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CRITICAL TRANSPORT PROPERTIES IN THE BINARY LIQUID PHASE TRANSITION

Robert Perl

Naval Ordnance Laboratory
White Oak, Maryland

7 September 1972

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13. ABSTRACT

Through various fluctuation-dissipation theorems, it is possible to relate critical transport coefficients to time and space integrals of correlation functions of the relevant fluxes. The anomaly in the critical transport properties is thus attributed to the cooperation of two effects: (1) the anomalous increase in the large-scale fluctuations of concentration variables contained in the flux, and (2) the anomalous increase in the lifetimes associated with these fluctuations. The fluctuation dissipation formula for the viscosity in terms of the stress tensor fluctuations reproduces the logarithmic temperature divergence of the shear viscosity. The excess viscosity, therefore, tends to reduce the critical Rayleigh linewidth predicted by Kawasaki. The effect of vertex corrections was investigated for both the shear viscosity and Rayleigh linewidth and found to be negligible in both cases.

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Rayleigh Linewidth						
Dynamical Sealing						

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This report is based on a dissertation submitted by the author to the University of Maryland in partial fulfillment of the requirements for a Ph.D. degree. It theoretically explains the wavenumber -, frequency-, and temperature-dependence of various transport coefficients observed in binary liquids in the vicinity of their critical points.

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Commander

Z. I. Slawsky
Z.I. SLAWSKY
By direction

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I. INTRODUCTION

A. Phenomenology

The critical temperature of a binary liquid (a two-component system) is the temperature above which the liquid exists in equilibrium as a homogeneous mixture of the two components in any specified concentration[1]. When the liquid having the critical concentration of each component is cooled below the critical temperature it begins to form two phases, separated by a well defined meniscus.

The equilibrium state of the two phases can be described by the temperature, pressure, and chemical potential of each component. However, it is more convenient to take the pressure P, temperature T, and concentration c, as independent variables. Near the critical point the equilibrium curve has the form shown in Fig. 1. Points within the shaded region represent those states in which phase separation takes place; the concentrations of the two phases are determined by the intersections of the curve with the horizontal line representing the temperature or pressure of the system. Points outside the shaded region represent states in which the system exists as a single phase in equilibrium. Near the critical point there are states for which the two phases can be in equilibrium with arbitrarily close values of the concentration, c and c + dc. If μ is the chemical potential of one of the components, then the equilibrium condition demands that

$$\left(\frac{\partial \mu}{\partial c}\right)_{P_c, T_c} = 0. \qquad (1)$$

It can be shown[1] that the equal time autocorrelation function of the concentration fluctuations is proportional to $(\frac{\partial \mu}{\partial c})^{-1}$. Therefore, the concentration fluctuations tend to have very large amplitudes near the critical point. If we consider the concentration as a local variable, which can vary in space and time, then it is convenient to define the order parameter $s(\vec{r},t)$, which in this case is the concentration fluctuation of one component about the equilibrium value:

$$S(\vec{r},t) \equiv C(\vec{r},t) - \langle c \rangle \quad , \qquad (2)$$

where $c(\vec{r},t)$ is the concentration at space-time point $(\vec{r},t)$, and $\langle c \rangle$ is the equilibrium, or ensemble average value of the concentration.

Light scattering measurements on binary liquids exhibit the phenomena known as critical opalescence[2], and critical slowing down[3]. Critical opalescence refers to the abnormally large amount of light scattering that occurs in the critical region. This is caused by the large regions of inhomogeneity that exist in the liquid. The size of these regions is characterized by the correlation length ξ. At temperatures far from the critical temperature T_c, the correlation length is very small, and of the order of magnitude of the molecular sizes. However, near T_c, the correlation length becomes very large, typically in the range of wavelengths of visible light. These large regions of inhomogeneity then act as scattering centers for incoming plane waves of light, and the liquid acquires a bluish tinge, characteristic of Rayleigh scattering, and then becomes murky, as it starts to separate into two phases.

Critical slowing down refers to the abnormally long lifetimes of the concentration fluctuations. This phenomenon is reflected by the vanishing of the particle diffusion coefficient at the critical point, as will be shown later. Thus, if an inhomogeneity arises, there will be almost no tendency for the molecules to move to the region of low concentration, and so, it will take longer for the system to return to equilibrium near the critical point.

We can, therefore, think of the critical region as a region where the order parameter fluctuations not only grow large in amplitude, but also become very long ranged, and very long lived. We will study how these phenomena affect various transport properties of the fluid.

B. Mean Field Theory

Mean field theory[4,5] presumes that the free energy density $\mathfrak{F}$ can be expanded in a power series in the order parameter $s(\vec{r},t)$. The first order term will be $-\mu s$ where μ is the field conjugate to s. In the case of the binary liquid μ is the difference in the chemical potential per unit mass of the two components, that is

$$\mu \equiv \frac{\mu_1}{m_1} - \frac{\mu_2}{m_2} \quad , \tag{3}$$

where m_i is the molecular mass of the ith component, and μ_i is its chemical potential. In the absence of a conjugate field (i.e., $\mu=o$), we presume the free energy density to be symmetric in s, and write

$$\mathcal{F}_{local} = \frac{a}{2}s^2 + \frac{b}{4}s^4 - \mu s \ . \tag{4}$$

Minimizing the free energy density gives the equilibrium equation of state

$$\mu = as + bs^3 \quad , \tag{5}$$

and the susceptibility χ:

$$\chi \equiv \lim_{s \to 0} \left(\frac{\partial s}{\partial \mu}\right) = a^{-1} \ . \tag{6}$$

We know that at the critical point, the susceptibility becomes infinite; therefore we presume that the parameter a is temperature dependent, and positive for $T>T_c$, and negative for $T<T_c$. We will, however presume that the parameter b has negligible temperature variation. Therefore, if $\mu=o$, the quadratic term in Eq. (4) is stable if $T>T_c$, and becomes unstable, corresponding to phase separation, for $T<T_c$, as shown in Fig. 2.

For an inhomogeneous liquid, however, we must also consider non-local terms involving gradients of the concentration. Since the fluid is isotropic, the first derivative enters as a scalar term proportional to $(\nabla s)^2$. A term proportional to $\nabla^2 s$ transforms to an insignificant surface term when integrated over the volume. Similarly, $s\nabla^2 s$ transforms into the integral of $(\nabla s)^2$. Thus, we add to the free energy density the term $\frac{Z^{-1}}{2}(\nabla s)^2$, where Z is a positive constant. Therefore,

$$\mathcal{F} = \mathcal{F}_{local} + \frac{Z^{-1}}{2}(\nabla s)^2$$

$$= \frac{a}{2}s^2 + \frac{Z^{-1}}{2}(\nabla s)^2 + \frac{b}{4}s^4 - \mu s \,. \tag{8}$$

We ignore all higher order terms.

All the thermodynamic properties of the system can be deduced from the partition function

$$Z_\Omega = \sum_{\{s\}} e^{-\beta\int_\Omega \mathcal{F} d^3r} \,, \tag{9}$$

where Ω is the volume of the system, and $\beta = T^{-1}$ in a system of units in which the Boltzmann constant is set equal to unity $(k_B \equiv 1)$.

At this point, it is convenient to expand the order parameter in a Fourier series over all possible wavenumbers, as follows:

$$S(\vec{r},t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}} S_{\vec{k}}(t)\, e^{i\vec{k}\cdot\vec{r}} \quad . \tag{10}$$

Then, if $\mu=o$, and we ignore the s^4 term,

$$F \equiv \int \mathcal{F} d^3r = \frac{1}{\Omega} \sum_{\vec{k}} \sum_{\vec{k}'} \left(\frac{a}{2} - \frac{Z^{-1}}{2} \vec{k}\cdot\vec{k}'\right) S_{\vec{k}} S_{\vec{k}'} \int d^3r\, e^{i(\vec{k}+\vec{k}')\cdot\vec{r}}$$

$$= \frac{1}{2} \sum_{\vec{k}} \left(a + Z^{-1} k^2\right) |S_{\vec{k}}|^2 , \tag{11}$$

and the Boltzmann factor becomes

$$e^{-\beta\int \mathcal{F} d^3r} = e^{-\frac{\beta}{2}\sum_{\vec{k}} (a+Z^{-1}k^2)|S_{\vec{k}}|^2}$$

$$= \prod_{\vec{k}} e^{-\frac{\beta}{2}(a+Z^{-1}k^2)|S_{\vec{k}}|^2} \quad . \tag{12}$$

Thus, by the equipartition theorem we see that the fluctuations of different wavenumbers are statistically independent, and that

$$\langle |S_{\vec{k}}|^2 \rangle = \frac{ZT}{\kappa^2 + k^2} , \tag{13}$$

where we have defined the inverse correlation length

$$\kappa \equiv \xi^{-1} = (aZ)^{1/2} \quad . \tag{14}$$

The vanishing of a at the critical point thus implies an infinite correlation length. If we define the spatial correlation function

$$G(\vec{r}_2,\vec{r}_1) \equiv \langle S(\vec{r}_2) S(\vec{r}_1) \rangle , \tag{15}$$

then translational invariance demands that

$$G(\vec{r}_2,\vec{r}_1) = G(\vec{r}_2-\vec{r}_1) \quad ,$$

and, therefore,

$$G(\vec{r}_{21}) = \int \frac{d^3k}{(2\pi)^3}\, g_{\vec{k}}\, e^{i\vec{k}\cdot\vec{r}_{21}} \quad , \qquad (16)$$

where

$$\vec{r}_{21} \equiv \vec{r}_2 - \vec{r}_1$$

If we substitute Eq. (10) into (15) we obtain

$$\begin{aligned} G(\vec{r}_{21}) &= \frac{1}{\Omega}\sum_{\vec{k}}\sum_{\vec{k}'}\langle s_{\vec{k}} s_{\vec{k}'}\rangle\, e^{i\vec{k}\cdot\vec{r}_2 + i\vec{k}'\cdot\vec{r}_1} \\ &= \frac{1}{\Omega}\sum_{\vec{k}}\langle |s_{\vec{k}}|^2\rangle\, e^{i\vec{k}\cdot\vec{r}_{21}} \quad . \qquad (17) \end{aligned}$$

Making the transformation

$$\frac{1}{\Omega}\sum_{\vec{k}} \longrightarrow \int \frac{d^3k}{(2\pi)^3} \quad , \qquad (18)$$

we can identify

$$g_{\vec{k}} = \langle |s_{\vec{k}}|^2\rangle \qquad (19)$$

Using Eq. (13), a special case of Eq. (19) is just the fluctuation - susceptibility theorem:

$$\frac{1}{T} g_{\vec{0}} = \frac{1}{T}\int d^3r_{21}\langle s(\vec{r}_2)\, s(\vec{r}_1)\rangle = \frac{Z}{\kappa^2} = a^{-1} \quad ,$$

or

$$\chi = \frac{1}{T}\int d^3 r_{21} \langle S(\vec{r}_2) S(\vec{r}_1)\rangle \quad . \tag{20}$$

This suggests the obvious generalization

$$\chi_{\vec{k}} = \frac{1}{T} g_{\vec{k}} = \frac{1}{T}\int d^3 r_{21}\, e^{-i\vec{k}\cdot\vec{r}_{21}} \langle S(\vec{r}_2) S(\vec{r}_1)\rangle \; . \tag{21}$$

Finally, if we substitute Eq. (13) into Eq. (16), then

$$G(r) = \int \frac{d^3 k}{(2\pi)^3} e^{i\vec{k}\cdot\vec{r}} \frac{ZT}{\kappa^2 + k^2} = \frac{ZT}{4\pi r} e^{-\kappa r} \; , \tag{22}$$

which is just a screened Coulomb type potential with a screening length equal to κ^{-1}, the correlation length of our system. Thus we see that in the critical region where the correlation length becomes very large, the range of the correlation function tends to infinity. Eq. (22) is a result first arrived at by Ornstein and Zernicke[6] in 1914.

We recall that the above results are only valid when we can neglect the fourth order term in the free energy density. However, as we get closer to the critical temperature, the coefficient of the quadratic term will tend to zero and the fourth order term will start to dominate. We observe that a change of scale by a factor λ in the order parameter induces the transformations $b \rightarrow b\lambda^4$ and $Z^{-1} \rightarrow Z^{-1}\lambda^2$, so that the quantity bZ^2, which has units of reciprocal energy times length, remains invariant. Thus if we define a length

$$\xi_0 \equiv (bZ^2 T_c)^{-1} \; , \tag{23}$$

then we expect that the above results of mean field theory should hold when $\frac{\xi}{\xi_0} << 1$, and start to break down when ξ becomes larger than ξ_0.

