4.3: Viscoelastic Model

Introduction

The Generalized Langevin Equation and Mode-Coupling theory are subsets of molecular hydrodynamics, the theory that was developed to bridge the gap between hydrodynamics and molecular dynamics. Hydrodynamics, which we discussed in chapter 3, describes the macroscopic, long time behavior of systems in the limit as *[Math Processing Error]* and *[Math Processing Error]*. It uses the transport coefficients *[Math Processing Error]*, *[Math Processing Error]*, and *[Math Processing Error]* to predict long time fluctuations. Molecular dynamics, which we discussed in section I of chapter 4 , describes the microscopic, short time behavior of systems in the limit as *[Math Processing Error]* and *[Math Processing Error]*. In this limit, systems behave as static liquid structures, and their dynamics are largely determined by the pairwise interaction potential.

In this section, we will use the GLE to derive the viscoelastic model for transverse current. By taking the appropriate limits, we can show that the results of the viscoelastic model are consistent with those of hydrodynamics and molecular dynamics, and that this model provides a successful bridge between the two limits.

Phenomenological Viscosity

Consider a constant shear force applied to a viscous liquid. At long times, the shear stress *[Math Processing Error]* in the liquid is related to the rate of strain *[Math Processing Error]* by

[Math Processing Error]

Liquids behaving in this fashion do not support shear waves. However, if the force is applied instantaneously, the system does not have the time to relax like a liquid. Instead, it behaves like an elastic solid. The stress is now proportional to the strain rather than the rate of strain. The short term response is

[Math Processing Error]

where *[Math Processing Error]* is the modulus of rigidity. When the liquid is behaving like a solid, it supports shear waves propagating at a speed of *[Math Processing Error]*.

To determine the time scale on which the liquid behaves like an elastic solid, define the constant

[Math Processing Error]

This is the Maxwell relaxation time. For the timescales *[Math Processing Error]* when

[Math Processing Error]

the system behaves like an elastic solid. For the timescales when

[Math Processing Error]

the system behaves like a viscous liquid.

Viscoelastic Approximation

To interpolate between the two extremes, we can write

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The Laplace transform of this equation yields

[Math Processing Error]

In the steady-state limit, as *[Math Processing Error]*

[Math Processing Error]

and in the high-frequency limit, as *[Math Processing Error]*

[Math Processing Error]

Transverse Current Correlation Function

We will use the transverse current correlation function to demonstrate the viscoelastic approximation. In Section I, we defined the transverse current as

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and the transverse current correlation function as

[Math Processing Error]

We have studied the transverse current in both the hydrodynamic limit *[Math Processing Error]* and the short-time expansion limit *[Math Processing Error]*. In chapter 3, we used the Navier Stokes equation to find an equation of motion for the transverse correlation function in the hydrodynamic limit

[Math Processing Error]

This has the solution

[Math Processing Error]

where *[Math Processing Error]* is the **shear viscosity**. Therefore, in the hydrodynamic limit, transverse current fluctuations decay exponentially with a rate determined by the shear viscosity *[Math Processing Error]*.

In section I of this chapter, we used the short-time expansion approximation to show that in the *[Math Processing Error]* limit, the transverse current correlation function can be written as

[Math Processing Error]

where the transverse frequency *[Math Processing Error]* is related to the transverse speed of sound *[Math Processing Error]* by

[Math Processing Error]

And the transverse speed of sound is given by

[Math Processing Error]

where *[Math Processing Error]* is the pairwise correlation function and *[Math Processing Error]* is the pairwise interaction potential. This frequency term can also be written as [3]

[Math Processing Error]

where *[Math Processing Error]* is the **shear modulus**. This indicates that at short times and wavelengths, the dissipation effects are diminished and transverse current fluctuations can propagate through the material with speed *[Math Processing Error]*.

Using the Generalized Langevin equation, we can generate a model for transverse current fluctuations that replicates the results of hydrodynamics and the short-time expansion when the appropriate limits are taken. Begin by writing the GLE for transverse current. Since the frequency matrix is zero, the GLE is written

[Math Processing Error]

where *[Math Processing Error]* is the memory function and *[Math Processing Error]* is the noise term. Multiplying through by *[Math Processing Error]* and taking the average gives us the equation of motion for the transverse current correlation function

[Math Processing Error]

Take a closer look at the memory kernel

[Math Processing Error]

The normalization factor is simply *[Math Processing Error]*. By writing the projection operator *[Math Processing Error]* as *[Math Processing Error]* and eliminating terms, this can be written

[Math Processing Error]

The equation of motion for the transverse current can be written as [5]

[Math Processing Error]

where *[Math Processing Error]* is the zx-component of the microscopic stress tensor

[Math Processing Error]

Then the memory kernel becomes

[Math Processing Error]

where *[Math Processing Error]* is defined as

[Math Processing Error]

This demonstrates that the memory kernel is proportional to *[Math Processing Error]*. Then the transverse current correlation function can be written

[Math Processing Error]

The memory kernel is the key element that links the two limits. In general, the presence of the propagator *[Math Processing Error]* makes it very difficult to evaluate *[Math Processing Error]* explicitly. However, the presence of *[Math Processing Error]* indicates that we can separate out fast and slow motions and use this to construct a form for *[Math Processing Error]* that will bridge the short and long time limits. To find this form, the viscoelastic model starts my assuming that the memory kernel has an exponential form:

[Math Processing Error]

where *[Math Processing Error]* is the **Maxwell relaxation time**, discussed above. Before using this function, it is necessary to specify the values of the two parameters, *[Math Processing Error]* and *[Math Processing Error]*. These can be found by taking the short and long time limits of the GLE and comparing them to the short-time expansion and hydrodynamic results, respectively.

