Microscopic Theory III: The Hydrodynamic Equations

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1 Microscopic Derivation

1.1 Local Equilibrium

- The basic idea of the local equilibrium ensemble is that every point in the system at a particular time can be described by an equilibrium ensemble.
- Each point of system is coarse-grained in the sense that it represents a region large enough to define local thermodynamic quantities, such as temperature and chemical potential.
- These thermodynamic quantities vary little over the length scale of the coarse graining.
- In an equilibrium system, the ensemble is constructed to give the proper total number $\langle N\rangle$, total momentum $\langle P\rangle$ (usually taken to be zero), and energy $\langle H\rangle$.
- If we require that the average over the probability density for this local equilibrium ensemble must give the correct values of the local mass (or number) density $n(\mathbf{r},t)$, momentum density $\mathbf{p}(\mathbf{r},t)$ and energy density $e(\mathbf{r},t)$.
- To generalize this to non-uniform, non-equilibrium systems, we define the appropriate densities for the above quantities:

$$\begin{aligned}
N(\mathbf{r}) &= \sum_{i=1}^{N} \delta(\mathbf{r}-\mathbf{r}_i) \\
\mathbf{P}(\mathbf{r}) &= \sum_{i=1}^{N} \mathbf{p}_i \delta(\mathbf{r}-\mathbf{r}_i) \\
E(\mathbf{r}) &= \sum_{i=1}^{N} e_i \delta(\mathbf{r}-\mathbf{r}_i) \quad \text{with} \quad e_i = \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{2m} + \sum_{j<i} U(|\mathbf{r}_{ij}|).
\end{aligned}$$

- We will require that the distribution function yields the correct average $\langle\cdots\rangle_L$ of these quantites, defined in a set $A(\mathbf{r}) = \{N(\mathbf{r}), \mathbf{P}(\mathbf{r}), E(\mathbf{r})\}$, at some initial time:

$$a(\mathbf{r}) \;=\; \overline{A(\mathbf{r})} = \langle A(\mathbf{r})\rangle_L\,.$$

- Applying the variational method of Gibbs to maximize the entropy subject to these constraints gives the distribution function:

$$\rho_L(\mathbf{r}^{(N)},\mathbf{p}^{(N)}) = \frac{\rho(\mathbf{r}^{(N)},\mathbf{p}^{(N)})\exp[A(\mathbf{r})*\phi(\mathbf{r})]}{\sum_{N=0}\int d\mathbf{r}^{(N)}d\mathbf{p}^{(N)}\,\rho(\mathbf{r}^{(N)},\mathbf{p}^{(N)})\exp[A(\mathbf{r})*\phi(\mathbf{r})]},$$

where ρ is the Grand Canonical distribution function, $A(\mathbf{r}) * B(\mathbf{r}) = \int_V d\mathbf{r}\, A(\mathbf{r}) \cdot \mathbf{B}(\mathbf{r})$, and $\phi(\mathbf{r})$ are Lagrange multipliers related to the constraint conditions.

- The Lagrange multipliers can be written as:

$$\begin{aligned}
\phi_n(\mathbf{r}) &= \beta(\mathbf{r}) \left[\mu(\mathbf{r}) - \frac{mv^2(\mathbf{r})}{2} \right] - \beta\mu^0 \\
\phi_e(\mathbf{r}) &= \beta - \beta(\mathbf{r}) \\
\phi_p(\mathbf{r}) &= \beta\mathbf{v}(\mathbf{r}),
\end{aligned}$$

  where $\beta(\mathbf{r}) = [k_B T(\mathbf{r})]^{-1}$, and $T(\mathbf{r})$, $\mu(\mathbf{r})$ and $\mathbf{v}(\mathbf{r})$ are the local temperature, chemical potential and velocity field.

- In equilibrium, the conjugate thermodynamic forces $\phi(\mathbf{r})$ vanish as the local thermodynamic quantities approach their equilibrium values.

- One can also write the local equilibrium distribution function as:

$$\begin{aligned}
\rho_L(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) &= \frac{1}{\Xi_L} \exp\left\{ - \int d\mathbf{r}\, \beta(\mathbf{r}) \left[E(\mathbf{r}) - \mathbf{v}(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}) - \psi(\mathbf{r}) N(\mathbf{r}) \right] \right\} \\
&= \frac{1}{\Xi_L} \exp\left\{ - \int d\mathbf{r}\, \beta(\mathbf{r}) \left[E^+(\mathbf{r}) - \mu(\mathbf{r}) N(\mathbf{r}) \right] \right\},
\end{aligned}$$

  where Ξ_L is a normalization factor, $\psi(\mathbf{r}) = \mu(\mathbf{r}) - mv^2(\mathbf{r})/2$, and we have introduced the internal energy density $E^+(\mathbf{r})$ defined to be the energy density in the stationary ensemble. To obtain this, we have used the fact that we can write:

$$\begin{aligned}
\mathbf{p}_j^+ &= \mathbf{p}_j - m\mathbf{v}(\mathbf{r}_j) \qquad \mathbf{P}^+(\mathbf{r}) = \sum_j \mathbf{p}_j^+ \delta(\mathbf{r} - \mathbf{r}_j) \\
\mathbf{P}(\mathbf{r}) &= \mathbf{P}^+(\mathbf{r}) + m\mathbf{v}(\mathbf{r}) N(\mathbf{r}) \\
E(\mathbf{r}) &= E^+(\mathbf{r}) + \mathbf{v}(\mathbf{r}) \cdot \mathbf{P}^+(\mathbf{r}) + \frac{m}{2} v^2(\mathbf{r}) N(\mathbf{r}).
\end{aligned}$$

- Note that at the initial time, since $\langle P^+(\mathbf{r}) \rangle = 0$,

$$\begin{aligned}
\langle \mathbf{P}(\mathbf{r}) \rangle_L &= m\mathbf{v}(\mathbf{r}) \langle N(\mathbf{r}) \rangle_L \\
\langle E(\mathbf{r}) \rangle_L &= \langle E^+(\mathbf{r}) \rangle_L + \frac{m}{2} v^2(\mathbf{r}) \langle N(\mathbf{r}) \rangle_L .
\end{aligned}$$

- Also note that if the thermodynamic forces are small, we can expand the local equilibrium distribution to obtain:

$$\rho_L(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) = \rho(\mathbf{r}^{(N)}, \mathbf{p}^{(N)}) \left(1 + \int d\mathbf{r} \hat{A}(\mathbf{r}) \cdot \phi(\mathbf{r}) + \cdot \right)$$

  where $\hat{A}(\mathbf{r}) = A(\mathbf{r}) - \langle A(\mathbf{r}) \rangle$ are the fluctuations of the set of hydrodynamic densities $A(\mathbf{r})$ from their *equilibrium* values.

- The evolution of the hydrodynamic variables can be written as

$$\begin{aligned}
\hat{A}_\alpha(\mathbf{r},t) &= e^{\mathcal{L}t}\hat{A}_\alpha(\mathbf{r}) \\
\delta a_\alpha(\mathbf{r},t) &= \overline{A}_\alpha(\mathbf{r},t) = \int d\mathbf{r}^{(N)}d\mathbf{p}^{(N)}\,\rho(0)e^{\mathcal{L}t}\hat{A}_\alpha(\mathbf{r}) \\
&= \int d\mathbf{r}^{(N)}d\mathbf{p}^{(N)}\,\rho_L\,e^{\mathcal{L}t}\hat{A}_\alpha(\mathbf{r}) \\
&\approx \langle A(\mathbf{r},t)\rangle - \langle A(\mathbf{r})\rangle + \int d\mathbf{r}'\,\left\langle \hat{A}(\mathbf{r},t)\hat{A}(\mathbf{r}')\right\rangle \cdot \phi(\mathbf{r}') \\
&= \left\langle \hat{A}(\mathbf{r},t)\hat{A}(\mathbf{r}')\right\rangle * \phi(\mathbf{r}')
\end{aligned}$$

  where we have assumed that the initial distribution function is of local equilibrium form.