C. Hydrodynamics

It is necessary to employ hydrodynamic equations of motion in calculating the time dependent correlation functions[7] of concentration and velocity. The time dependence of the concentration[3] is derived from the continuity equation

$$\frac{\partial S}{\partial t} + \vec{\nabla}\cdot\vec{J} = 0 \quad , \tag{24}$$

where $\vec{J}$ is the particle current, given by

$$\vec{J}(\vec{r},t) = S(\vec{r},t)\,\vec{v}(\vec{r},t) \quad , \tag{25}$$

where $\vec{v}(\vec{r},t)$ is the fluid velocity at space time point $(\vec{r},t)$. It is also possible to write a constitutive equation, analogous to Ohm's Law in electricity:

$$\vec{J} = -\lambda\vec{\nabla}\mu \quad , \tag{26}$$

where λ is the particle conductivity. If we make use of the definition of the susceptibility, then we can write

$$\vec{\nabla}\mu = \frac{1}{\left(\frac{\partial S}{\partial \mu}\right)}\vec{\nabla}S = \frac{1}{\chi}\vec{\nabla}S \quad , \tag{27}$$

and Eq. (24) becomes

$$\frac{\partial S}{\partial t} = D\nabla^2 S \quad , \tag{28}$$

where

$$D = \frac{\lambda}{\chi} \tag{29}$$

This is just the diffusion equation, with D equal to the particle diffusion coefficient. More generally, we have the equation for the wavenumber dependent concentration fluctuation

$$\frac{d}{dt} S_{\vec{k}}(t) = -\Gamma_{\vec{k}} S_{\vec{k}}(t) , \tag{30}$$

where $\Gamma_{\vec{k}}$ is the decay rate of the $\vec{k}$th mode, given by

$$\Gamma_{\vec{k}} = D_{\vec{k}} k^2 = \frac{\lambda_{\vec{k}}}{\chi_{\vec{k}}} k^2 . \tag{31}$$

The solution of Eq. (30) is just

$$S_{\vec{k}}(t) = e^{-\Gamma_{\vec{k}} t} S_{\vec{k}}(0) , \qquad t > 0 , \tag{32}$$

and

$$g_{\vec{k}}(t_{21}) = \langle S_{\vec{k}}(t_2) S_{\vec{k}}(t_1) \rangle = \langle |S_{\vec{k}}|^2 \rangle e^{-\Gamma_{\vec{k}} |t_{21}|} \tag{33}$$

To determine the velocity autocorrelation function, one makes use of the equipartition theorem to calculate the equal time value, and the Navier-Stokes equation to calculate the time dependence. First, we Fourier analyze the velocity field,

$$\vec{v}(\vec{r}, t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}} \vec{v}_{\vec{k}}(t) e^{i\vec{k}\cdot\vec{r}} , \tag{34}$$

and resolve $\vec{v}_{\vec{k}}(t)$ into orthogonal components

$$\vec{v}_{\vec{k}}(t) = \sum_{\mu=1}^{2} \hat{\varepsilon}_{\vec{k}\mu} v_{\vec{k}\mu}(t) . \tag{35}$$

We have only two directions of polarization, since we will only be interested in the transverse velocity modes, with $\hat{\varepsilon}_{\vec{k}\mu}$ representing a unit vector along the direction of polarization, such that

$$\vec{k}\cdot\hat{\varepsilon}_{\vec{k}\mu} = 0 \,, \qquad \mu = 1,2 . \tag{36}$$

We can write the kinetic energy of the fluid as

$$E_{kinetic} = \int \frac{1}{2}\rho v^2 d^3r$$

$$= \frac{\rho}{2\Omega}\sum_{\vec{k},\mu}\sum_{\vec{k}',\mu'} v_{\vec{k}\mu} v_{\vec{k}'\mu'}\, \hat{\varepsilon}_{\vec{k}\mu}\cdot\hat{\varepsilon}_{\vec{k}'\mu'} \int e^{i(\vec{k}+\vec{k}')\cdot\vec{r}} d^3r$$

$$= \frac{1}{2}\rho \sum_{\vec{k}}\sum_{\mu=1}^{2} |v_{\vec{k}\mu}|^2 . \tag{37}$$

The equipartition theorem then implies that

$$\frac{\rho}{2}\langle |v_{\vec{k}\mu}|^2 \rangle = \frac{T}{2} \,,$$

or

$$\langle |v_{\vec{k}\mu}|^2 \rangle = \frac{T}{\rho} \tag{38}$$

where ρ is the mass density of the fluid. Again we have the situation that different velocity modes are statistically independent. To determine the time dependence of the velocity modes we make use of the linearized Navier-Stokes equation:

$$\rho\frac{\partial}{\partial t}\vec{v}(\vec{r},t) = \vec{\nabla}\cdot\overleftrightarrow{T}(\vec{r},t) \,, \tag{39}$$

where $\overleftrightarrow{T}$ is the stress tensor, whose cartesian components are given by

$$\mathcal{T}_{ij} = -p\delta_{ij} + \eta\left[\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right] + \delta_{ij}\left(\zeta - \frac{2}{3}\eta\right)(\vec{\nabla}\cdot\vec{v}) \quad , \tag{40}$$

where p is the hydrostatic pressure, and η and ζ are the shear and bulk viscosities, respectively. If we separate out the transverse components of the velocity, that is the part for which

$$\vec{\nabla}\cdot\vec{v}(\vec{r},t) = 0 \quad , \tag{41}$$

then Eq. (39) becomes

$$\frac{\partial}{\partial t} v_i(\vec{r},t) = \frac{\eta}{\rho}\nabla^2 v_i(\vec{r},t) \quad , \tag{42}$$

or

$$\frac{d}{dt} v_{k\mu}(t) = -\frac{\eta}{\rho} k^2 v_{k\mu}(t) \quad , \tag{43}$$

and thus we can write the velocity correlation function as

$$\langle v_{k\mu}(t_2)\, v_{-k\mu}(t_1)\rangle = \frac{T}{\rho}\, e^{-\frac{\eta}{\rho}k^2|t_{21}|} \quad . \tag{44}$$

We note that the velocity equal time correlation function is not k-dependent, whereas the equal time concentration correlation function has the k-dependent, and also temperature dependent Ornstein-Zernicke form. We also note that the velocity modes will decay much faster than the concentration modes in the critical region, because we expect that D will go to zero strongly while $\frac{\eta}{\rho}$ will either have a weak divergence or stay finite.

In this chapter we have developed the tools of mean field theory and hydrodynamics, which will be indispensable in our analysis of the critical variation of transport coefficients. In each case we will relate the transport coefficient to an integral over all space and time of a correlation function of the relevant fluctuating quantities[8,9]. To evaluate these integrals we will need to use the concentration and velocity autocorrelation functions, which we have just derived.

II. CRITICAL SHEAR VISCOSITY

A. Fluctuation-Dissipation Formula

The wavenumber and frequency dependent shear viscosity $\eta_{\vec{q}}(\omega)$ can be computed from a fluctuation-dissipation formula relating the viscosity to the Fourier transform over space and time of the autocorrelation function of the local, time dependent, off-diagonal component of the stress tensor $\mathcal{T}_{xz}(\vec{r},t)$[10,11]. That is

$$\eta_{\vec{q}}(\omega) = \frac{1}{2T}\int d^3r_{21}\, dt_{21} \langle \mathcal{T}_{xz}(\vec{r}_2,t_2)\,\mathcal{T}_{xz}(\vec{r}_1,t_1)\rangle e^{i(\vec{q}\cdot\vec{r}_{21}-\omega t_{21})} , \quad (1)$$

where T is the absolute temperature in a system of units in which the Boltzmann constant is set equal to unity ($k_B \equiv 1$), and where $\vec{r}_{21}=\vec{r}_2-\vec{r}_1$ and $t_{21}=t_2-t_1$ are relative space and time separations.

To calculate the excess viscosity in the critical region it is necessary to relate the local time dependent stress tensor to the order parameter fluctuations, which become very large in amplitude, extremely far ranging, and very long lived. This is accomplished by identifying the Ginzburg-Landau free energy density with a Lagrangian density, and using a canonical expression relating the stress tensor to the Lagrangian density.

The most probable configuration of a system is that which maximizes the partition function Z_Ω, or equivalently, minimizes the total free energy $\int \mathcal{F} d^3r$, since

$$Z_\Omega = \sum_{\{s\}} e^{-\beta \int \mathcal{F} d^3r} , \tag{2}$$

where $\sum_{\{s\}}$ denotes the sum over all possible configurations in space of the order parameter s. Thus, if we consider the free energy density $\mathcal{F}$ to be a functional of the order parameter and its gradient, i.e.

$$\mathcal{F} = \mathcal{F}[s, s_i] , \quad i = 1, 2, 3 , \tag{3}$$

where

$$s_i \equiv \frac{\partial s}{\partial x_i} , \tag{4}$$

then the problem of the most probable configuration of the system is equivalent to minimizing the free energy, and, thereby, becomes a problem in the calculus of variations, where the variation of the integral over all space of $\mathcal{F}$ is zero:

$$\delta \int d^3r \, \mathcal{F}[s, s_i] = 0 , \tag{5}$$

or, the functional derivative of $\mathcal{F}$ with respect to s vanishes:

$$\frac{\delta \mathcal{F}}{\delta s} = 0 . \tag{6}$$

Eq. (5) then becomes

$$\delta \int d^3r \, \mathcal{F}[s, s_i] = \int d^3r \left\{ \mathcal{F}[s + \delta s, s_i + \delta s_i] - \mathcal{F}[s, s_i] \right\}$$

$$= \int d^3r \left[\frac{\partial \mathcal{F}}{\partial s} \delta s + \sum_{i=1}^{3} \frac{\partial \mathcal{F}}{\partial s_i} \delta s_i \right] = 0 . \tag{7}$$

If we note that

$$\delta s_i = \delta \frac{\partial s}{\partial x_i} = \frac{\partial}{\partial x_i}(s+\delta s) - \frac{\partial}{\partial x_i} s = \frac{\partial}{\partial x_i}(\delta s) , \tag{8}$$

and if we integrate the second term in Eq. (7) by parts, ignoring surface terms, we get

$$\int d^3r\, \delta s \left[\frac{\partial \mathcal{F}}{\partial s} - \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \frac{\partial \mathcal{F}}{\partial s_i} \right] = 0 . \tag{9}$$

For arbitrary variations δs, this leads to the Euler-Lagrange equation

$$\frac{\partial \mathcal{F}}{\partial s} - \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \frac{\partial \mathcal{F}}{\partial s_i} = 0 . \tag{10}$$

Therefore, we can employ a canonical formalism, with the free energy density analogous to the Lagrangian density in scalar field theory[12].

We can, therefore, use the absence of explicit coordinate dependence of the free energy density $\mathcal{F}$ to derive an expression for the stress tensor $\mathcal{T}_{ij}$. Under an infinitesimal displacement

$$x_i' = x_i + \epsilon_i \tag{11}$$

the free energy density changes by the amount

$$\delta \mathcal{F} = \mathcal{F}' - \mathcal{F} = \sum_{i=1}^{3} \epsilon_i \frac{\partial \mathcal{F}}{\partial x_i} . \tag{12}$$

If, however, $\mathcal{F}$ has no explicit coordinate dependence, then

$$\delta \mathcal{F} = \frac{\partial \mathcal{F}}{\partial s} \delta s + \sum_{i=1}^{3} \frac{\partial \mathcal{F}}{\partial s_i} \delta s_i , \tag{13}$$

where

$$\delta s = s(\vec{r}+\vec{\epsilon}) - s(\vec{r}) = \sum_{j=1}^{3} \epsilon_j \frac{\partial s}{\partial x_j} = \sum_{j=1}^{3} \epsilon_j s_j \ . \tag{14}$$

But, by the Euler-Lagrange equation, Eq. (13) becomes

$$\delta\mathcal{F} = \sum_{i=1}^{3} \left[\left(\frac{\partial}{\partial x_i} \frac{\partial \mathcal{F}}{\partial s_i} \right) \delta s + \frac{\partial \mathcal{F}}{\partial s_i} \left(\frac{\partial}{\partial x_i} \delta s \right) \right]$$

$$= \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \left(\frac{\partial \mathcal{F}}{\partial s_i} \delta s \right) = \sum_{i=1}^{3} \frac{\partial}{\partial x_i} \left(\frac{\partial \mathcal{F}}{\partial s_i} \sum_{j=1}^{3} \epsilon_j s_j \right)$$

$$= \sum_{j=1}^{3} \sum_{i=1}^{3} \epsilon_j \frac{\partial}{\partial x_i} \left(\frac{\partial \mathcal{F}}{\partial s_i} s_j \right) \ . \tag{15}$$