The Short Time Limit

The value of *[Math Processing Error]* at short times can be obtained by comparing the GLE at time *[Math Processing Error]* to the short time expansion of the transverse correlation function. To find the GLE at time *[Math Processing Error]*, take its time derivative

[Math Processing Error]

The first two terms of the short time expansion of the correlation function are

[Math Processing Error]

The second derivative of this expansion gives

[Math Processing Error]

Comparison of equations (4.38) and (4.35) shows that

[Math Processing Error]

Further, we see that in this limit the material supports propagating waves. The form of the waves can be found by solving the differential equation Eq.(4.38), and is given by

[Math Processing Error]

where *[Math Processing Error]* and the speed of the waves are *[Math Processing Error]*.

The Hydrodynamic Limit

The value of *[Math Processing Error]* at long times can be obtained by comparing the hydrodynamic equation to the long time limit of the GLE for *[Math Processing Error]* :

[Math Processing Error]

To take the long time limit of this equation, note that the memory function will generally be characterized by some relaxation time *[Math Processing Error]*. When the time *[Math Processing Error]* is much greater than this relaxation time, the major contribution to the integral will come when *[Math Processing Error]*. Therefore, we can approximate *[Math Processing Error]*. With this approximation, the correlation function can be taken out of the integral in the GLE:

[Math Processing Error]

where the integration limit has been extended to *[Math Processing Error]* to indicate that we are taking the long time limit.

This result should be identical to the hydrodynamic solution in the long time and long wavelength limit. By taking the long wavelength limit *[Math Processing Error]* and comparing to the hydrodynamic result (Eq.(4.35)), we see that this only holds when:

[Math Processing Error]

The Viscoelastic Solution

We now have the information we need to construct the explicit form of the viscoelastic memory kernel.

[Math Processing Error]

From the short time limit, we found that *[Math Processing Error]*, which allows us to write

[Math Processing Error]

From the long time limit, we know that

[Math Processing Error]

Now, plug in the exponential memory kernel for *[Math Processing Error]*

[Math Processing Error]

The elastic modulus has no time dependence, so it can be taken out of the integral

[Math Processing Error]

Finally, evaluate the integral to find the Maxwell relaxation time at *[Math Processing Error]*. It is reasonable to assume that the Maxwell relaxation time remains constant over all *[Math Processing Error]* values. Therefore, the Maxwell relaxation time can be written as the ratio of the shear viscosity coefficient of the liquid to the modulus of rigidity of the elastic solid at *[Math Processing Error]*.

[Math Processing Error]

When *[Math Processing Error]* is small compared to the time *[Math Processing Error]*, the viscosity term dominates and the system will behave as a viscous liquid. However, when *[Math Processing Error]* is large compared to the time *[Math Processing Error]*, the system does not have time to respond to a stimulus as a viscous liquid. The modulus of rigidity dominates, and the material will behave as an elastic solid, supporting propagating shear waves.

Finally, we can use the Maxwell relaxation time to write the explicit form of the viscoelastic memory kernel.

[Math Processing Error]

With this memory kernel in hand, we can now go on to find an explicit solution to the transverse current correlation function.

To find the equation for the viscoelastic wave, we first find the Laplace transform of the transverse current correlation function

[Math Processing Error]

Now, solve this equation using the exponential memory kernel *[Math Processing Error]*. The Laplace transform of an exponential function is well defined

[Math Processing Error]

Therefore, the Laplace transform of the viscoelastic memory kernel is

[Math Processing Error]

Plug this into the the Laplace transform of the transverse current correlation function

[Math Processing Error]

Since function is quadratic, it is relatively easy to find the reverse Laplace transform, using the same method as that presented in section 4.2.C.2, or reference [1].

[Math Processing Error]

where the eigenvalues *[Math Processing Error]*are given by the solutions to the quadratic equation *[Math Processing Error]* :

[Math Processing Error]

Complex eigensolutions exist if

[Math Processing Error]

Recall that [Math Processing Error]. Then we can rewrite the above inequality in terms of the wavenumber

[Math Processing Error]

Define the critical wavenumber, [Math Processing Error]. For more information on the viscoelastic approximation and its application to transverse current, please see Chapter 6 of Molecular Hydrodynamics by Jean-Pierre Boon and Sidney Yip [3] and chapter 3 and chapter 6 of Dynamics of the Liquid State by Umberto Balucani [5].