- Thus we see that the time behavior of the non-equilibrium average is *identical* to that of fluctuations of correlation functions in equilibrium. These are easier to analyze.

1.2 Equilibrium Correlation Functions

- We are interested in evaluating time-dependent correlation functions of fluctuations of the hydrodynamic densities about their equilibrium values at times and length-scales that are coarse-grained: i.e. long compared to microscopic time and length scales.

- **POSTULATE:** The long-time dynamics of the correlation functions can be expressed in terms of a set of slow modes of the system that are well-separated in their time scale of evolution from all other dynamical variables of the system.
  - We will focus on the dynamics of these slow modes, and how they determine the long-time behavior of all dynamical variables of the system.

- We can express the length constraint by focusing on the small k values Fourier transform of the densities $A(\mathbf{k})$ and their fluctuations $\hat{A}(\mathbf{k})$.
  - Note that the $k = 0$ limit of these densities corresponds to the total number N, total momentum $\mathbf{P}$, and total energy $E = H$ of the system, all of which are conserved by the dynamics.
  - This implies that $\lim_{k\to 0}\dot{A}(\mathbf{k}) = 0$, and we expect that $\dot{A}(\mathbf{k}) \sim \mathbf{k}$.
  - Thus, for small values of $k < k_c$, $\dot{A}(\mathbf{k})$ *must be small.*
  - The minimal set of slow modes for dynamics on long length scales *must include* the 5 hydrodynamic densities.
  - Any other density of a constant of the motion must also be included.
  - Other slow variables must be specified by *physical arguments* as being relevant on long time scales under the conditions of the system: Simple examples include slow vibrational modes of molecules or the director of long molecules in high density.

- We will take the basis set of slow variables to be the simplest possible set, namely $A(\mathbf{k})$.

- We extract the slow component of any dynamical variable $B(\mathbf{k})$ by projecting it onto the slow basis set with a projection operator:

$$\mathcal{P}B(\mathbf{k}) = \left\langle B(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \hat{\mathbf{A}}(\mathbf{k}).$$

  - The slow part of the evolution of $B^s(\mathbf{k},t)$ arises due to the evolution of the projection onto the slow basis set:

$$B^s(\mathbf{k},t) \;=\; \left\langle B(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \hat{\mathbf{A}}(\mathbf{k},t).$$

  - Thus it is clear we need to describe the time evolution of our slow basis set.

- The Liouville equation and our favorite operator identity are used to obtain the equation of motion of our slow set:
  - We define the random fluctuations $\mathbf{K}(\mathbf{k},t)$ by

$$\mathbf{K}(\mathbf{k},t) \;=\; e^{(1-\mathcal{P})\mathcal{L}t}(1-\mathcal{P})\mathcal{L}\hat{\mathbf{A}}(\mathbf{k}) = e^{\mathcal{Q}\mathcal{L}t}\mathcal{Q}\mathcal{L}\hat{\mathbf{A}}(\mathbf{k}).$$

    which has the properties

$$\begin{aligned}
\langle \mathbf{K}(\mathbf{k},t)\rangle &= \langle \mathbf{K}(\mathbf{k},0)\rangle = \left\langle \dot{A}(\mathbf{k})\right\rangle - \left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \left\langle \hat{A}(\mathbf{k})\right\rangle = 0 \\
\langle \mathbf{K}(\mathbf{k},t)\mathbf{A}(\mathbf{k})^*\rangle &= \left\langle \mathbf{K}(\mathbf{k},t)\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle - \langle \mathbf{K}(\mathbf{k},t)\mathbf{A}(\mathbf{k})^*\rangle = 0 \\
\mathbf{K}(\mathbf{k},0) &= \mathcal{Q}\dot{A}(\mathbf{k}) = \dot{A}(\mathbf{k}).
\end{aligned}$$

  - Our often-used operator identity gives

$$e^{\mathcal{L}t}\mathcal{Q}\mathcal{L}\hat{\mathbf{A}}(\mathbf{k}) \;=\; \mathbf{K}(\mathbf{k},t) + \int_0^\infty d\tau\, e^{\mathcal{L}(t-\tau)}\mathcal{P}\mathcal{L}\mathbf{K}(\mathbf{k},\tau).$$

  - Inserting this relation in:

$$\dot{A}(\mathbf{k},t) \;=\; e^{\mathcal{L}t}(\mathcal{P}+\mathcal{Q})\mathcal{L}\hat{\mathbf{A}}(\mathbf{k})$$

    yields the exact equation

$$\begin{aligned}
\dot{A}(\mathbf{k},t) &= \left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \hat{A}(\mathbf{k},t) \\
&\quad + \int_0^\infty d\tau\, e^{\mathcal{L}(t-\tau)} \left\langle \mathcal{L}\mathbf{K}(\mathbf{k},\tau)\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \hat{A}(\mathbf{k}) + \mathbf{K}(\mathbf{k},t) \\
&= \left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \hat{A}(\mathbf{k},t) \\
&\quad + \int_0^\infty d\tau\, \left\langle \mathcal{L}\mathbf{K}(\mathbf{k},\tau)\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \hat{A}(\mathbf{k},t-\tau) + \mathbf{K}(\mathbf{k},t) \\
&= \left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \cdot \hat{A}(\mathbf{k},t) \\
&\quad - \int_0^\infty d\tau\, \left\langle \mathbf{K}(\mathbf{k},\tau)\dot{A}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \hat{A}(\mathbf{k},t-\tau) + \mathbf{K}(\mathbf{k},t)
\end{aligned}$$

  - The first term is called the *Euler* term, and it is proportional to k.
  - The second term is called the *Dissipative* term, and it is proportional to k^2.
  - The third term is the *fluctuating force* term.

- To obtain an equation for the equilibrium correlation function, we multiply by $\hat{\mathbf{A}}(\mathbf{k})^*$ and average over the equilibrium probability density to obtain

$$\begin{aligned}\left\langle \dot{\mathbf{A}}(\mathbf{k},t)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle &= \left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle^{-1} \cdot \left\langle \hat{A}(\mathbf{k},t)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \\ &\quad - \int_0^\infty d\tau \, \langle \mathbf{K}(\mathbf{k},\tau)\mathbf{K}(\mathbf{k})^* \rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \hat{A}(\mathbf{k},t-\tau)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle\end{aligned}$$

  where we have used the properties of the fluctuating force.