If we equate Eqs. (12) and (15) we obtain

$$\sum_{j=1}^{3} \sum_{i=1}^{3} \epsilon_j \frac{\partial}{\partial x_i} \left[\frac{\partial \mathcal{F}}{\partial s_i} s_j - \delta_{ij} \mathcal{F} \right] = 0 \ , \tag{16}$$

or

$$\sum_{i=1}^{3} \frac{\partial}{\partial x_i} \mathcal{T}_{ij} = 0 \ , \tag{17}$$

where we identify $\mathcal{T}_{ij}$ with the stress tensor, which we define by

$$\mathcal{T}_{ij} \equiv \frac{\partial \mathcal{F}}{\partial s_i} s_j - \delta_{ij} \mathcal{F} \ . \tag{18}$$

In particular, let us now consider the Ginzburg-Landau equation for the free energy density

$$\mathcal{F}[s, \nabla s] = \frac{a}{2} s^2 + \frac{Z^{-1}}{2} (\nabla s)^2 + \frac{b}{4} s^4 - \mu s \ , \tag{19}$$

where, in the binary liquid we identify the order parameter s with the excess local concentration, and μ with the chemical potential, then the Euler-Lagrange equation provides us with the "equation of motion," or in this case the equation of state:

$$\mu = as + bs^3 - Z^{-1}\nabla^2 s \quad , \tag{20}$$

and the off diagonal component of the stress tensor:

$$\begin{aligned} \mathcal{T}_{xz}(\vec{r},t) &= \frac{\partial \mathcal{F}}{\partial s_x} s_z = Z^{-1} s_x s_z \\ &= Z^{-1}\left[\frac{\partial}{\partial x} s(\vec{r},t)\right]\left[\frac{\partial}{\partial z} s(\vec{r},t)\right] . \end{aligned} \tag{21}$$

We note the μs term in the diagonal components of the stress tensor, so that the divergence of the stress tensor will contain a term ∇(sμ), which is recognizable as the force per unit volume caused by the gradient in the chemical potential density. This, in turn is equal to the time rate of change of momentum density, or momentum density flow, in a region of fluid Thus, we can justify the choice of unity as the arbitrary constant factor involved in the definition of the stress tensor, Eqs. (16)-(18).

From now on it will be convenient to work in wavenumber space, rather than configuration space. This is accomplished by Fourier transforming the order parameter as follows:

$$s(\vec{r},t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}} S_{\vec{k}}(t)\, e^{i\vec{k}\cdot\vec{r}} \tag{22}$$

$$S_{\vec{k}}(t) = \frac{1}{\Omega^{1/2}} \int d^3r\, s(\vec{r},t)\, e^{-i\vec{k}\cdot\vec{r}} , \tag{23}$$

where Ω is the volume of the system. In the thermodynamic limit it is possible to transform the sum over $\vec{k}$ into an integral over $\vec{k}$ by the prescription:

$$\frac{1}{\Omega} \sum_{\vec{k}} \longrightarrow \int^{k_0} \frac{d^3k}{(2\pi)^3} , \tag{24}$$

where the upper limit of integration is a Debye cutoff.

Similarly, if we Fourier transform the local stress tensor:

$$\mathcal{T}_{xz}(\vec{r},t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}} \mathcal{T}_{xz}^{\vec{k}}(t)\, e^{i\vec{k}\cdot\vec{r}} \tag{25}$$

$$\mathcal{T}_{xz}^{\vec{k}}(t) = \frac{1}{\Omega^{1/2}} \int d^3r\, \mathcal{T}_{xz}(\vec{r},t)\, e^{-i\vec{k}\cdot\vec{r}} , \tag{26}$$

then by Eqs. (21) and (22), (26) becomes

$$\mathcal{T}_{xz}^{\vec{k}}(t) = \frac{Z^{-1}}{\Omega^{1/2}} \sum_{\vec{l}} l_x (k_z - l_z)\, S_{\vec{l}}(t)\, S_{\vec{k}-\vec{l}}(t) . \tag{27}$$

We can now rewrite the fluctuation-dissipation formula for the shear viscosity, Eq. (1):

$$\eta_{\vec{q}}(\omega) = \frac{1}{2T} \int dt_{21}\, e^{i\omega t_{21}} \frac{1}{\Omega} \sum_{\vec{k}} \sum_{\vec{k}'} \left\langle \mathcal{T}_{xz}^{\vec{k}}(t_2)\, \mathcal{T}_{xz}^{\vec{k}'}(t_1) \right\rangle \int d^3r_{21}\, e^{i(\vec{k}\cdot\vec{r}_2 + \vec{k}'\cdot\vec{r}_1 - \vec{q}\cdot\vec{r}_{21})} . \tag{28}$$

Translational invariance of the stress tensor demands that $\vec{k}' = -\vec{k}$, so that Eq. (28) becomes

$$\eta_{\vec q}(\omega) = \frac{1}{2T}\int dt_{21}\, e^{i\omega t_{21}} \frac{1}{\Omega}\sum_{\vec k}\langle \mathcal{T}_{xz}^{\vec k}(t_2)\, \mathcal{T}_{xz}^{-\vec k}(t_1)\rangle \int d^3 r_{21}\, e^{i(\vec k-\vec q)\cdot\vec r_{21}}$$

$$= \frac{1}{2T}\int dt_{21}\, e^{i\omega t_{21}} \sum_{\vec k}\langle \mathcal{T}_{xz}^{\vec k}(t_2)\, \mathcal{T}_{xz}^{-\vec k}(t_1)\rangle\, \delta_{\vec k,\vec q}$$

$$= \frac{1}{2T}\int dt_{21}\, e^{i\omega t_{21}} \langle \mathcal{T}_{xz}^{\vec q}(t_2)\, \mathcal{T}_{xz}^{-\vec q}(t_1)\rangle \quad . \qquad (29)$$

To calculate the anomalous part of the shear viscosity in the critical region, we substitute the contribution to $\mathcal{T}_{xz}^{\vec q}(t)$ of the concentration fluctuations, namely Eq. (27), so that Eq. (29) becomes

$$\Delta\eta_{\vec q}(\omega) = -\frac{1}{2TZ^2\Omega}\int dt_{21}\, e^{i\omega t_{21}} \sum_{\vec \ell}\sum_{\vec \ell'} \ell_x(q_z-\ell_z)\,\ell'_x(q_z+\ell'_z)$$

$$\times\ \langle S_{\vec\ell}(t_2)\, S_{\vec q-\vec\ell}(t_2)\, S_{\vec\ell'}(t_1)\, S_{-\vec q-\vec\ell'}(t_1)\rangle \quad . \qquad (30)$$

At this point we have to consider the correlation function in the above equation. We must correlate two components of the order parameter at time t_1 with two other components at time t_2. We will make a decoupling approximation, which we will justify later. This approximation suggests that we treat this correlation function as the sum of all possible products of two correlation functions of the form $\langle s_{k_1}(t_2) s_{k_2}(t_1)\rangle$. In Feynman diagram notation, this is equivalent to considering only graphs of the form:

(31)

Later we will show that higher order graphs do not contribute to the shear viscosity. Thus we will write

$$\langle S_{\vec{\ell}}(t_2)\, S_{\vec{q}-\vec{\ell}}(t_2)\, S_{\vec{\ell}'}(t_1)\, S_{-\vec{q}-\vec{\ell}'}(t_1)\rangle =$$

$$\langle S_{\vec{\ell}}(t_2)\, S_{\vec{\ell}'}(t_1)\rangle \langle S_{\vec{q}-\vec{\ell}}(t_2)\, S_{-\vec{q}-\vec{\ell}'}(t_1)\rangle + \langle S_{\vec{\ell}}(t_2)\, S_{-\vec{q}-\vec{\ell}'}(t_1)\rangle \langle S_{\vec{q}-\vec{\ell}}(t_2)\, S_{\vec{\ell}'}(t_1)\rangle$$

$$= \delta_{\vec{\ell}',-\vec{\ell}} \langle S_{\vec{\ell}}(t_2)\, S_{-\vec{\ell}}(t_1)\rangle \langle S_{\vec{q}-\vec{\ell}}(t_2)\, S_{-\vec{q}+\vec{\ell}}(t_1)\rangle$$

$$+ \delta_{\vec{\ell}',-\vec{q}+\vec{\ell}} \langle S_{\vec{\ell}}(t_2)\, S_{-\vec{\ell}}(t_1)\rangle \langle S_{\vec{q}-\vec{\ell}}(t_2)\, S_{-\vec{q}+\vec{\ell}}(t_1)\rangle$$

$$= \langle S_{\vec{\ell}}(t_2)\, S_{-\vec{\ell}}(t_1)\rangle \langle S_{\vec{q}-\vec{\ell}}(t_2)\, S_{-\vec{q}+\vec{\ell}}(t_1)\rangle \left(\delta_{\vec{\ell}',-\vec{\ell}} + \delta_{\vec{\ell}',-\vec{q}+\vec{\ell}}\right). \quad (32)$$

If we assume that the order parameter fluctuations decay exponentially with a wavenumber dependent lifetime $\Gamma_{\vec{\ell}}^{-1}$ we can write each time dependent correlation function as the equal time correlation function times a decaying exponential as follows:

$$\langle S_{\vec{\ell}}(t_2)\, S_{-\vec{\ell}}(t_1)\rangle = \langle |S_{\vec{\ell}}|^2\rangle\, e^{-\Gamma_{\vec{\ell}}|t_2-t_1|} \quad . \tag{33}$$

If we substitute Eqs. (32) and (33) into (30) we obtain

$$\Delta\eta_{\vec{q}}(\omega) = -\frac{1}{2TZ^2\Omega}\sum_{\vec{\ell}}\sum_{\vec{\ell}'} \ell_x \ell'_x (q_z-\ell_z)(q_z+\ell'_z)\langle |S_{\vec{\ell}}|^2\rangle\langle |S_{\vec{q}-\vec{\ell}}|^2\rangle$$

$$\times(\delta_{\vec{\ell}',-\vec{\ell}} + \delta_{\vec{\ell}',-\vec{q}+\vec{\ell}})\int_{-\infty}^{\infty} dt_{21}\, e^{i\omega t_{21}}\, e^{-(\Gamma_{\vec{\ell}}+\Gamma_{\vec{q}-\vec{\ell}})|t_{21}|} \quad . \tag{34}$$

In the above equation we will take $\vec{q}$ to be along the z-axis, so that Eq. (34) becomes

$$\Delta\eta_{\vec{q}}(\omega) = \frac{1}{2TZ^2\Omega}\sum_{\vec{\ell}} \ell_x(q_z-\ell_z)\left[\ell_x(q_z-\ell_z)-\ell_x\ell_z\right]$$

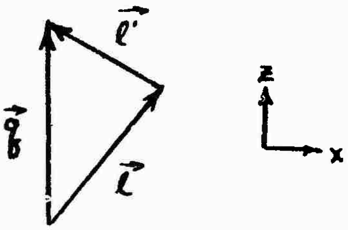
$$\times \quad \langle |S_{\vec{\ell}}|^2\rangle\langle |S_{\vec{q}-\vec{\ell}}|^2\rangle\, \frac{2(\Gamma_{\vec{\ell}}+\Gamma_{\vec{q}-\vec{\ell}})}{\omega^2+(\Gamma_{\vec{\ell}}+\Gamma_{\vec{q}-\vec{\ell}})^2} \quad . \tag{35}$$

To exhibit and make use of the symmetry in the above expression it is convenient to make the substitution

$$\vec{\ell}' \equiv \vec{q}-\vec{\ell}$$

$$\ell'_z = q-\ell_z \tag{36}$$

$$\ell'_x = -\ell_x$$



then

$$\Delta\eta_{\vec{q}}(\omega) = -\frac{1}{2TZ^2\Omega}\sum_{\vec{\ell}} \ell_x \ell'_x \ell'_z(\ell'_z-\ell_z)\langle |S_{\vec{\ell}}|^2\rangle\langle |S_{\vec{\ell}'}|^2\rangle$$

$$\times \quad \frac{2(\Gamma_{\vec{\ell}}+\Gamma_{\vec{\ell}'})}{\omega^2+(\Gamma_{\vec{\ell}}+\Gamma_{\vec{\ell}'})^2} \quad . \tag{37}$$

If we note that we can write

$$\ell_z' = \frac{1}{2}(\ell_z' - \ell_z) + \frac{1}{2}(\ell_z' + \ell_z) \tag{38}$$

then only the first term will contribute to Eq. (37), because the second term will antisymmetrize (37). Then

$$\Delta\eta_{\vec{k}}(\omega) = \frac{-1}{2TZ^2\Omega} \sum_{\vec{\ell}} \ell_x \ell_x' (\ell_z' - \ell_z)^2 \langle |S_{\vec{\ell}}|^2 \rangle \langle |S_{\vec{\ell}'}|^2 \rangle \frac{(\Gamma_{\vec{\ell}} + \Gamma_{\vec{\ell}'})}{\omega^2 + (\Gamma_{\vec{\ell}} + \Gamma_{\vec{\ell}'})^2} . \tag{39}$$

Now we are in a position to apply the above formula to a few special cases.

