{k})\right\rangle\\ &= \int_0^t d\tau\,\boldsymbol{\mathcal{U}}(\boldsymbol{k},\tau)\left[-k^2\overline{n}_t(\boldsymbol{k},t-\tau) + \beta e_t n_{t_0} i\boldsymbol{k}\cdot\boldsymbol{E}(\boldsymbol{k},t-\tau)\right]. && (140)\end{aligned}$$

The Laplace transform of this reads

$$z\overline{n}_t(\boldsymbol{k}, z) \quad = \quad \tilde{U}(\boldsymbol{k}, z)\left[-k^2\overline{n}_t(\boldsymbol{k}, z) + \beta e_t n_{t_0} i\boldsymbol{k}\cdot\tilde{\boldsymbol{E}}(\boldsymbol{k}, z)\right] + n_t(\boldsymbol{k}.t = 0). \tag{141}$$

1.5.2 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 (138) this immediately follows as

$$\mathcal{P}\Delta\mathcal{L}\log\rho_0 \quad = \quad \frac{\beta}{M} i\boldsymbol{k}\cdot\boldsymbol{G}(\boldsymbol{k})\sum_l\left[n_{l_0}\phi_l(-\boldsymbol{k}, t)\right], \tag{142}$$

with M the average total mass. This contributes an external force term to the Navier-Stokes equations. Furthermore, as follows from (139), 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

$$\frac{\partial\overline{\rho}(\boldsymbol{k}, t)}{\partial t} \quad = \quad -i\boldsymbol{k}\cdot\overline{\boldsymbol{G}}(\boldsymbol{r}, t), \tag{143}$$

$$\begin{aligned}\frac{\partial\overline{\boldsymbol{G}}(\boldsymbol{k}, t)}{\partial t} \quad = \quad & -i\boldsymbol{k}\left[\overline{p}(\boldsymbol{k}, t) + \sum_l n_{l_0}\phi_l(\boldsymbol{k}, t)\right] \\ & -\frac{k^2}{n_0 m}\int_0^t d\tau\,\left[\eta(\boldsymbol{k}, \tau)\overline{\boldsymbol{G}}(\boldsymbol{k}, t-\tau) + \{\kappa(\boldsymbol{k}, \tau) + \frac{d-2}{d}\eta(\boldsymbol{k}, \tau)\}\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\cdot\overline{\boldsymbol{G}}(\boldsymbol{k}, t-\tau)\right] \\ & -\frac{k^2 n_0\beta_0^2\hat{\boldsymbol{k}}}{V}\int_0^t d\tau\,\left\langle\mathcal{P}_\perp(\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k})\,|\,e^{\widehat{\mathcal{L}}\tau}\mathcal{P}_\perp\hat{\boldsymbol{k}}\cdot\widehat{\boldsymbol{J}}_q(\boldsymbol{k})\right\rangle k_B\overline{T}(\boldsymbol{k}, t-\tau).\end{aligned} \tag{144}$$

$$\begin{aligned}\frac{\partial\overline{\sigma}(\boldsymbol{k}, t)}{\partial t} \quad = \quad & -\frac{k^2}{n_0 T_0}\int_0^t d\tau\,\left[\lambda(\boldsymbol{k}, \tau)\overline{T}(\boldsymbol{k}, t-\tau) + \sum_l L_{el}(\boldsymbol{k}, \tau)\left[\overline{\tilde{\nu}}_l(\boldsymbol{k}, t-\tau) + \beta\phi_l(\boldsymbol{k}, t-\tau)\right]\right] \\ & -\frac{k_B\beta_0^2 k^2}{m n_0 V}\int_0^t d\tau\,\left\langle\mathcal{P}_\perp\hat{\boldsymbol{k}}\cdot\widehat{\boldsymbol{J}}_q(\boldsymbol{k})\,|\,e^{\widehat{\mathcal{L}}\tau}\mathcal{P}_\perp\hat{\boldsymbol{k}}\hat{\boldsymbol{k}}\boldsymbol{:}\widehat{\mathsf{P}}(\boldsymbol{k})\right\rangle\hat{\boldsymbol{k}}\cdot\overline{\boldsymbol{G}}(\boldsymbol{k}, t-\tau),\end{aligned} \tag{145}$$

$$\begin{aligned}\frac{\partial\overline{\rho}_l(\boldsymbol{k}, t)}{\partial t} \quad - \quad & \frac{\rho_{l_0}}{\rho_0}\frac{\partial\overline{\rho}(\boldsymbol{k}, t)}{\partial t} = -k^2\int_0^t d\tau\,\sum_n L_{ln}(\boldsymbol{k}, \tau)\left[\overline{\tilde{\nu}}_n(\boldsymbol{k}, t-\tau) + \beta\phi_n(\boldsymbol{k}, t-\tau)\right] \\ & +k^2\int_0^t d\tau\, L_{le}(\boldsymbol{k}, \tau)\overline{\beta}(\boldsymbol{k}, t-\tau).\end{aligned} \tag{146}$$

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