- The equations involve a time convolution, that is simply expressed by taking the Laplace transform:

$$\begin{aligned}z\left\langle \mathbf{A}(\mathbf{k},z)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle - \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle &= \left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle^{-1} \cdot \left\langle \hat{A}(\mathbf{k},z)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \\ &\quad - \langle \mathbf{K}(\mathbf{k},z)\mathbf{K}(\mathbf{k})^* \rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \hat{A}(\mathbf{k},z)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle\end{aligned}$$

- We can define the Euler and Dissipative parts of the hydrodynamic matrix $\mathbf{M}(\mathbf{k},z)$ according to

$$\begin{aligned}\mathbf{M}^E(\mathbf{k}) &= \left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle^{-1} \\ \mathbf{M}^D(\mathbf{k},z) &= -\int_0^\infty dt \, e^{-zt} \, \langle \mathbf{K}(\mathbf{k},t)\mathbf{K}(\mathbf{k})^* \rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle^{-1} \\ &= -\langle \mathbf{K}(\mathbf{k},z)\mathbf{K}(\mathbf{k})^* \rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle^{-1}\end{aligned}$$

- Solving the Laplace transform equation gives

$$\begin{aligned}\left\langle \mathbf{A}(\mathbf{k},z)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle &= \left[z\mathbf{I} - \mathbf{M}(\mathbf{k},z)\right]^{-1} \cdot \left\langle \mathbf{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \\ G_{\mathbf{AA}}(\mathbf{k},z) &= \left\langle \mathbf{A}(\mathbf{k},z)\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \mathbf{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle^{-1} = \left[z\mathbf{I} - \mathbf{M}(\mathbf{k},z)\right]^{-1}.\end{aligned}$$

1.3 The Euler Matrix

- Let us examine the contribution of the Euler part $\mathbf{M}^E(\mathbf{k})$ to the hydrodynamic matrix.
- Note that the matrix requires evaluation of the static correlation function $\left\langle \dot{A}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle^{-1}$ and therefore the time derivatives of the densities $\hat{\mathbf{A}}(\mathbf{k})$.
- Let us consider them individually:

$$\begin{aligned}\dot{\hat{N}}(\mathbf{k}) &= \sum_{j=1}^N \frac{d}{dt} e^{i\mathbf{k}\cdot\mathbf{r}_j} - \frac{d}{dt}\langle N \rangle \, \delta_{k,0} \\ &= \sum_{j=1}^N i\mathbf{k}\cdot\dot{\mathbf{r}}_j e^{i\mathbf{k}\cdot\mathbf{r}_j} = i\mathbf{k}\cdot\sum_{j=1}^N \frac{\mathbf{p}_j}{m} e^{i\mathbf{k}\cdot\mathbf{r}_j} \\ &= \frac{i\mathbf{k}}{m}\cdot\mathbf{P}(\mathbf{k}).\end{aligned}$$

  - If we choose $\hat{\mathbf{k}} = \hat{\mathbf{z}}$, then $\hat{\mathbf{k}}\cdot\mathbf{P}(\mathbf{k}) = P^z(\mathbf{k})$.

  - Recall that the set $\mathbf{A}(\mathbf{k})$ is $\{\hat{N}(\mathbf{k}), \hat{E}(\mathbf{k}), \mathbf{P}(\mathbf{k})\}$, so $\left\langle \dot{N}(\mathbf{k})\mathbf{A}_\alpha(\mathbf{k})^*\right\rangle = \left\langle \dot{N}(\mathbf{k})P^z(\mathbf{k})^*\right\rangle \delta_{\alpha,P^z}$, and

$$\left\langle \dot{N}(\mathbf{k})\mathbf{A}_\alpha(\mathbf{k})^*\right\rangle = \frac{ik}{m}\left\langle P^z(\mathbf{k})P^z(\mathbf{k})^*\right\rangle \delta_{\alpha P^z} = \frac{ik\,m}{\beta}\,\delta_{\alpha,P^z}.$$

- Thus, we can conclude

$$\mathbf{M}^E_{NN}(\mathbf{k}) = 0 \qquad \mathbf{M}^E_{NP}(\mathbf{k}) = i\mathbf{k} \qquad \mathbf{M}^E_{NE}(\mathbf{k}) = 0.$$

- Now consider the momentum density $\mathbf{P}(\mathbf{k})$ for small k:

$$\begin{aligned}
\dot{\mathbf{P}}(\mathbf{k}) &= \frac{i\mathbf{k}}{m}\cdot\sum_j \mathbf{p}_j\mathbf{p}_j e^{i\mathbf{k}\cdot\mathbf{r}_j} + \sum_j \dot{\mathbf{p}}_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \qquad \text{but since}\\
\dot{\mathbf{p}}_j &= \sum_{l\neq j}\mathbf{F}_{jl}\\
\sum_{j,l\neq j}\dot{\mathbf{p}}_j e^{i\mathbf{k}\cdot\mathbf{r}_j} &= \sum_{l,j\neq l}\dot{\mathbf{p}}_l e^{i\mathbf{k}\cdot\mathbf{r}_l} = \sum_{l,j\neq l}\mathbf{F}_{lj}e^{i\mathbf{k}\cdot\mathbf{r}_l} = \frac{1}{2}\sum_{j,l\neq j}\left(\mathbf{F}_{jl}e^{i\mathbf{k}\cdot\mathbf{r}_j} + \mathbf{F}_{lj}e^{i\mathbf{k}\cdot\mathbf{r}_l}\right)\\
&= \frac{1}{2}\mathbf{F}_{jl}\left(e^{i\mathbf{k}\cdot\mathbf{r}_j} - e^{i\mathbf{k}\cdot\mathbf{r}_l}\right) = frac12\mathbf{F}_{jl}\left(e^{i\mathbf{k}\cdot\mathbf{r}_j} - e^{i\mathbf{k}\cdot\mathbf{r}_l}\right)\\
&= \sum_{j,l\neq j}\frac{1}{2}\mathbf{F}_{jl}\left(1 - e^{-i\mathbf{k}\cdot(\mathbf{r}_j-\mathbf{r}_l)}\right)e^{i\mathbf{k}\cdot\mathbf{r}_j} \approx \frac{1}{2}\sum_{j,l\neq j}\mathbf{F}_{jl}i\mathbf{k}\cdot(\mathbf{r}_j - \mathbf{r}_l)\,e^{i\mathbf{k}\cdot\mathbf{r}_j}\\
&= i\mathbf{k}\cdot\frac{1}{2}\sum_{j,l\neq j}\mathbf{r}_{jl}\mathbf{F}_{jl}e^{i\mathbf{k}\cdot\mathbf{r}_j}
\end{aligned}$$

so for small k, we can write

$$\dot{\mathbf{P}}(\mathbf{k}) = i\mathbf{k}\cdot\tau(\mathbf{k}) \qquad \tau(\mathbf{k}) = \sum_j\left(\frac{\mathbf{p}_j\mathbf{p}_j}{m} + \frac{1}{2}\sum_{l\neq j}\mathbf{r}_{jl}\mathbf{F}_{jl}\right)e^{i\mathbf{k}\cdot\mathbf{r}_j}.$$

where $\tau(\mathbf{k})$ is the *microscopic stress tensor.*

  - Note that $\tau(\mathbf{k})$ is an even-ranked tensor, and an even function of momentum variables $\mathbf{p}_j$ that couples only to even functions of the momenta. Hence averages of the form $\left\langle\tau(\mathbf{k})\hat{\mathbf{A}}_\alpha(\mathbf{k})^*\right\rangle$ vanish if $\alpha = P^z, P^x, P^y$ and is proportional to the unit tensor $\mathbf{I}$ if $\alpha = \hat{N}, \hat{E}$ for an isotropic system.
  - As is evident from the virial formula for the pressure, the equilibrium average of the stress tensor gives the (hydrostatic or internal) pressure since

$$\langle\tau(\mathbf{k})\rangle = \langle\tau\rangle\left(1 + O\left((k\xi)^2\right)\right) = \langle\tau_{xx}\rangle\,\mathbf{I} = P_h V\mathbf{I}.$$