B. Temperature Dependence at Zero Frequency and Wavenumber

At zero frequency and wavenumber, $\vec{\ell}' = -\vec{\ell}$, $\omega = 0$, and Eq. (39) becomes

$$\Delta\eta(\kappa) \equiv \Delta\eta_{\vec{0}}(0) = \frac{1}{TZ^2\Omega} \sum_{\vec{\ell}} \frac{\ell_x^2 \ell_z^2}{\Gamma_{\vec{\ell}}} \langle |S_{\vec{\ell}}|^2 \rangle^2 , \tag{40}$$

where κ^{-1} is the correlation length. In the critical region we will use the Ornstein-Zernicke formula for the wavenumber dependent order parameter correlation function, namely

$$g_{\vec{\ell}} = \langle |S_{\vec{\ell}}|^2 \rangle = \frac{ZT}{\kappa^2 + \ell^2} . \tag{41}$$

For the linewidth of the order parameter fluctuations we will use a modification of the Kawasaki[13,14] formula:

$$\Gamma_{\vec{\ell}} = \frac{T\ell^2}{6\pi\eta_0} (\kappa^2 + \ell^2)^{1/2} K\left(\frac{\ell}{\kappa}\right) , \tag{42}$$

where η_0 is the non-anomalous, background shear viscosity, which is the component of the shear viscosity not influenced by the critical fluctuations. The Kawasaki scaling function K(z) is a slowly varying function with a minimum value, K(o), of 1, and a maximum value K(∞) of $\frac{3\pi}{8}$ (=1.18), explicitly given by:

$$K(z) = \frac{3}{4}(1+z^2)^{1/2}\left[\frac{1}{z^2} + \left(\frac{1}{z} - \frac{1}{z^3}\right)\tan^{-1} z\right] . \tag{43}$$

Experimentally, it has been found that the linewidth behaves as if the scaling function were constant and equal to its high wavenumber limit, $\frac{3\pi}{8}$, and η_o replaced by an experimentally fitted parameter $\bar{\eta}$, about 29% larger than the background viscosity η_o. Therefore, we assume that

$$\Gamma_{\vec{\ell}} = \frac{T\ell^2}{16\bar{\eta}}(\kappa^2 + \ell^2)^{\frac{1}{2}} . \tag{44}$$

Substituting Eqs. (41) and (44) into (40) we get

$$\frac{\Delta\eta(\kappa)}{\bar{\eta}} = \frac{16}{\Omega}\sum_{\vec{\ell}} \frac{\ell_x^2 \ell_z^2}{\ell^2(\kappa^2+\ell^2)^{5/2}} . \tag{45}$$

We first calculate the angular average:

$$\left\langle \frac{\ell_x^2 \ell_z^2}{\ell^4} \right\rangle_{\theta,\phi} = \frac{1}{4\pi}\int_0^{\pi} \sin\theta\, d\theta \int_0^{2\pi} d\phi \left[\sin^2\theta \cos^2\phi \cos^2\theta\right]$$

$$= \frac{1}{4\pi}\int_0^{\pi} \cos^2\theta \sin^3\theta\, d\theta \int_0^{2\pi} \cos^2\phi\, d\phi$$

$$= \frac{1}{4}\int_{-1}^{1} \mu^2(1-\mu^2)\, d\mu = \frac{1}{2}\left(\frac{1}{3} - \frac{1}{5}\right) = \frac{1}{15} , \tag{46}$$

so that Eq. (45), upon transforming the sum to an integral through Eq. (24), becomes

$$\frac{\Delta\eta(\kappa)}{\bar{\eta}} = 16\left(\frac{4\pi}{15}\right)\frac{1}{(2\pi)^3}\int_0^{k_D}\frac{\ell^4\,dk}{(\kappa^2+\ell^2)^{5/2}}$$

$$= \frac{8}{15\pi^2}\int_0^{k_D}\frac{\ell^4\,d\ell}{(\kappa^2+\ell^2)^{5/2}} \quad . \qquad (47)$$

To evaluate the above integral we make the trigonometric substitution:

$$\ell = \kappa\tan\theta \qquad (48)$$

so that

$$\int_0^{k_D}\frac{\ell^4\,d\ell}{(\kappa^2+\ell^2)^{5/2}} = \int_0^{\tan^{-1}\frac{k_D}{\kappa}}\frac{\tan^4\theta}{\sec^3\theta}\,d\theta = \int_0^{\tan^{-1}\frac{k_D}{\kappa}}\frac{\sin^2\theta}{\cos^2\theta}\cos^3\theta\left[\frac{1}{\cos^2\theta}-1\right]$$

$$= \int_0^{\tan^{-1}\frac{k_D}{\kappa}}\frac{\sin^2\theta}{\cos\theta}\,d\theta - \int_0^{\tan^{-1}\frac{k_D}{\kappa}}\sin^2\theta\cos\theta\,d\theta$$

$$= \left[-\sin\theta + \ln\tan\left(\frac{\pi}{4}+\frac{\theta}{2}\right) - \frac{1}{3}\sin^3\theta\right]_0^{\tan^{-1}\frac{k_D}{\kappa}} \quad . \qquad (49)$$

In the critical region, where the correlation length becomes very large, $\frac{k_D}{\kappa} >> 1$, and

$$\tan^{-1}\frac{k_D}{\kappa} \simeq \frac{\pi}{2} - \frac{\kappa}{k_D} \quad . \qquad (50)$$

Therefore:

$$\int_0^{k_D} \frac{\ell^4 d\ell}{(\kappa^2+\ell^2)^{5/2}} \approx -\frac{4}{3} + \ln\tan\left(\frac{\pi}{2} - \frac{\kappa}{2k_D}\right)$$

$$\approx -\frac{4}{3} + \ln\frac{2k_D}{\kappa} \qquad (51)$$

to the lowest order in $\frac{\kappa}{k_D}$. Thus for zero wavenumber and zero wavelength, we have:

$$\frac{\Delta\eta(\kappa)}{\bar{\eta}} = \frac{8}{15\pi^2}\left[\ln\frac{2k_D}{\kappa} + C_\eta^{(0)}\right], \qquad (52)$$

with

$$C_\eta^{(0)} \approx -\frac{4}{3} \approx -1.333\,. \qquad (53)$$

Assuming that κ vanishes like

$$\kappa \propto \left|\frac{T-T_c}{T_c}\right|^\nu, \qquad (54)$$

then

$$\frac{\Delta\eta(\kappa)}{\bar{\eta}} \approx \frac{8}{15\pi^2}\left[-\nu\ln\left|\frac{T-T_c}{T_c}\right| + \text{constant}\right]. \qquad (55)$$

Therefore, if $\frac{\Delta\eta(\kappa)}{\bar{\eta}}$ is plotted against $\ln\left|\frac{T-T_c}{T_c}\right|$, the slope of the line that results should be $-\frac{8\nu}{15\pi^2}$[15,16].

The critical shear viscosity of the binary system 3-methylpentane-nitroethane has been investigated by Stein, Allen, and Allegra[17], who found a slope of -.039. The critical exponent ν for the divergence of the correlation length has been found to be equal to .616 for the 3-methylpentane-nitroethane system, which would yield a theoretical slope of -.033, a value 15% lower than experiment.

C. Fourier-Laplace Transform of Critical Shear Viscosity

In the calculation of the correction to the Rayleigh linewidth due to the anomalous shear viscosity it will be useful to know the Fourier-Laplace transform of the critical shear viscosity, defined by

$$\Delta\eta^*_{\vec{q}}(p) \equiv \frac{1}{T}\int_0^\infty dt_{21}\, e^{-pt_{21}} \int d^3r_{21}\, e^{-i\vec{q}\cdot\vec{r}_{21}} \langle J_{xz}(\vec{r}_2,t_2)\, J_{xz}(\vec{r}_1,t_1)\rangle \,. \quad (56)$$

This will only modify the frequency factor of Eq. (39) as follows:

$$\Delta\eta^*_{\vec{q}}(p) = \frac{-1}{2TZ^2\Omega} \sum_{\vec{\ell}} \ell_x \ell'_x (\ell'_z - \ell_z)^2 \frac{\langle |S_{\vec{\ell}}|^2\rangle \langle |S_{\vec{\ell}'}|^2\rangle}{p + \Gamma_{\vec{\ell}} + \Gamma_{\vec{\ell}'}} \,. \quad (57)$$

We will calculate this quantity at the critical temperature $T=T_c$, where

$$g_{\vec{\ell}} \equiv \langle |S_{\vec{\ell}}|^2\rangle = \frac{ZT}{\ell^2} \,, \quad (58)$$

$$\Gamma_{\vec{\ell}} = \frac{T}{16\eta}\,\ell^3 \,. \quad (59)$$

If we convert the Laplace frequency to wavenumber units, by the equation

$$Q \equiv 4\left(\frac{\bar{\eta}\,p}{T}\right)^{1/3} \tag{60}$$

and insert Eqs. (24), (58), (59) and (60) into (57), we obtain

$$\frac{\Delta\eta^{*}_{\vec{q}}(Q)}{\bar{\eta}} = \frac{1}{\pi^{3}}\int^{k_D}\frac{d^{3}\ell}{\ell^{2}\ell'^{2}}\cdot\frac{\ell_x^{2}(\ell_z'-\ell_z)^{2}}{\ell^{3}+\ell'^{3}+\frac{1}{4}Q^{3}} \; . \tag{61}$$

Let us now consider the important special case $\vec{q}=\vec{o}$. Then we can say $\vec{\ell}'=-\vec{\ell}$, and Eq. (61) becomes

$$\frac{\Delta\eta^{*}_{\vec{o}}(Q)}{\bar{\eta}} = \frac{4}{\pi^{3}}\int^{k_D}\frac{d^{3}\ell}{\ell^{4}}\;\frac{\ell_x^{2}\ell_z^{2}}{2\ell^{3}+\frac{1}{4}Q^{3}}$$

$$= \frac{2}{\pi^{3}}\cdot\frac{4\pi}{15}\int_{0}^{k_D}\frac{\ell^{2}\,d\ell}{\ell^{3}+\left(\frac{Q}{2}\right)^{3}}$$

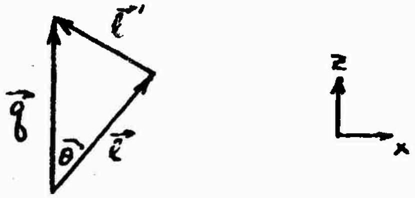
$$= \frac{8}{15\pi^{2}}\cdot\frac{1}{3}\,\ln\left[\frac{k_D^{3}+\left(\frac{Q}{2}\right)^{3}}{\left(\frac{Q}{2}\right)^{3}}\right]$$

$$\approx \frac{8}{15\pi^{2}}\,\ln\frac{2k_D}{Q} \tag{62}$$

for small enough Laplace frequency to consider $Q \ll k_D$. Again we get the $\frac{8}{15\pi^2}$ times a logarithm term, with the inverse correlation length replaced by the frequency in wavenumber units, as we would expect from the principle of dynamic scaling[18,19]. Because of the convenient definition of Q, we have no additive constant to the logarithm, as we had in the case of zero wavenumber and frequency. Equivalently we can say that $(\ln\ \kappa - C_\eta^{(o)})$ is to be replaced by ln Q, or that Q scales as $\kappa e^{-C_\eta^{(o)}}$, i.e.

$$\kappa \rightarrow Q e^{c_{\eta}^{(0)}} = Q e^{-4/3} = .26Q \tag{63}$$

Returning now to the more general case, where $\vec{q} = \vec{\ell} + \vec{\ell}'$, or graphically:



,

it is convenient to transform the integral over $\mu = \cos\theta$, to an integral over ℓ' through the law of cosines:

$$\ell'^2 = \ell^2 + q^2 - 2q\ell\mu \quad , \tag{64}$$

or

$$\mu = \frac{\ell^2 - \ell'^2 + q^2}{2q\ell} \tag{65}$$

$$d\mu = -\frac{\ell' d\ell'}{q\ell} \tag{66}$$

$$\ell_x^2 = \ell^2 \sin^2\theta \cos^2\phi = \ell^2 \cos^2\phi \, (1-\mu^2) \quad , \tag{67}$$

$$1 - \mu^2 = 1 - \frac{\ell^4 + \ell'^4 + q^4 - 2\ell^2\ell'^2 - 2q^2\ell'^2 + 2q^2\ell^2}{4q^2\ell^2}$$

$$= \frac{2q^2(\ell^2 + \ell'^2) - q^4 - (\ell'^2 - \ell^2)^2}{4q^2\ell^2} \quad , \tag{68}$$

$$\ell_y' - \ell_y = q - 2\ell\mu = q - \frac{\ell^2 - \ell'^2 + q^2}{q} = \frac{\ell'^2 - \ell^2}{q} \quad . \tag{69}$$

Noting that the integration over the aximuthal angle gives a factor of $\int_0^{2\pi}\cos^2\phi\,d\phi = \pi$, and substituting Eqs. (64)-(69) into (61), we find:

$$\frac{\Delta\eta^*_{\vec{q}}(Q)}{\bar{\eta}} = \frac{1}{\pi^2}\int_0^{k_D} d\ell\,\ell^2 \int_{|q-\ell|}^{(q+\ell)} \frac{\ell' d\ell'}{q\ell}\cdot\frac{\ell^2[2q^2(\ell^2+\ell'^2)-\,.\,.\,-(\ell'^2-\ell^2)^2]}{4q^2k^2(\ell^3+\ell'^3+\frac{1}{4}Q^3)}\;\frac{(\ell'^2-\ell^2)^2}{q^2\ell^2\ell'^2}\;. \qquad (70)$$

If we transform to dimensionless units, where

$$\left.\begin{aligned} u &\equiv \frac{\ell}{q} \\ u' &\equiv \frac{\ell'}{q} \end{aligned}\right\}\;, \qquad (71)$$

$$P \equiv \frac{64\bar{\eta}\rho}{Tq^3} = \frac{4\rho}{Tq^3/16\bar{\eta}}\;, \qquad (72)$$

then Eq. (70) becomes

$$\frac{\Delta\eta^*_{\vec{q}}(P)}{\bar{\eta}} = \frac{1}{4\pi^2}\int_0^{\frac{k_D}{q}}\frac{du}{u}\int_{|u-1|}^{(u+1)}\frac{du'}{u'}\cdot\frac{(u'^2-u^2)^2}{(u^3+u'^3+\frac{1}{4}P)}\left[2(u^2+u'^2)-1-(u'^2-u^2)^2\right]\;, \qquad (73)$$

where the region of integration is shaded in Fig. 6.

The double integral in Eq. (73) is more readily evaluated by a 45° rotation of the axes; letting

$$\left.\begin{aligned} x &= u'+u \\ x' &= u'-u \end{aligned}\right\}\;, \qquad (74)$$

$$\left.\begin{aligned} u' &= \tfrac{1}{2}(x+x') \\ u &= \tfrac{1}{2}(x-x') \end{aligned}\right\}\;, \qquad (75)$$

then, the Jacobian of the transformation is

$$\left|\frac{\partial(u,u')}{\partial(x,x')}\right| = \begin{vmatrix} \frac{1}{2} & -\frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{vmatrix} = \frac{1}{2} \tag{76}$$

and

$$uu' = \frac{1}{4}(x^2 - x'^2) \quad , \tag{77}$$

$$u'^2 - u^2 = (u'-u)(u'+u) = xx' \quad , \tag{78}$$

$$\begin{aligned} \left[2(u^2+u'^2) - 1 - (u'^2-u^2)^2\right] &= x^2 + x'^2 - 1 - x^2x'^2 \\ &= (x^2-1)(1-x'^2) \quad , \end{aligned} \tag{79}$$

$$u^3 + u'^3 = \frac{1}{4}(x^3 + 3xx'^2) \; . \tag{80}$$

Substituting Eqs. (75)-(80) into (73) we obtain

$$\begin{aligned} \frac{\Delta\eta^*_q(P)}{\bar\eta} &= \frac{1}{4\pi^2}\int_1^{\frac{2k_0}{q}}\int_{-1}^{1} \frac{\frac{1}{2}dx\,dx'}{\frac{1}{4}(x^2-x'^2)} \; \frac{x^2x'^2(x^2-1)(1-x'^2)}{\frac{1}{4}(x^3+3xx'^2+P)} \\ &= \frac{4}{\pi^2}\int_1^{\frac{2k_0}{q}} dx\,x^2(x^2-1)\int_0^1 \frac{dx'\,x'^2(1-x'^2)}{(x^2-x'^2)(x^3+3xx'^2+P)} \\ &= \frac{8}{15\pi^2}\,f(q,P) \end{aligned} \tag{81}$$

where the function f(q,P) is defined by:

$$f(q,P) \equiv \frac{15}{2}\int_1^{\frac{2k_0}{q}} dx\,x^2(x^2-1)\int_0^1 \frac{dx'\,x'^2(1-x'^2)}{(x^2-x'^2)(x^3+3xx'^2+P)} \; . \tag{82}$$

Noting that the double integral in the above equation ranges over values of x larger than unity, and values of x' smaller than unity, we can approximate it by neglecting x' and unity when added or subtracted from x, so that a first approximation to f(q,P) is:

$$f_o(q,P) = \frac{15}{2}\int_1^{\frac{2k_D}{q}} \frac{x^2dx}{x^3+P}\int_0^1 dx\,x'^2(1-x'^2)$$

$$= \ln\left[\frac{\left(\frac{2k_D}{q}\right)^3+P}{1+P}\right]^{\frac{1}{3}}$$

$$\approx \ln\frac{2k_D}{(q^3+Q^3)^{1/3}} \quad . \qquad (83)$$

Again we recover the logarithmic dependence. If either the wavenumber or frequency is very large, such that q and Q are of different orders of magnitude, then the ratio of the excess shear viscosity to the total shear viscosity is equal to $8/15\pi^2$ times the natural logarithm of the ratio of $2k_D$ to the larger of q or Q.

We note that f(q,P) depends on q only through the upper limit of the x integral in Eq. (82). Thus, if we subtract $f_o(q,P)$ from f(q,P), then at least to order $\frac{q}{2k_D}$ we can extend the limit to infinity, having subtracted out the divergent part. If we define

$$\sigma_\eta(q,P) \equiv f(q,P) - f_o(q,P) = \sigma_\eta(P) \quad , \qquad (84)$$

then the scaling function σ_η will only be a function of P, which is proportional to the ratio of the Laplace frequency to the cube of the wavenumber. Therefore, if we subtract Eq. (83) from (82) and extend the integral to infinity, then we have

$$\sigma_\eta(P) = \frac{15}{2}\int_1^\infty dx\,x^2\int_0^1 dx\,x'^2(1-x'^2)\left[\frac{(x^2-1)}{(x^2-x'^2)(x^3+3xx'^2+P)} - \frac{1}{x^3+P}\right]$$

$$= -\frac{15}{2}\int_1^\infty dx\,x^2\int_0^1 dx'\,x'^2(1-x'^2)\left[\frac{(1-x'^2)}{(x^2-x'^2)(x^3+3xx'^2+P)} + \frac{3xx'^2}{(x^3+P)(x^3+3xx'^2+P)}\right] \quad (85)$$

It is possible to perform the x' integration if we let

$$a(x) \equiv (x^3+P)^{1/2} \quad , \qquad (86)$$

$$b(x) \equiv (3x)^{1/2} \quad , \qquad (87)$$

then

$$\sigma_\eta(P) = -\frac{15}{2}\int_1^\infty dx\,x^2\int_0^1 dx'\,x'^2(1-x'^2)\left[\frac{(1-x'^2)}{(x^2-x'^2)(a^2+b^2x'^2)} + \frac{b^2x'^2}{a^2(a^2+b^2x'^2)}\right]$$

$$= -\frac{15}{2}\int_1^\infty \frac{dx\,x^2}{a^2+b^2x^2}\int_0^1 dx\,x'^2(1-x'^2)\left[\frac{(1-x'^2)}{(x^2-x'^2)} + \frac{b^2(1-x'^2)}{(a^2+b^2x'^2)} + \frac{b^2(a^2+b^2x^2)x'^2}{a^2(a^2+b^2x'^2)}\right]$$

$$= -\frac{15}{2}\int_1^\infty \frac{dx\,x^2}{a^2+b^2x^2}\left\{\int_0^1 \frac{dx'\,x'^2(1-x'^2)^2}{(x^2-x'^2)} + \int_0^1 \frac{dx'\,x'^2(1-x'^2)(1+\frac{b^2}{a^2}x^2x'^2)}{(\frac{a^2}{b^2}+x'^2)}\right\}$$

$$= -\frac{15}{2}\int_1^\infty \frac{x^2dx}{a^2+b^2x^2}\left\{J_1(x) + J_2(x)\right\} \quad , \qquad (88)$$

where,

$$J_1(x) \equiv \int_0^1 \frac{dx' x'^2 (1-x'^2)^2}{x^2 - x'^2} \quad , \tag{89}$$

and

$$J_2(x) = \int_0^1 \frac{dx' x'^2 (1-x'^2)\left(1 + \frac{b^2}{a^2} x^2 x'^2\right)}{\frac{a^2}{b^2} + x'^2} \quad . \tag{90}$$

To evaluate $J_1(x)$, it is convenient to make a hyberbolic substitution:

$$\begin{aligned} x' &= x \tanh \theta \quad , \\ x^2 - x'^2 &= x^2(1 - \tanh^2 \theta) = x^2 \operatorname{sech}^2 \theta \quad , \\ dx' &= x \operatorname{sech}^2 \theta \, d\theta \quad , \end{aligned} \tag{91}$$

so that

$$\begin{aligned} J_1(x) &= \int_0^{\tanh^{-1}\frac{1}{x}} \frac{x \operatorname{sech}^2 \theta \; x^2 \tanh^2 \theta (1 - x^2 \tanh^2 \theta)^2 \, d\theta}{x^2 \operatorname{sech}^2 \theta} \\ &= x \int_0^{\tanh^{-1}\frac{1}{x}} \tanh^2 \theta (1 - 2x^2 \tanh^2 \theta + x^4 \tanh^4 \theta) \, d\theta \; . \end{aligned} \tag{92}$$

Noting that:

$$\left.\begin{aligned} \int \tanh^2 \theta \, d\theta &= \int (1 - \operatorname{sech}^2 \theta) \, d\theta = \theta - \tanh \theta \\ \int \tanh^4 \theta \, d\theta &= \int \tanh^2 \theta (1 - \operatorname{sech}^2 \theta) \, d\theta = \theta - \tanh \theta - \tfrac{1}{3} \tanh^3 \theta \\ \int \tanh^6 \theta \, d\theta &= \int \tanh^4 \theta (1 - \operatorname{sech}^2 \theta) \, d\theta = \theta - \tanh \theta - \tfrac{1}{3} \tanh^3 \theta - \tfrac{1}{5} \tanh^5 \theta \end{aligned}\right\} \tag{93}$$

we compute

$$J_1(x) = (1-x^2)^2\left(x\tanh^{-1}\frac{1}{x} - 1\right) + \frac{1}{3}(2-x^2) - \frac{1}{5}$$

$$= (1-x^2)^2\left(x\tanh^{-1}\frac{1}{x} - 1\right) + \frac{1}{3}(1-x^2) + \frac{2}{15} \quad . \qquad (94)$$

To evaluate $J_2(x)$, it is convenient to make a trigonometric substitution:

$$x' = \frac{a}{b}\tan\theta$$

$$\frac{a^2}{b^2} + x'^2 = \frac{a^2}{b^2}(1+\tan^2\theta) = \frac{a^2}{b^2}\sec^2\theta \qquad (95)$$

$$dx' = \frac{a}{b}\sec^2\theta\, d\theta$$

so that

$$J_2(x) = \int_0^{\tan^{-1}\frac{b}{a}} \frac{\frac{a}{b}\sec^2\theta\, \frac{a^2}{b^2}\tan^2\theta\left(1-\frac{a^2}{b^2}\tan^2\theta\right)(1+x^2\tan^2\theta)\,d\theta}{\frac{a^2}{b^2}\sec^2\theta} \qquad (96)$$

$$= \frac{a}{b}\int_0^{\tan^{-1}\frac{b}{a}} \left[\tan^2\theta - \left(\frac{a^2}{b^2} - x^2\right)\tan^4\theta - \frac{a^2}{b^2}x^2\tan^6\theta\right] d\theta \; .$$