- Away from the critical point where the correlation length ξ of $g(r)$ is short, for small k with $k\xi << 1$, we can approximate all static correlation functions by their small k values:

$$\langle A(\mathbf{k})B(\mathbf{k})^*\rangle = \langle AB\rangle\left(1 + O\left((k\xi)^2\right)\right)$$

- Under these conditions, noting that

$$\left(\frac{\partial \langle B\rangle}{\partial \beta\mu}\right)_{\beta,V} = \left\langle \hat{B}\hat{N}\right\rangle \qquad \left(\frac{\partial \langle B\rangle}{\partial(-\beta)}\right)_{\beta\mu,V} = \left\langle \hat{B}\hat{E}\right\rangle$$

  we can write

$$\begin{aligned}\left\langle \dot{\mathbf{P}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} &= i\mathbf{k}\cdot\left\langle \tau(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \\ &= i\mathbf{k}\cdot\frac{\partial P_h}{\partial\phi_\alpha}\frac{\partial\phi_\alpha}{\partial A_\beta}\end{aligned}$$

  where $\alpha = \{\beta\mu, -\beta\}$ are conjugate thermodynamic forces, and we have used the fact that $\left\langle \hat{\mathbf{A}}\hat{\mathbf{A}}\right\rangle^{-1}_{\alpha\beta} = \frac{\partial\phi_\alpha}{\partial\hat{\mathbf{A}}_\beta}$. These relations imply that to leading ordering in $k\xi$

$$\mathbf{M}^E_{PN}(\mathbf{k}) = i\mathbf{k}\cdot\left(\frac{\partial P_h\,\mathbf{I}}{\partial n}\right)_e \qquad \mathbf{M}^E_{PP}(\mathbf{k}) = 0 \qquad \mathbf{M}^E_{PE}(\mathbf{k}) = i\mathbf{k}\cdot\left(\frac{\partial P_h\,\mathbf{I}}{\partial e}\right)_n$$

- Considering the equation for the energy density $E(\mathbf{k})$ is slightly more complicated algebraically, but the same sort of manipulations as those above can be carried out to obtain

$$\begin{aligned}\dot{E}(\mathbf{k}) &= i\mathbf{k}\cdot\mathbf{J}_E(\mathbf{k}) \\ \mathbf{J}_E(\mathbf{k}) &= \sum_j\left[\frac{\mathbf{p}_j e_j}{m} + \frac{1}{2}\sum_{l\neq j}\mathbf{r}_{jl}\mathbf{F}_{jl}\cdot\frac{\mathbf{p}_j+\mathbf{p}_l}{m}\right]e^{i\mathbf{k}\cdot\mathbf{r}_j},\end{aligned}$$

  which is odd in momenta and hence couples only to the momentum density $\mathbf{P}(\mathbf{k})$.

- A useful identity to note is:

$$\begin{aligned}\left\langle \dot{E}(\mathbf{k})\mathbf{P}(\mathbf{k})^*\right\rangle &= -\left\langle E(\mathbf{k})\dot{\mathbf{P}}(\mathbf{k})^*\right\rangle = \left\langle \hat{E}(\mathbf{k})\tau(\mathbf{k})^*\right\rangle\cdot i\mathbf{k} \approx i\mathbf{k}\cdot\left\langle \tau\hat{E}\right\rangle \\ &= i\mathbf{k}\cdot V\left(\frac{\partial P_h\,\mathbf{I}}{\partial(-\beta)}\right)_{\beta\mu,V}.\end{aligned}$$

- Using the fact that $d(\beta\mu) = \tilde{h}d\beta + \beta\tilde{V}dP$, where $\tilde{X} = X/\langle N\rangle$ and $tildeh$ is the enthalpy per particle, we can write

$$\left(\frac{\partial P_h}{\partial(-\beta)}\right)^{\beta\mu} = \frac{\tilde{h}}{\beta\tilde{V}}.$$

- To leading order in $k\xi$, we obtain:

$$\mathbf{M}^E_{EN}(\mathbf{k}) = 0 \qquad \mathbf{M}^E_{EP}(\mathbf{k}) = i\mathbf{k}\frac{h}{mn} \qquad \mathbf{M}^E_{EE}(\mathbf{k}) = 0.$$

1.4 The Dissipative Matrix $\mathbf{M}^D(\mathbf{k}, z)$:

- Recall the definition of the stochastic force appearing in the dissipative matrix $\mathbf{M}^D(\mathbf{k}, z)$:

$$\begin{aligned}\mathbf{M}^D(\mathbf{k}, z) &= -\left\langle \mathbf{K}(\mathbf{k}, z)\mathbf{K}(\mathbf{k})^*\right\rangle\cdot\left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^*\right\rangle^{-1} \\ \mathbf{K}(\mathbf{k}, t) &= e^{\mathcal{QL}t}\mathcal{Q}\dot{\hat{\mathbf{A}}}(\mathbf{k}).\end{aligned}$$

- We have already evaluated the time derivatives to find:

$$\dot{N}(\mathbf{k}) \quad = \quad \frac{i\mathbf{k}}{m} \cdot \mathbf{P}(kk) \qquad \dot{\mathbf{P}}(\mathbf{k}) = i\mathbf{k} \cdot \tau(\mathbf{k}) \qquad \dot{E}(\mathbf{k}) = i\mathbf{k} \cdot \mathbf{J}_E(\mathbf{k}).$$

- Recall from the definition of the projection operator $\mathcal{Q}$ that $\mathcal{Q}\hat{\mathbf{A}}_\alpha(\mathbf{k}) = 0$, so $\mathcal{Q}\mathbf{P}(\mathbf{k}) = 0$ and hence the equation for N has *no* stochastic force component.

- We therefore can write:

$$\mathbf{K}_N(\mathbf{k}) \quad = \quad 0 \qquad \mathbf{K}_{\mathbf{P}}(\mathbf{k}) = i\mathbf{k} \cdot \tau^D(\mathbf{k}) \qquad \mathbf{K}_E(\mathbf{k}) = i\mathbf{k} \cdot \mathbf{J}_E^D(\mathbf{k}),$$

  where we have defined $\mathbf{X}^D = \mathcal{Q}\mathbf{X}$.

- We will keep only the leading order terms of the dissipative matrix:

$$\begin{aligned} \langle \mathbf{K}(\mathbf{k},\tau)\mathbf{K}(\mathbf{k})^* \rangle &= i\mathbf{k} \cdot \left\langle \mathbf{J}^D(\mathbf{k},\tau)\mathbf{J}^D(\mathbf{k})^* \right\rangle \cdot (-i\mathbf{k}) \\ &\approx \mathbf{k} \cdot \left\langle \mathbf{J}^D(\tau)\mathbf{J}^D \right\rangle \cdot \mathbf{k}. \end{aligned}$$

  - Note that as before, $\mathbf{J}_E^D$ is odd in momentum and τ^D is even in momentum, so we expect little coupling between E and $\mathbf{P}$ in the dissipative matrix and none *directly* with the number density N, although coupling *does* arise through the $\left\langle \hat{\mathbf{A}}\hat{\mathbf{A}} \right\rangle^{-1}$ matrix.

- Considering the energy flux term, by isotropy:

$$\mathbf{k} \cdot \left\langle \mathbf{J}_E^D(\tau)\mathbf{J}_E^D \right\rangle \cdot \mathbf{k} = k^2 \left\langle \mathbf{J}_{E,x}^D(\tau)\mathbf{J}_{E,x}^D \right\rangle$$

- As before, we consider dynamics on time scales long compared to a microscopic time scale τ_m but short compared to the hydrodynamic time scale $\tau_h \sim k^2$. We expect that due to the projected dynamics, the time correlation functions in the dissipative matrix decay quickly on a time scale on the order of τ_m. Thus, for $\tau_m << t << \tau_h$, we can write:

$$\int_0^t d\tau \left\langle \mathbf{J}_{E,x}^D(\tau)\mathbf{J}_{E,x}^D \right\rangle \quad \approx \quad \int_0^\infty d\tau \left\langle \mathbf{J}_{E,x}^D(\tau)\mathbf{J}_{E,x}^D \right\rangle = \left\langle \mathbf{J}_{E,x}^D(z=0)\mathbf{J}_{E,x}^D \right\rangle.$$

- We define the *thermoal conductivity* by the *Green-Kubo relation*:

$$\lambda \quad = \quad \frac{\int_0^\infty d\tau \left\langle \mathbf{J}_{E,x}^D(\tau)\mathbf{J}_{E,x}^D \right\rangle}{V k_B T^2}$$

  and use the same sort of thermodynamic manipulations used earlier to obtain

$$\begin{aligned} \mathbf{M}_{EN}^D(\mathbf{k}) &= -k^2\lambda \left(\frac{\partial T}{\partial n}\right)_e \\ \mathbf{M}_{E\mathbf{P}}^D(\mathbf{k}) &= O\left(k^3\right) \qquad \mathbf{M}_{EE}^D(\mathbf{k}) = -k^2\lambda \left(\frac{\partial T}{\partial e}\right)_n. \end{aligned}$$

- For the momentum, we find that $\mathbf{P}$ only couples to $\mathbf{P}$ to order k^2, and so

$$\mathbf{M}_{\mathbf{PP}}^D(\mathbf{k}) \quad = \quad -\int_0^\infty d\tau \left(\mathbf{k} \cdot \left\langle \tau^D(\tau)\tau^D \right\rangle \cdot \mathbf{k}\right) / (m \langle N \rangle k_B T).$$

- In general, isotropy implies that:

$$\begin{aligned}
\langle \alpha_{ij}\beta_{kl}\rangle &= A\delta_{ij}\delta_{kl} + B\delta_{ik}\delta_{jl} + C\delta_{il}jk \qquad \text{and since } \tau_{ij} = \tau_{ji} \\
\left\langle \tau^{D}(\tau)_{ij}\tau^{D}_{kl}\right\rangle &= A\delta_{ij}\delta_{kl} + B\left(\delta_{ik}\delta_{jl} + \delta_{il}jk\right) \\
A &= \int_0^\infty d\tau \left\langle \tau^{D}_{xx}(\tau)\tau^{D}_{xx}\right\rangle \\
B &= \int_0^\infty d\tau \left\langle \tau^{D}_{xz}(\tau)\tau^{D}_{xz}\right\rangle .
\end{aligned}$$

- Defining longitudinal and transverse momentum components by $P_l(\mathbf{k}) = \hat{\mathbf{k}}\cdot\mathbf{P}(\mathbf{k})$ and $P_t(\mathbf{k}) = \hat{\mathbf{k}}\times\mathbf{P}(\mathbf{k})$, we see that the transverse momenta are uncoupled from other variables and

  $$\begin{aligned}
  \mathbf{M}^{D}_{P_tP_t}(\mathbf{k}) &= -k^2\frac{B}{\langle N\rangle m k_B T} = -k^2\frac{\eta}{mn} \\
  \eta &= \frac{1}{Vk_BT}\int_0^\infty d\tau \left\langle \tau^{D}_{xz}(\tau)\tau^{D}_{xz}\right\rangle
  \end{aligned}$$

  is the Green-Kubo relation for the *shear viscosity.*

- The longitudinal components are:

  $$\begin{aligned}
  \mathbf{M}^{D}_{P_lP_l}(\mathbf{k}) &= -k^2\frac{A+2B}{\langle N\rangle m k_B T} = -k^2\frac{\zeta + 4\eta/3}{mn} \\
  \zeta + 4\eta/3 &= \frac{1}{Vk_BT}\int d\tau \left\langle \tau^{D}_{xx}(\tau)\tau^{D}_{xx}\right\rangle .
  \end{aligned}$$

- Putting the Eulear and Dissipative parts of the matrix together, we obtain the matrix for the coupled N, P_l and E components:

  $$\mathbf{M}(\mathbf{k}) \;=\; \begin{pmatrix} 0 & \frac{ik}{m} & 0 \\ ik\left(\frac{\partial P_h}{\partial n}\right)_e & -k^2\frac{\zeta+4\eta/3}{mn} & ik\left(\frac{\partial P_h}{\partial e}\right)_n \\ -k^2\lambda\left(\frac{\partial T}{\partial n}\right)_e & ik\frac{h}{mn} & -k^2\lambda\left(\frac{\partial T}{\partial e}\right)_n \end{pmatrix}$$

  and the equation of the correlation functions

  $$G_{AA}(\mathbf{k},z) \;=\; \left[z\mathbf{I} - \mathbf{M}(\mathbf{k})\right]^{-1}.$$

- The matrix can be diagonalized to obtain the *hydrodynamic modes* and the eigenvalues of the matrix $\mathbf{M}$:

  $$\begin{aligned}
  &S^{\pm}(\mathbf{k}) = \tfrac{\chi_n}{c_0}\hat{N}(\mathbf{k}) + \tfrac{\chi_e}{c_0}\hat{E}(\mathbf{k}) \pm P_l(\mathbf{k}) &\qquad& \mathbf{M}_{SS}(\mathbf{k}) = \pm ic_0k - \Gamma_S k^2 \\
  &T(\mathbf{k},t) = \hat{E}(\mathbf{k}) - \tfrac{h}{n}\hat{N}(\mathbf{k}) && \mathbf{M}_{TT}(\mathbf{k}) = -\Gamma_T k^2
  \end{aligned}$$

  where χ_n and χ_e are $\left(\frac{\partial P_h}{\partial e}\right)_n$ and $\left(\frac{\partial P_h}{\partial n}\right)_e$ respectively, and c_0 is the zero frequency sound speed and the Γ_S and Γ_T are the sound and thermal damping coefficients defined in the last set of notes.

- Note that we have obtained microscopic expressions (Green-Kubo) for the transport coefficients appearing in the equations above. These expressions involve the projected dynamics via $\exp\{\mathcal{QL}t\}$. To leading order in k, the projected dynamics can be replaced by the unprojected dynamics since $\mathcal{L}(1 - Pt)B = \dot{B} + O(k)$.

- The Assumptions:

  1. For non-equilibrium systems, the hydrodynamic equations require linear displacement from equilibrium.
  2. The correlation lengths are all short so that $k\xi << 1$.
  3. The magnitude of k is small enough to enforce a clear separation of time scales with $\tau_h >> \tau_m$.
  4. The complete set of slow modes consists of the linear densities of the hydrodynamic variables N, E and $\mathbf{P}$.