Noting that

$$\left.\begin{aligned} \int \tan^2\theta\, d\theta &= \int(\sec^2\theta - 1)\,d\theta = \tan\theta - \theta \\ \int \tan^4\theta\, d\theta &= \int \tan^2\theta(\sec^2\theta-1)\,d\theta = -(\tan\theta - \theta) + \frac{1}{3}\tan^3\theta \\ \int \tan^6\theta\, d\theta &= \int \tan^4\theta(\sec^2\theta - 1)\,d\theta = (\tan\theta - \theta) - \frac{1}{3}\tan^3\theta + \frac{1}{5}\tan^5\theta \end{aligned}\right\} , \qquad (97)$$

we compute

$$J_2(x) = \left[1 + \frac{a^2}{b^2} - x^2 - \frac{a^2}{b^2}x^2\right]\left[1 - \frac{a}{b}\tan^{-1}\frac{b}{a}\right] - \left[\frac{a^2}{b^2} - x^2 - \frac{a^2}{b^2}x^2\right]\frac{b^2}{3a^2} - \frac{b^2x^2}{5a^2}$$

$$= (1-x^2)\left(1+\frac{a^2}{b^2}\right)\left(1-\frac{a}{b}\tan^{-1}\frac{b}{a}\right) - \frac{1}{3}(1-x^2) + \frac{2}{15}\frac{b^2x^2}{a^2}. \qquad (98)$$

Therefore:

$$J_1(x) + J_2(x) = (1-x^2)\left[(1-x^2)\left(x\tanh^{-1}\frac{1}{x} - 1\right) + \left(1+\frac{a^2}{b^2}\right)\left(1-\frac{a}{b}\tan^{-1}\frac{b}{a}\right)\right]$$

$$+ \frac{2}{15}\left(1 + \frac{b^2x^2}{a^2}\right), \qquad (99)$$

and by Eq. (88)

$$\sigma_\eta(P) = -\frac{15}{2}\int_1^\infty \frac{x^2dx}{4x^3+P}\left\{(1-x^2)\left[(1-x^2)\left(x\tanh^{-1}\frac{1}{x} - 1\right)\right.\right.$$

$$\left.\left. + \left(1+\frac{x^3+P}{3x}\right)\left(1-\left(\frac{x^3+P}{3x}\right)^{1/2}\tan^{-1}\left(\frac{3x}{x^3+P}\right)^{1/2}\right)\right] + \frac{2}{15}\left(\frac{4x^3+P}{x^3+P}\right)\right\}. \qquad (100)$$

To study the behavior of $\sigma_\eta(P)$ for very large values of P it is simplest to refer back to Eq. (85), and note that for large enough values of P, we can neglect the term $3xx'^2$ compared to x^3+P, so that Eq. (85) becomes, approximately

$$\sigma_\eta(P) \approx -\frac{15}{2}\int_1^\infty dx\,x^2\int_0^1 dx'x'^2(1-x'^2)\left[\frac{(1-x'^2)}{x^2(x^3+P)} + \frac{3xx'^2}{(x^3+P)^2}\right]$$

$$= -\frac{15}{2}\int_0^1 dx\,x'^2(1-x'^2)\left\{(1-x'^2)\int_1^\infty\frac{dx}{x^3+P} + 3x'^2\int_1^\infty\frac{x^3dx}{(x^3+P)^2}\right\}$$

$$= -\frac{15}{2}\int_0^1 dx'\,x'^2(1-x'^2)\left\{(1+2x'^2)\int_1^\infty \frac{dx}{x^3+P} - 3x'^2 P\int_1^\infty \frac{dx}{(x^3+P)^2}\right\}. \tag{101}$$

We can see that the above expression will vary as $P^{-2/3}$ to lowest order in P^{-1}. In fact if we define

$$I(P) \equiv \int_1^\infty \frac{dx}{x^3+P}\;, \tag{102}$$

then

$$\int_1^\infty \frac{dx}{(x^3+P)^2} = -\frac{d}{dP} I(P)\;. \tag{103}$$

Evaluating I(P) we find:

$$I(P) \equiv \int_1^\infty \frac{dx}{x^3+P} = \frac{1}{3}P^{-2/3}\left[\frac{1}{2}\ln\frac{P^{2/3}-P^{1/3}+1}{P^{2/3}+2P^{1/3}+1} + \sqrt{3}\left(\frac{\pi}{2} - \tan^{-1}\frac{2-P^{1/3}}{\sqrt{3}\,P^{1/3}}\right)\right]$$

$$\simeq \frac{2\pi}{3\sqrt{3}}P^{-2/3}\;, \tag{104}$$

and

$$-\frac{d}{dP} I(P) \approx \frac{2}{3}\cdot\frac{2\pi}{3\sqrt{3}}P^{-5/3}\;. \tag{105}$$

Thus Eq. (101) becomes

$$\sigma_\eta(P) \approx -\frac{15}{2}P^{-2/3}\left[\frac{2\pi}{3\sqrt{3}}\int_0^1 dx'\,x'^2(1-x'^2)(1+2x'^2) - \frac{4\pi}{3\sqrt{3}}\int_0^1 dx'\,x'^4(1-x'^2)\right]$$

$$= -\frac{15}{2}P^{-2/3}\,\frac{2\pi}{3\sqrt{3}}\left[\frac{26}{15\cdot 7} - \frac{12}{15\cdot 7}\right]$$

$$= -\frac{2\pi}{3\sqrt{3}}P^{-2/3} \simeq -1.209\,P^{-2/3}\;. \tag{106}$$

The scaling function was calculated for various values of P, by numerically integrating Eq. (100). In the process we transformed the infinite range of integration to a finite one by the transformation

$$x = \tan\phi \quad , \tag{107}$$

and

$$\int_1^\infty g(x)\,dx = \int_{\pi/4}^{\pi/2} g(\tan\phi)\sec^2\phi\,d\phi \tag{108}$$

The results are plotted in Figs. (3)-(5).

We note that for the special case P=0, we have

$$\sigma_\eta(0) = -\frac{15}{8}\int_1^\infty \frac{dx}{x}\left\{(1-x^2)\left[(1-x^2)\left(x\tanh^{-1}\frac{1}{x}-1\right) + \left(1+\frac{x^2}{3}\right)\left(1-\frac{x}{\sqrt{3}}\tan^{-1}\frac{\sqrt{3}}{x}\right)\right] + \frac{8}{15}\right\}$$

$$\approx -0.633 . \tag{109}$$

Eq. (85) was also used to calculate the initial slope of the scaling function, as follows:

$$\sigma_\eta'(0) = \frac{15}{2}\int_1^\infty dx\,x^2 \int_0^1 dx'\,x'^2(1-x'^2)\left[\frac{1}{x^6} - \frac{(x^2-1)}{(x^2-x'^2)(x^2+3x'^2)x^2}\right]$$

$$= \frac{15}{2}\int_1^\infty \frac{dx}{x^4}\int_0^1 dx'\,x'^2(1-x'^2) - \frac{15}{2}\int_0^1 dx'\,x'^2(1-x'^2)\int_1^\infty \frac{dx\,(x^2-1)}{(x^2-x'^2)(x^2+3x'^2)}$$

$$= \frac{1}{3} - \frac{15}{2}\int_0^1 dx'\,x'^2(1-x'^2)\int_1^\infty \frac{dx\,(x^2-1)}{(x^2-x'^2)(x^2+3x'^2)}$$

$$= \frac{1}{3} + \frac{15}{2}\int_0^1 dx'\,x'^2(1-x'^2)\left\{\frac{(1-x'^2)}{16x'^4}\int_1^\infty dx\left[\frac{1}{x^2-x'^2} - \frac{1}{x^2+3x'^2}\right] - \frac{(3x'^2+1)}{4x'^2}\int_1^\infty \frac{dx}{(x^2+3x'^2)^2}\right\}$$

$$= \frac{1}{3} + \frac{15}{2}\int_0^1 dx'(1-x'^2)\left\{\frac{(1-x'^2)}{16x'^2}\left[\frac{1}{2x'}\ln\frac{1+x'}{1-x'} - \frac{1}{\sqrt{3}x'}\left(\frac{\pi}{2} - \tan^{-1}\frac{1}{\sqrt{3}x'}\right)\right]\right.$$

$$\left. - \frac{1}{24x'^2}\left[\frac{1}{\sqrt{3}x'}(3x'^2+1)\left(\frac{\pi}{2} - \tan^{-1}\frac{1}{\sqrt{3}x'}\right) - 1\right]\right\} .$$

$$\approx 0.254 \quad . \tag{110}$$

Therefore, for small P

$$\sigma_\eta(P) \approx -0.633 + 0.254\,P \tag{111}$$

The integrals in Eqs. (109) and (110) were evaluated numerically. Details of their evaluation, along with the general evaluation of $\sigma_\eta(P)$, Eq. (100), can be found in the Appendix.

The wavenumber dependence of the critical shear viscosity in the low frequency limit can now be written as

$$\frac{\Delta\eta_q(0)}{\bar{\eta}} = \frac{8}{15\pi^2}\left[\ln\frac{2k_D}{q} - 0.633\right] , \tag{112}$$

or equivalently we can say that κ and q scale as

$$-\ln\kappa - 1.333 \leftrightarrow -\ln q - 0.633$$

or

$$\kappa \leftrightarrow q e^{-0.700}$$

$$\kappa \leftrightarrow .497\,q \, . \tag{113}$$

In this chapter we have calculated the critical shear viscosity by use of the fluctuation dissipation theorem, and have verified the experimentally observed logarithmic divergence.

We have also shown how the correlation length, wavenumber, and frequency scale with respect to each other.

III. WAVENUMBER DEPENDENCE OF THE CRITICAL RAYLEIGH LINEWIDTH

A. General Formalism

The Rayleigh linewidth $\Gamma_{\vec{q}}$ is the decay rate of the $\vec{q}$-wavenumber mode of the concentration fluctuations. It is given by the formula

$$\Gamma_{\vec{q}} = D_{\vec{q}}\, q^2 \quad , \tag{1}$$

where $D_{\vec{q}}$ is the $\vec{q}$-dependent diffusion coefficient. The diffusion coefficient is equal to the ratio of the conductivity $\lambda_{\vec{q}}$ to the susceptibility $\chi_{\vec{q}}$. The susceptibility is proportional to the equal time value of the correlation function of the $\vec{q}$-mode of the order parameter,

$$\chi_{\vec{q}} = \frac{1}{T} \langle |S_{\vec{q}}|^2 \rangle \quad . \tag{2}$$

By the use of a fluctuation-dissipation formula, we can relate the conductivity to a space-time integral of the correlation function of the solute particle current[14]. That is,

$$\lambda_{\vec{q}} = \frac{1}{2T} \int_{-\infty}^{\infty} dt_{21} \int d^3 r_{21}\, e^{-i\vec{q}\cdot\vec{r}_{21}} \langle J_{\hat{q}}(\vec{r}_2,t_2)\, J_{\hat{q}}(\vec{r}_1,t_1) \rangle \, , \tag{3}$$

where $J_{\hat{q}}(r,t)$ is the component along the $\hat{q}$-direction of the local solute particle current, which is equal to the second order product of the concentration fluctuation s times the local fluid velocity $\vec{v}$,

$$J_{\hat{q}}(\vec{r},t) = s(\vec{r},t)\, \hat{q}\cdot\vec{v}(\vec{r},t) \, . \tag{4}$$

Therefore, any simultaneous fluctuations in the concentration and velocity fields lead to nonvanishing contributions to the current, according to Eq. (4). Such fluctuations in the current in turn give a contribution to the conductivity by Eq. (3).