- Comments:

  - For general non-equilibrium systems, can generalize the discussion here to include mode-coupling terms to be discussed below. These lead to a more general local equilibrium ensemble that should be approached more rapidly than the "linear" local equilibrium ensemble used here. This ensemble can be used to derive non-linear hydrodynamic equations.
  - The correlation length ξ is generally short-ranged for liquids except near the critical point, as we discussed in the context of static structure.
  - If one is interested in larger values of k, the k-ordering scheme must be used carefully. In addition, additional "kinetic" modes that are slow relaxing may become important. In many situtations, we have some control over what length scales we are examining.
  - It turns out the set of slow modes is not sufficient and the Green-Kubo expressions for the transport coefficients do not match well with simulation data at very long times. We will now analyze why this may be the case.

1.5 Application of Formalism: Light Scattering Spectrum

- Recall that the intensity of scattered light of an incident wave with wavevector $\mathbf{k}_i$ and frequency ω_i is related to the dynamic structure factor $F(\mathbf{k}, t) = \left\langle \hat{N}(\mathbf{k}, t)\hat{N}(\mathbf{k})^* \right\rangle$ by

$$I_{\text{scatt}}(\mathbf{k}, \omega) \sim \text{Re}\left\langle \hat{N}(\mathbf{k}, z = -i\omega)\hat{N}(\mathbf{k})^* \right\rangle = \text{Re}\int_0^\infty dt\, e^{i\omega t}\, F(\mathbf{k}, t),$$

  where $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$, $\omega = \omega_f - \omega_i$, where $\mathbf{k}_f$ and ω_f are the wavevector and frequency of the scattered light.

- Using the hydrodynamic theory developed here, we find:

$$\begin{aligned} I_{\text{scatt}}(\mathbf{k}, \omega) &\sim \left\langle \hat{N}\hat{N} \right\rangle \text{Re}\left[\frac{c_v}{2c_p}\left(\frac{1}{-i\omega - z_+(\mathbf{k})} + \frac{1}{-i\omega - z_-(\mathbf{k})}\right) + \frac{c_p - c_v}{c_p}\frac{1}{-i\omega - z_T(k)}\right] \\ &= \left\langle \hat{N}\hat{N} \right\rangle \left[\frac{c_v}{2c_p}\left(\frac{k^2\Gamma_S}{k^4\Gamma_S^2 + (\omega - c_0k)^2} + \frac{k^2\Gamma_S}{k^4\Gamma_S^2 + (\omega + c_0k)^2}\right) + \frac{c_p - c_v}{c_p}\frac{\Gamma_T k^2}{k^4\Gamma_T^2 + \omega^2}\right] \end{aligned}$$

  - Width of peaks determined by damping coefficients $\Gamma_{S,T}k^2$, so peaks are very narrow for small k.
  - Peak heights increase as $(\Gamma_{S,T}k^2)^{-1}$.

  - There are contributions for local thermal fluctuations (Rayleigh peak) and travelling sound waves (Brillouin peaks), which have total intensities:

$$\begin{aligned} I_R &\sim \frac{c_p - c_v}{c_p} \int_{-\infty}^{\infty} d\omega \, \frac{\Gamma_T k^2}{k^4 \Gamma_T^2 + \omega^2} = \pi \frac{c_p - c_v}{c_p} \\ I_B &\sim \frac{c_v}{c_p} \pi \end{aligned}$$

    and hence $I_R / I_B = (c_p - c_v)/c_v$.
  - In liquids, $c_p \approx c_v$, so the Brillouin peak is small.
  - In gases, $c_p > c_v$ and the Brillouin peak is large.
  - Position of center Brillouin peaks at $c_0 k$, so sound speed can be read off from peak position.

2 Mode Coupling Theory

At long times, Alder and Wainwright showed that numerical simulations of simple liquids deviated from the form predicted by linear hydrodynamics. An additional long time, non-exponential relaxation was observed that they called a "long time tail" of the form $t^{-d/2}$. What could be missing in the theory? Clearly, an infinite number of additional slow modes must exist that are coupled to the linear equations. What are these modes?

- The argument of what variables constitutes the slow basis set for small values of k was based on the fact that time derivatives of conserved densities are proportional to k.

- Consider the "bi-linear" modes, $B(\mathbf{k}, \mathbf{k}') = \hat{\mathbf{A}}(\mathbf{k} - \mathbf{k}')\hat{\mathbf{A}}(\mathbf{k}')$, with both k and k' small:

$$\dot{B}(\mathbf{k}, \mathbf{k}') = i(\mathbf{k} - \mathbf{k}') \cdot \left[\mathbf{J}(\mathbf{k} - \mathbf{k}') \hat{\mathbf{A}}(\mathbf{k}') \right] + i\mathbf{k}' \cdot \left[\mathbf{J}(\mathbf{k}') \hat{\mathbf{A}}(\mathbf{k} - \mathbf{k}') \right].$$

  - Clearly, B is *also* slowly varying since both k and k' are small.
  - The projection of dynamical variables therefore has an additional slow component not accounted for in the theory. This must be important since

$$\langle \mathbf{K}(\mathbf{k}, \tau) B(\mathbf{k}, \mathbf{k}') \rangle \neq 0$$

    since $\mathcal{Q}B \neq 0$.

- Consider the effect of just including the bi-linear variables $B(\mathbf{k}, \mathbf{k}')$: we are therefore including an *infinite* number of modes since we have the freedom to choose any value of $\mathbf{k}'$ we wish, as long as its magnitude is smaller than some cut-off k_c.

- We write our basis set for a particular choice of $\mathbf{k}'$ as:

$$\begin{aligned} \mathbf{Q}(\mathbf{k}, \mathbf{k}') &= \begin{pmatrix} \hat{\mathbf{A}}(\mathbf{k}) \\ \mathbf{Q}^{(2)}(\mathbf{k} - \mathbf{k}', \mathbf{k}') \end{pmatrix} \\ \mathbf{Q}^{(2)}(\mathbf{k} - \mathbf{k}', \mathbf{k}') &= \hat{\mathbf{A}}(\mathbf{k} - \mathbf{k}')\hat{\mathbf{A}}(\mathbf{k}') - \left\langle \hat{\mathbf{A}}(\mathbf{k} - \mathbf{k}')\hat{\mathbf{A}}(\mathbf{k}')\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \left\langle \hat{\mathbf{A}}(\mathbf{k})\hat{\mathbf{A}}(\mathbf{k})^* \right\rangle \cdot \hat{\mathbf{A}}(\mathbf{k}) \end{aligned}$$

  to make it orthogonal in *mode order* $\langle \mathbf{Q}_i \mathbf{Q}_j \rangle = \langle \mathbf{Q}_i \mathbf{Q}_j \rangle \delta_{ij}$.

- If we follow our derivation of the hydrodynamic equations with the extended basis set using a projection operator that projects onto the new basis set, we obtain a larger (actually infinite) matrix that we can write in block form:

$$\mathbf{M}(\mathbf{k},z) \;=\; \begin{pmatrix} \mathbf{M}_{11}(\mathbf{k},z) & \mathbf{M}_{12}(\mathbf{k},\mathbf{k}',z) \\ \mathbf{M}_{21}(\mathbf{k},\mathbf{k}',z) & \mathbf{M}_{22}(\mathbf{k},\mathbf{k}',z) \end{pmatrix}$$

  where

$$\mathbf{M}_{ij} = \left[\left\langle \dot{\mathbf{Q}}_i \mathbf{Q}_j^* \right\rangle - \left\langle \mathbf{K}_i(z) \mathbf{K}_j^* \right\rangle\right] \cdot \langle \mathbf{Q}\mathbf{Q}^* \rangle_{jj}^{-1} .$$

- Note that the $1-1$ sub-block of this matrix is like the linear-linear matrix we had before except that the fluctuating force uses the new projection operator, which removes projections onto $\mathbf{Q}^{(2)}$ as well as $\hat{\mathbf{A}}$.

- We can write the correlation functions of the basis set as:

$$G_{QQ}(z) \;=\; \langle \mathbf{Q}(z)\mathbf{Q}^* \rangle * \langle \mathbf{Q}\mathbf{Q}^* \rangle^{-1} = [z\mathbf{I} - \mathbf{M}(z)]^{-1}$$

- Our original correlation functions of the linear densities are contained in the $1-1$ sub-block of the matrix $[z\mathbf{I} - \mathbf{M}(z)]^{-1}$.

- To find the contribution of the bi-linear modes to the linear-linear correlation functions, we can used the matrix identity

$$\begin{bmatrix} \mathsf{a} & \mathsf{c} \\ \mathsf{d} & \mathsf{b} \end{bmatrix}^{-1} = \begin{bmatrix} [\mathsf{a} - \frac{\mathsf{c}\,\mathsf{d}}{\mathsf{b}}]^{-1} & -[\mathsf{a} - \frac{\mathsf{c}\,\mathsf{d}}{\mathsf{b}}]^{-1}\mathsf{c}\mathsf{b}^{-1} \\ -[\mathsf{b} - \frac{\mathsf{d}\,\mathsf{c}}{\mathsf{a}}]^{-1}\mathsf{d}\mathsf{a}^{-1} & [\mathsf{b} - \frac{\mathsf{d}\,\mathsf{c}}{\mathsf{a}}]^{-1} \end{bmatrix},$$

  where $a = z\mathbf{I} - \mathbf{M}_{11}$, $b = z\mathbf{I} - M_{22}$. $c = -\mathbf{M}_{12}$, $d = -M_{21}$ and we have used the shorthand notation

$$\frac{\mathsf{A}\,\mathsf{B}}{\mathsf{C}} \;\equiv\; \mathsf{A} \cdot \mathsf{C}^{-1} \cdot \mathsf{B}.$$

- Examining the $1-1$ sub-block we see that

$$\begin{aligned} G_{11}(\mathbf{k},z) &= \left[z\mathbf{I} - \mathbf{M}_{11} - \mathbf{M}_{12}\left[z\mathbf{I} - \mathbf{M}_{22}\right]^{-1}\mathbf{M}_{21}\right]^{-1} \\ &= \left[z\mathbf{I} - \tilde{\mathbf{M}}\right]^{-1} \\ \tilde{\mathbf{M}}(\mathbf{k},z) &= \mathbf{M}_{11}(\mathbf{k},z) + \sum_{\mathbf{k}',\mathbf{k}''} \mathbf{M}_{12}(\mathbf{k};\mathbf{k},\mathbf{k}')\left[z\mathbf{I} - \mathbf{M}_{22}\right]^{-1}(\mathbf{k},\mathbf{k}';\mathbf{k},\mathbf{k}'')\mathbf{M}_{21}(\mathbf{k},\mathbf{k}'';\mathbf{k}) \end{aligned}$$

- The linear-linear term $\mathbf{M}_{11}$ looks a lot like our original hydrodynamic matrix, with the Green-Kubo expressions for transport coefficient.

- What is the matrix $[z\mathbf{I} - \mathbf{M}_{22}]^{-1} = \mathsf{b}^{-1}$? Note that it is almost

$$G_{22} = \left[\mathsf{b} - \frac{\mathsf{d}\,\mathsf{c}}{\mathsf{a}}\right]^{-1} = [z\mathbf{I} - \mathbf{M}_{22} - \mathbf{M}_{21}[z\mathbf{I} - \mathbf{M}_{11}]^{-1}\mathbf{M}_{12}]^{-1}$$

  except for the additional $\mathbf{M}_{21}[z\mathbf{I} - \mathbf{M}_{11}]^{-1}\mathbf{M}_{12}$ term.

- Need a systematic way of examining the relative importance of higher-order correlation functions.

2.1 The N-ordering method

In the N-ordering approach, one assigns to each cumulant of an average appearing in the equations an order of N (the number of particles). The starting point is to consider cumulants, which we denote by "$\langle\langle\cdots\rangle\rangle$". For a product of linear densities, the cumulant expansion consists of all possible ways of combining the densities into groups, i.e.,

$$\begin{aligned}
\langle A\rangle &= \langle\langle A\rangle\rangle \\
\langle AB\rangle &= \langle\langle AB\rangle\rangle + \langle\langle A\rangle\rangle\langle\langle B\rangle\rangle \\
\langle ABC\rangle &= \langle\langle ABC\rangle\rangle + \langle\langle AB\rangle\rangle\langle\langle C\rangle\rangle \\
&\quad + \langle\langle AC\rangle\rangle\langle\langle B\rangle\rangle + \langle\langle BC\rangle\rangle\langle\langle A\rangle\rangle \\
&\quad + \langle\langle A\rangle\rangle\langle\langle B\rangle\rangle\langle\langle C\rangle\rangle,
\end{aligned}$$

and so on. The assignment of N-orders is based on the observation that each cumulant containing n linear densities is of order $N(\xi/a)^{3(n-1)}$, where a is the average distance between particles.

- As an example, consider the cumulant of a linear-linear correlation function of the number density $N_{\mathbf{k}}$, defined as can be formally written as

$$\begin{aligned}
\langle\langle N_{\mathbf{k}}N_{\mathbf{k}}^*\rangle\rangle &= \langle N_{\mathbf{k}}N_{\mathbf{k}}^*\rangle - \langle N_{\mathbf{k}}\rangle\langle N_{\mathbf{k}}^*\rangle\,\delta_{k0} \\
&= [\langle N\rangle + \left\langle N(N-1)e^{i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2)}\right\rangle](1-\delta_{\mathbf{k}0}) \\
&\quad + [\left\langle N^2\right\rangle - \langle N\rangle^2]\delta_{\mathbf{k}0}.
\end{aligned}$$

For $\mathbf{k}=0$, the cumulant expansion of $\langle N_{\mathbf{k}}N_{\mathbf{k}}^*\rangle$ is given by $\langle(N-\langle N\rangle)^2\rangle$, which, in the grand canonical ensemble, is of order $\langle N\rangle$. For $\mathbf{k}\neq 0$, the expression is proportional to N as well, because particles beyond the correlation length ξ will not contribute to the average of $\exp(i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2))$, so that

$$\langle N(N-1)\exp(i\mathbf{k}\cdot(\mathbf{r}_1-\mathbf{r}_2))\rangle \propto N(N-1)\frac{\xi^3}{V} = O(N).$$

- Within this approach, a 4-point function factors as follows:

$$\begin{aligned}
\left\langle \mathbf{Q}^{(2)}(\mathbf{k},\mathbf{q})\mathbf{Q}^{(2)}(\mathbf{k},\mathbf{q}')^*\right\rangle &= \left\langle \hat{\mathbf{A}}(\mathbf{k}-\mathbf{q})\hat{\mathbf{A}}(\mathbf{k}-\mathbf{q})^*\right\rangle\left\langle \hat{\mathbf{A}}(\mathbf{q})\hat{\mathbf{A}}(\mathbf{q})^*\right\rangle(\delta_{\mathbf{q},\mathbf{q}'}+\delta_{\mathbf{q}',\mathbf{k}-\mathbf{q}}) \\
&\quad + \langle\langle \mathbf{Q}^{(2)}(\mathbf{k},\mathbf{q})\mathbf{Q}^{(2)}(\mathbf{k},\mathbf{q}')^*\rangle\rangle.
\end{aligned}$$

- Note that the first term is of order N^2, whereas the second term is of order N.
  - Even though the second term is order N^{-1}, smaller than the first, there are two unrestricted wavevectors $\mathbf{q}$ and $\mathbf{q}'$, so that there are *many such terms.*
  - When summing over wavevectors such as $\mathbf{q}$ and $\mathbf{q}'$, the finite measure of these sums M may compensate for lower N-order, so that terms of order N^2 may have corrections of the form $N^2(M/N)$.
- Using these principles, it is easy to show that $\mathbf{M}_{12}\sim N^{-1}$, $\mathbf{M}_{21}\sim N^0$, $M_{11}\sim N^0$.