At this point, it is useful to make a decoupling approximation, separating the concentration fluctuations from the velocity fluctuations. We can do this if we note that the transverse velocity fluctuations do not lead to any concentration changes in the liquid, and as a result have much lower frequency components than the longitudinal modes. Consequently, the transverse velocity modes make a much greater contribution to the integral in Eq. (3). Therefore, we can ignore the longitudinal velocity modes, and decouple the transverse modes from the concentration modes. This assumption now lets us write the integral in Eq. (3) in factorized form, as follows:

$$\lambda_{\vec{q}} = \frac{1}{2T}\int_{-\infty}^{\infty} dt_{21} \int d^3 r_{21}\, e^{-i\vec{q}\cdot\vec{r}_{21}} \langle S(\vec{r}_2,t_2) S(\vec{r}_1,t_1)\rangle \langle \hat{q}\cdot\vec{v}(\vec{r}_2,t_2)\,\hat{q}\cdot\vec{v}(\vec{r}_1,t_1)\rangle . \quad (5)$$

It will be convenient for us to work in wavenumber and frequency space. Therefore, we will Fourier transform the concentration and velocity fields as follows:

$$s(\vec{r},t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{\ell}} \int \frac{d\nu}{2\pi}\, s_{\vec{\ell}}(\nu)\, e^{i(\vec{\ell}\cdot\vec{r}-\nu t)} , \quad (6)$$

$$\vec{v}(\vec{r},t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}} \int \frac{d\omega}{2\pi}\, \vec{v}_{\vec{k}}(\omega)\, e^{i(\vec{k}\cdot\vec{r}-\omega t)} . \quad (7)$$

If we make use of the translational invariance in space and time of both the concentration and velocity modes:

$$\langle S_{\vec{\ell}}(\nu)\, S_{\vec{\ell}'}(\nu')\rangle = 2\pi\,\delta(\nu+\nu')\,\delta_{\vec{\ell}',-\vec{\ell}}\,\langle |S_{\vec{\ell}}(\nu)|^2\rangle\ , \tag{8}$$

$$\langle -\hat{q}\cdot\vec{v}_{\vec{k}}(\omega)\,\hat{q}\cdot\vec{v}_{\vec{k}'}(\omega')\rangle = 2\pi\,\delta(\omega+\omega')\,\delta_{\vec{k}',-\vec{k}}\,\langle |\hat{q}\cdot\vec{v}_{\vec{k}}(\omega)|^2\rangle\ , \tag{9}$$

and we recall the Fourier transforms of the delta functions

$$\int_{-\infty}^{\infty} dt\, e^{-i(\omega+\nu)t} = 2\pi\,\delta(\omega+\nu)\ , \tag{10}$$

$$\int d^3r\, e^{i(\vec{\ell}+\vec{k}-\vec{q})\cdot\vec{r}} = \Omega\,\delta_{\vec{\ell},\vec{q}-\vec{k}}\ , \tag{11}$$

then Eq. (5) becomes

$$\lambda_{\vec{q}} = \frac{1}{2T\Omega}\sum_{\vec{k}}\int\frac{d\omega}{2\pi}\,\langle |S_{\vec{q}-\vec{k}}(\omega)|^2\rangle\langle |\hat{q}\cdot\vec{v}_{\vec{k}}(\omega)|^2\rangle . \tag{12}$$

For the concentration fluctuations we will use the Ornstein-Zernicke form, with a decay time of Γ. That is,

$$\langle |S_{\vec{k}'}(\omega)|^2\rangle = \int_{-\infty}^{\infty} dt_{21}\, e^{i\omega t_{21}}\langle S_{\vec{k}'}(t_2)\, S_{\vec{k}'}(t_1)\rangle$$

$$= \langle |S_{\vec{k}'}|^2\rangle \int_{-\infty}^{\infty} dt_{21}\, e^{i\omega t_{21}}\, e^{-\Gamma_{\vec{k}'}|t_{21}|}$$

$$= \langle |S_{\vec{k}'}|^2\rangle\,\mathcal{L}(\omega;\Gamma_{\vec{k}'})\ , \tag{13}$$

where $\langle|s_{\vec{k}}|^2\rangle$ is the equal time correlation function, and $\mathcal{L}(\omega;\Gamma_{\vec{k}})$ is the Lorentzian function of the frequency ω with a half-width of $\Gamma_{\vec{k}}$, given by:

$$\mathcal{L}(\omega;\Gamma) \equiv \int_{-\infty}^{\infty} dt\, e^{i\omega t} e^{-\Gamma|t|} = \frac{1}{\Gamma+i\omega} + \frac{1}{\Gamma-i\omega} = \frac{2\Gamma}{\Gamma^2+\omega^2}\,. \tag{14}$$

We can resolve each velocity mode into its two components of polarization:

$$\vec{v}_{\vec{k}}(t) = \sum_{\mu=1}^{2} \hat{\varepsilon}_{\vec{k}\mu}\, v_{\vec{k}\mu}(t) \quad , \tag{15}$$

where $\hat{\varepsilon}_{\vec{k}1}$ and $\hat{\varepsilon}_{\vec{k}2}$ are two orthogonal unit vectors in a plane which is normal to the direction of k as shown in Fig. 7. If q is an arbitrary direction, and if $\hat{q}\cdot\hat{k}=\cos\theta$ defines the angle between $\hat{q}$ and $\hat{k}$, then since $\vec{v}_{\vec{k}}$ is normal to $\vec{k}$, then we can pick one direction of polarization normal to both $\hat{k}$ and $\hat{q}$, say $\hat{\varepsilon}_{\vec{k}2}$, and then write

$$\hat{q}\cdot\hat{\varepsilon}_{\vec{k}1} = \sin\theta \quad , \tag{16}$$

and thus

$$\langle|\hat{q}\cdot\vec{v}_{\vec{k}}(\omega)|^2\rangle = \sin^2\theta\,\langle|v_{\vec{k}1}(\omega)|^2\rangle\,. \tag{17}$$

We can write $\langle|v_{\vec{k}1}(\omega)|^2\rangle$ as the Fourier transform of the time correlation function of $v_{\vec{k}1}(t)$ as follows

$$\langle|v_{\vec{k}1}(\omega)|^2\rangle = \int_{-\infty}^{\infty} dt_{21}\, e^{i\omega t_{21}} \langle v_{\vec{k}1}(t_2)\, v_{-\vec{k}1}(t_1)\rangle\,. \tag{18}$$

The equal time correlation function is given by the equipartition theorem of statistical mechanics:

$$\langle |v_{\vec{k}1}|^2 \rangle = \frac{T}{\rho} \quad , \tag{19}$$

where ρ is the equilibrium mass density of the liquid. The time dependence of the transverse velocity modes is given by the Navier-Stokes equation, which states that they decay at a rate equal to $\frac{\eta}{\rho}k^2$, where η is the shear viscosity. Therefore:

$$\langle v_{\vec{k}1}(t_2)\, v_{-\vec{k}1}(t_1) \rangle = \frac{T}{\rho}\, e^{-\frac{\eta}{\rho}k^2 |t_{21}|} \quad , \tag{20}$$

and

$$\langle |v_{\vec{k}1}(\omega)|^2 \rangle = \frac{T}{\rho}\, \mathcal{L}\left(\omega;\ \frac{\eta_{\vec{k}}(\omega)}{\rho} k^2\right) \quad , \tag{21}$$

where we have inserted the wavenumber and frequency dependent value of the shear viscosity for η.

If we insert Eqs. (13), (17) and (21) into (12), we obtain

$$\lambda_{\vec{q}} = \frac{1}{2\rho\Omega} \sum_{\vec{k}} \langle |S_{\vec{q}-\vec{k}}|^2 \rangle \left[1 - (\hat{k}\cdot\hat{q})^2\right] \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\, \mathcal{L}(\omega; \Gamma_{\vec{q}-\vec{k}})\, \mathcal{L}\left(\omega;\ \frac{\eta_{\vec{k}}(\omega) k^2}{\rho}\right). \tag{22}$$

In the above equation we essentially have the product of two Lorentzians, if $\eta_{\vec{k}}(\omega)$ has a weak frequency dependence. Since the first Lorentzian has a much smaller width than the second one, we can replace the second one by its variation in the neighborhood of $\omega=0$, that is we make the approximation

$$\mathcal{L}\left(\omega; \frac{\eta_{\vec{k}}(\omega)}{\rho} k^2\right) \approx \mathcal{L}\left(0; \frac{\eta_{\vec{k}}(\omega)}{\rho} k^2\right) = \frac{2\rho}{\eta_{\vec{k}}(\omega) k^2} \ , \tag{23}$$

and, therefore:

$$\lambda_{\vec{q}} = \frac{1}{\Omega} \sum_{\vec{k}} \frac{1}{k^2} \langle |S_{\vec{q}-\vec{k}}|^2 \rangle \left[1 - (\hat{q}\cdot\hat{k})^2\right] \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\mathcal{L}(\omega; \Gamma_{\vec{q}-\vec{k}})}{\eta_{\vec{k}}(\omega)} \ . \tag{24}$$

B. Kawasaki Theory

Let us now investigate the important special case, where the shear viscosity is independent of frequency and wavenumber, and we can write

$$\eta_{\vec{k}}(\omega) = \bar{\eta} \ . \tag{25}$$

Then

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \mathcal{L}(\omega; \Gamma_{\vec{q}-\vec{k}}) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \int_{-\infty}^{\infty} dt\, e^{i\omega t} e^{-\Gamma_{\vec{q}-\vec{k}}|t|} = \int_{-\infty}^{\infty} dt\, e^{-\Gamma_{\vec{q}-\vec{k}}|t|} \delta(0) = 1 \ , \tag{26}$$

and

$$\lambda_{\vec{q}} = \frac{1}{8\pi^3 \bar{\eta}} \int \frac{d^3k}{k^2} \langle |S_{\vec{q}-\vec{k}}|^2 \rangle \left[1 - (\hat{q}\cdot\hat{k})^2\right] \tag{27}$$

If we assume an Ornstein-Zernicke form:

$$\langle |S_{\vec{q}-\vec{k}}|^2 \rangle = \frac{ZT}{\kappa^2 + (\vec{q}-\vec{k})^2} \tag{28}$$

then Eq. (27) becomes:

$$\lambda_{\vec{q}} = \frac{ZT}{8\pi^3 \bar{\eta}} \cdot 2\pi \int_0^{\infty} dk \int_{-1}^{1} \frac{d\mu (1-\mu^2)}{q^2 + \kappa^2 + k^2 - 2qk\mu}$$

$$= \frac{ZT}{4\pi^2\bar{\eta}}\int_{-1}^{1} d\mu(1-\mu^2)\int_{0}^{\infty}\frac{dk}{(q^2+\kappa^2)-2q\mu k+k^2}$$

$$= \frac{ZT}{4\pi^2\bar{\eta}}\int_{-1}^{1} d\mu(1-\mu^2)\left[\frac{1}{\sqrt{\kappa^2+q^2(1-\mu^2)}}\tan^{-1}\frac{k-q\mu}{\sqrt{\kappa^2+q^2(1-\mu^2)}}\right]_{k=0}^{k=\infty}$$

$$= \frac{ZT}{4\pi^2\bar{\eta}}\int_{-1}^{1}\frac{d\mu(1-\mu^2)}{\sqrt{\kappa^2+q^2(1-\mu^2)}}\left[\frac{\pi}{2}+\tan^{-1}\frac{q\mu}{\sqrt{\kappa^2+q^2(1-\mu^2)}}\right]. \qquad (29)$$

The second term in the brackets of the above expression does not contribute because it is an odd function of μ. To evaluate the above integral, we substitute:

$$\left.\begin{aligned} w &= 1-\mu^2 \\ \mu &= (1-w)^{1/2} \\ d\mu &= -\frac{dw}{2(1-w)^{1/2}} \end{aligned}\right\}, \qquad (30)$$

then

$$\lambda_{\vec{q}} = \frac{ZT}{8\pi\bar{\eta}}\int_{0}^{1}\frac{w\,dw}{(1-w)^{1/2}(\kappa^2+q^2w)^{1/2}}$$

$$= \frac{ZT}{8\pi\bar{\eta}}\left\{\frac{(1-w)^{1/2}(\kappa^2+q^2w)^{1/2}}{-q^2}\Bigg|_{w=0}^{w=1} + \frac{(q^2-\kappa^2)}{2q^2}\cdot\frac{2}{q}\tan^{-1}\frac{q(1-w)^{1/2}(\kappa^2+q^2w)^{1/2}}{-(\kappa^2+q^2w)}\Bigg|_{w=0}^{w=1}\right\}$$

$$= \frac{ZT}{8\pi\bar{\eta}q}\left\{\frac{\kappa}{q}+\left(1-\frac{\kappa^2}{q^2}\right)\tan^{-1}\frac{q}{\kappa}\right\}$$

$$= \frac{ZT}{6\pi\bar{\eta}(q^2+\kappa^2)^{1/2}}K\left(\frac{q}{\kappa}\right), \qquad (31)$$

which is just the Kawasaki result, where $K(x)$ is the Kawasaki scaling function[13,14], given by:

$$K(x) = \frac{3}{4}(1+x^2)^{1/2}\left[\frac{1}{x^2} + \left(\frac{1}{x} - \frac{1}{x^3}\right)\tan^{-1}x\right] . \tag{32}$$