- If we look at the *diagonal* corrections to $\mathbf{M}_{11}$, i.e.

$$\tilde{\mathbf{M}}(\mathbf{k}, z) = \mathbf{M}_{11}(\mathbf{k}, z) + \sum_{\mathbf{q}} \mathbf{M}_{12}(\mathbf{k}; \mathbf{k}, \mathbf{q}) \left[z\mathbf{I} - \mathbf{M}_{22}\right]^{-1} (\mathbf{k}, \mathbf{q}; \mathbf{k}, \mathbf{q}) \mathbf{M}_{21}(\mathbf{k}, \mathbf{q}; \mathbf{k})$$

  then we find that in the thermodynamic limit

$$\left[z\mathbf{I} - \mathbf{M}_{22}\right]^{-1} \left(1 + O(N^{-1})\right) = G^d_{22}(\mathbf{k}, \mathbf{q}, z)$$

- To leading N-order, $G^d_{22}(z)$ is the Laplace transform of the time correlation function

$$\begin{aligned} G^d_{22}(t) &= \left\langle \mathbf{Q}^{(2)}(\mathbf{k}-\mathbf{q}, \mathbf{q}; t) \mathbf{Q}^{(2)}(\mathbf{k}-\mathbf{q}, \mathbf{q})^* \right\rangle \cdot \left\langle \mathbf{Q}^{(2)}(\mathbf{k}-\mathbf{q}, \mathbf{q}) \mathbf{Q}^{(2)}(\mathbf{k}-\mathbf{q}, \mathbf{q})^* \right\rangle^{-1} \\ &= G_{11}(\mathbf{k}-\mathbf{q}, t) G_{11}(\mathbf{q}, t) \left(1 + O(N^{-1})\right) \end{aligned}$$

- The overall N-order is $M * N^{-1} * 1 * 1 = M/N$, which contrasts to the $O(1)$ term $\mathbf{M}_{11}(\mathbf{k}, t)$.
- This gives us self-consistent equations for the $G_{11}(t)$!
  - This equation is the foundation of mode-coupling theories of the glass transition, in which a non-linear, integral equation for the dynamic structure factor $F(\mathbf{k}, t)$.
  - In glasses and very dense fluids, one typically focuses on *short wavelength* phenomena, where typical length scales are on the order of the first solvation shell (first peak in structure factor). On these length scales, one can appeal to kinetic theory to look for extensions of the hydrodynamic modes to short length scales. Typically, there is an *extended heat mode* that looks like the number density on very short length scales. This mode is slow due to caging effects, and looks like a self-diffusion mode and very short length scales. Often one simply approximates this mode by the density mode.
- The off-diagonal terms are of lower N-order, but retain an additional sum (over $\mathbf{k}''$) that compensates and makes the leading off-diagonal contribution of order $(M/N)^2$.
- If we retain terms of M/N only, then we can use the fact that the $G_{11}(t)$ are exponentially-decaying to this order, as the correction terms to this behavior are at least of order M/N.
- Considering the coupling via the shear modes where $G_{11}(\eta_i, \eta_i; t) = \exp\{-k^2 \eta t\}$. The mode-coupling term is:

$$\begin{aligned} \mathbf{M}^{mc}_{11}(\mathbf{k}, t) &= \sum_{\mathbf{q}}^{k_c} \mathbf{M}_{12}(\mathbf{k}; \mathbf{k}-\mathbf{q}) e^{-(\mathbf{k}-\mathbf{q})^2 \eta t} e^{-k^2 \eta t} \mathbf{M}_{21}(\mathbf{k}-\mathbf{q}, \mathbf{q}; \mathbf{k}) \\ &\sim Ck^2 \frac{V}{(2\pi)^3} \int d\mathbf{q}\, e^{-2q^2 t} \\ &= Ck^2 \frac{4\pi V}{(2\pi)^3} \left[\int_0^\infty dq\, q^2 e^{-2q^2 t} - \int_{k_c}^\infty dq\, q^2 e^{-2q^2 t} \right] \\ &\to Ck^2 \frac{4\pi V}{(2\pi)^3} \frac{\pi^{1/2}}{4(2\eta t)^{3/2}} + \text{fast decaying term.} \end{aligned}$$

  where C is some constant and we have used the fact that the leading contribution to this integral comes from the "Euler" part of the the $\mathbf{M}_{12}$ and $\mathbf{M}_{21}$ vertices, which are terms strictly proportional to $\mathbf{k}$.

- The mode-coupling contribution to the matrix $\mathbf{M}_{11}(\mathbf{k}, t)$ has a "long-time tail" contribution of $t^{-3/2}$ in 3-dimensions.

- The Laplace transform $\mathbf{M}_{11}^{mc}(\mathbf{k}, z) \sim k^2 z^{1/2}$, so that the $z = 0$ limit exists (renormalization of transport coefficient).

- In lower dimension, $\mathbf{M}_{11}^{mc}(\mathbf{k}, t) \sim k^2 t^{-d/2}$, so the contribution to the transport coefficients (time integral) diverge! Hydrodynamics in infinite, 2-d systems is not valid.

- The simple bi-linear contribution is of form $\mathbf{M}_{11}^{mc}(\mathbf{k}, z) \sim k^2 / \ln(z + \eta k^2)$. Contributions from other modes also diverge and must be treated. Including all orders gives the asymptotic form $k^2 \ln^{-1/2}(z + \eta k^2)$.

- Comments

  1. In principle, all mode-orders must be included and dealt with perturbatively.
  2. Find the non-analytic k dependence of the dispersion relation, i.e. determine the k dependence of the generalized hydrodynamic modes. Inclusion of the bi-linear densities introduces an infinite number of terms between order k^2 and k^3.
  3. Typically, the ordering parameter $M/N \sim k_c^3 V/N \sim (k_c \xi)^3 << 1$, so perturbation series is an effective expansion. Problems can develop when either k_c becomes large (very dense fluids) or ξ becomes long-ranged through either critical fluctuations or long *dynamical* correlation lengths.
  4. Tagged particle correlations can be treated similarly, with slightly different N-ordering behavior.
  5. The inclusion of all mode-orders can be used to:
     - Derive the Stokes-Einstein law for tagged particle motion.
     - Rigorously develop theories of the glass transition without making assumptions about the statistical properties of the random forces $\mathbf{K}(t)$.
     - Examine dynamics in critical systems.