C. First Order Effect of Critical Viscosity

Now let us return to the general case of Eq. (24), and assume that we can write

$$\eta_{\vec k}(\omega) = \eta_0 + \Delta\eta_{\vec k}(\omega) \quad , \tag{33}$$

where $\Delta\eta_{\vec k}(\omega)$ is the critical wavenumber and frequency dependent viscosity, and η_0 is the background, or ideal viscosity. If the anomalous viscosity is a small part of the total viscosity, then to first order we can write:

$$\eta_{\vec k}(\omega)^{-1} = \left[\eta_0 + \Delta\eta_{\vec k}(\omega)\right]^{-1} = \eta_0^{-1}\left[1 - \frac{\Delta\eta_{\vec k}(\omega)}{\eta_0}\right] . \tag{34}$$

We will now consider the wavenumber dependent conductivity at the critical temperature where $\kappa = 0$. Thus to lowest order

$$\begin{aligned} \lambda_{\vec q}^{(0)} &= \frac{ZT}{6\pi\eta_0 q}\,\sigma(\infty) \\ &= \frac{ZT}{16\eta_0 q} \quad , \end{aligned} \tag{35}$$

and the first order correction is, then by Eq. (24):

$$\Delta\lambda_{\vec q} = -\frac{1}{\eta_0^2\Omega}\sum_{\vec k}\frac{1}{k^2}\left\langle |S_{\vec q-\vec k}|^2\right\rangle\left[1-(\hat q\cdot\hat k)^2\right]\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\alpha(\omega;\Gamma_{\vec q-\vec k})\,\Delta\eta_{\vec k}(\omega) . \tag{36}$$

By Eq. (39) of the previous chapter, we have

$$\Delta\eta_{\vec{k}}(\omega) = \frac{1}{\Omega}\sum_{\vec{\ell}} \psi(\vec{\ell},\vec{\ell}')\,\mathcal{L}(\omega;\Gamma_{\vec{\ell}}+\Gamma_{\vec{\ell}'}), \tag{37}$$

where

$$\vec{\ell}+\vec{\ell}' = \vec{k} \quad ,$$

and

$$\psi(\vec{\ell},\vec{\ell}') \equiv -\frac{1}{4TZ^2}\,\ell_x\ell_x'(\ell_z'-\ell_z)^2\langle|S_{\vec{\ell}}|^2\rangle\langle|S_{\vec{\ell}'}|^2\rangle\ . \tag{38}$$

Therefore, Eq. (36) becomes

$$\Delta\lambda_{\vec{q}} = -\frac{1}{\eta_0^2\Omega}\sum_{\vec{k}}\frac{1}{k^2}\left[1-(\hat{q}\cdot\hat{k})^2\right]\langle|S_{\vec{q}-\vec{k}}|^2\rangle\frac{1}{\Omega}\sum_{\vec{\ell}}\psi(\vec{\ell},\vec{\ell}')\int\frac{d\omega}{2\pi}\mathcal{L}(\omega;\Gamma_{\vec{q}-\vec{k}})\mathcal{L}(\omega;\Gamma_{\vec{\ell}}+\Gamma_{\vec{\ell}'}) \tag{39}$$

But

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\mathcal{L}(\omega;\gamma_1)\mathcal{L}(\omega;\gamma_2) = \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dt\,dt'\,e^{i\omega(t+t')}e^{-\gamma_1|t|}e^{-\gamma_2|t'|}$$

$$= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}dt\,dt'\,\delta(t+t')e^{-\gamma_1|t|}e^{-\gamma_2|t|} = \int_{-\infty}^{\infty}dt\,e^{-(\gamma_1+\gamma_2)|t|} = \frac{2}{\gamma_1+\gamma_2}\ , \tag{40}$$

so that Eq. (39) becomes:

$$\Delta\lambda_{\vec{q}} = -\frac{1}{\eta_0^2\Omega}\sum_{\vec{k}}\frac{1}{k^2}\left[1-(\hat{q}\cdot\hat{k})^2\right]\langle|S_{\vec{q}-\vec{k}}|^2\rangle\frac{1}{\Omega}\sum_{\vec{\ell}}\psi(\vec{\ell},\vec{\ell}')\frac{2}{\Gamma_{\vec{\ell}}+\Gamma_{\vec{\ell}'}+\Gamma_{\vec{q}-\vec{k}}} \tag{41}$$

$$= -\frac{1}{\eta_0^2\Omega}\sum_{\vec{k}}\frac{1}{k^2}\left[1-(\hat{q}\cdot\hat{k})^2\right]\langle|S_{\vec{q}-\vec{k}}|^2\rangle\,\Delta\eta^*_{\vec{k}}(\Gamma_{\vec{q}-\vec{k}})\ , \tag{42}$$

where $\Delta\eta^*_{\vec{k}}(\Gamma_{\vec{q}-\vec{k}})$ is the Fourier-Laplace transform of the anomalous shear viscosity, evaluated at the Laplace frequency equal to the relaxation rate of the $\vec{q}-\vec{k}$ concentration mode. Previously, we have found that

$$\Delta\eta^*_{\vec{k}}(p) = \frac{8\bar{T}}{15\pi^2}\left\{\ln\frac{2k_D}{\left[k^3+\frac{64\bar{\eta}p}{T}\right]^{1/3}} + \sigma_\eta\left(\frac{64\bar{\eta}p}{Tk^3}\right)\right\} . \tag{43}$$

At the critical temperature T_c we can use the formulae:

$$\langle|S_{\vec{q}-\vec{k}}|^2\rangle = \frac{ZT}{(\vec{q}-\vec{k})^2} , \tag{44}$$

and

$$\Gamma_{\vec{q}-\vec{k}} = \frac{T}{16\bar{\eta}}|\vec{q}-\vec{k}|^3 . \tag{45}$$

Inserting Eqs. (43), (44) and (45) into (42) we obtain

$$\Delta\lambda_{\vec{q}} = -\frac{ZT}{\eta_0}\cdot\frac{\bar{\eta}}{\eta_0}\cdot\frac{1}{\Omega}\sum_{\vec{k}}\frac{\left[1-(\hat{q}\cdot\hat{k})^2\right]}{k^2k'^2}\cdot\frac{8}{15\pi^2}\left[\ln\frac{2k_D}{(k^3+4k'^3)^{1/3}}+\sigma_\eta\left(\frac{4k'^3}{k^3}\right)\right], \tag{46}$$

where

$$\vec{k}+\vec{k}' = \vec{q} . \tag{47}$$

If we choose the polar axis to be along the direction of $\vec{q}$, and convert the sum in Eq. (46) to an integral, and change to dimensionless variables, according to the transformation:

$$\left.\begin{aligned} u &= \frac{k}{q} \\ u' &\equiv \frac{k'}{q} = (u^2+1-2u\mu)^{1/2} \end{aligned}\right\} , \tag{48}$$

then

$$\Delta\lambda_{\vec{q}} = -\frac{ZT}{4\pi^2\eta_0 q}\cdot\frac{\bar{\eta}}{\eta_0}\cdot\frac{8}{15\pi^2}\int_0^\infty du\int_{-1}^{1}\frac{d\mu(1-\mu^2)}{(u^2+1-2u\mu)^{1/2}}\left[\ln\frac{2k_D}{q}+\sigma_\eta\left(\frac{4u'^3}{u^3}\right)-\frac{1}{3}\ln(u^3+4u'^3)\right]. \quad (49)$$

Only the first term in the brackets of the above equation has any dependence on q. When integrated, the other terms will give constants. Therefore, let us first examine the coefficient of the ln $\frac{2k_D}{q}$ term:

$$\int_0^\infty du\int_{-1}^{1}\frac{d\mu(1-\mu^2)}{(u^2+1-2u\mu)} = \int_{-1}^{1}d\mu(1-\mu^2)\int_0^\infty\frac{du}{1-2\mu u+u^2}$$

$$= \int_{-1}^{1}d\mu(1-\mu^2)\left[\frac{1}{(1-\mu^2)^{1/2}}\tan^{-1}\frac{u-\mu}{(1-\mu^2)^{1/2}}\right]_{u=0}^{u=\infty}$$

$$= \int_{-1}^{1}d\mu(1-\mu^2)^{1/2}\left[\frac{\pi}{2}+\sin^{-1}\mu\right] = \pi\int_0^1 d\mu(1-\mu^2)^{1/2} = \pi\int_0^{\pi/2}\sin^2\theta\, d\theta = \frac{\pi^2}{4}. \quad (50)$$

Therefore, we can write the first order correction to the conductivity as follows:

$$\Delta\lambda_{\vec{q}} = -\frac{ZT}{16\eta_0 q}\cdot\frac{8}{15\pi^2}\frac{\bar{\eta}}{\eta_0}\left[\ln\frac{2k_D}{q}+C_\lambda\right], \quad (51)$$

where C_λ is just a numerical constant given by

$$C_\lambda = \frac{4}{\pi^2}\int_0^\infty du\int_{-1}^{1}\frac{d\mu(1-\mu^2)}{u'^2}\left[\sigma_\eta\left(\frac{4u'^3}{u^3}\right)-\frac{1}{3}\ln(u^3+4u'^3)\right]. \quad (52)$$

Thus, to within a constant Eq. (51) is the result we would have obtained if we had inserted

$$\eta = \eta_0 + \Delta\eta_{\vec{q}} \quad (53)$$

into the Kawasaki formula for q>>κ:

$$\lambda_{\vec{q}} = \frac{ZT}{16\eta q} . \tag{54}$$

We will evaluate $C_{\bar{\lambda}}$ through the use of two successive transformations. First we will transform the integral over μ to an integral over u' by

$$\left.\begin{aligned} \mu &= \frac{1}{2u}\left(u^2+1-u'^2\right) \\ d\mu &= -\frac{u'du'}{u} \\ 1-\mu^2 &= 1-\frac{u^4+1+u'^4+2u^2-2u'^2-2u^2u'^2}{4u^2} \\ &= \frac{1}{4u^2}\left[2(u^2+u'^2)-1-(u'^2-u^2)^2\right] \end{aligned}\right\} , \tag{55}$$

so that Eq. (52) becomes

$$C_\lambda = \frac{1}{\pi^2}\int_0^\infty \frac{du}{u^3}\int_{|u-1|}^{(u+1)} \frac{du'}{u'}\left[2(u^2+u'^2)-1-(u'^2-u^2)^2\right]\left[\sigma_\eta\left(\frac{4u'^3}{u^3}\right)-\frac{1}{3}\ln\left(u^3+4u'^3\right)\right] , \tag{56}$$

where the region of integration is the diagonal strip shown in Fig. 6. Noting that the term involving the viscosity scaling function depends only on the ratio of u' to u, we transform to polar coordinates so that the unavoidable numerical integration be a single integral instead of a double integral. We let

$$\left.\begin{aligned} u &= v\cos\phi \\ u' &= v\sin\phi \\ du\,du' &= v\,dv\,d\phi \end{aligned}\right\} , \tag{57}$$

then

$$C_\lambda = \frac{1}{\pi^2}\int_0^{\pi/2}\frac{d\phi}{\sin\phi\cos^3\phi}\int_{v_1(\phi)}^{v_2(\phi)}\frac{dv}{v^3}\left[2v^2-1-v^4\cos^2 2\phi\right]\left[\sigma_\eta(4\tan^3\phi)-\tfrac{1}{3}\ln(\cos^3\phi+4\sin^3\phi)-\ln v\right], \tag{58}$$

where $v_1(\phi)$ is the intersection of the ray ϕ = constant with the line $u'+u = 1$, and $v_2(\phi)$ is the intersection of the same ray with the appropriate one of the two lines $|u'-u| = 1$, or,

$$v_1(\phi) = (\cos\phi + \sin\phi)^{-1} \quad , \tag{59}$$

$$v_2(\phi) = |\cos\phi - \sin\phi|^{-1} \quad . \tag{60}$$

We can rewrite Eq. (58) as follows

$$C_\lambda = \frac{1}{\pi^2}\int_0^{\pi/2}\frac{d\phi}{\sin\phi\cos^3\phi}\left\{\Psi_1(\phi)\left[\sigma_\eta(4\tan^3\phi)-\tfrac{1}{3}\ln(\cos^3\phi + 4\sin^3\phi\right]-\Psi_2(\phi)\right\} , \tag{61}$$

where $\Psi_1(\phi)$ and $\Psi_2(\phi)$ are the radial integrals:

$$\Psi_1(\phi) \equiv \int_{v_1(\phi)}^{v_2(\phi)}\frac{dv}{v^3}\left[2v^2-1-v^4\cos^2 2\phi\right] \quad , \tag{62}$$

$$\Psi_2(\phi) \equiv \int_{v_1(\phi)}^{v_2(\phi)}\frac{dv}{v^3}\ln v\left[2v^2-1-v^4\cos^2 2\phi\right] \quad . \tag{63}$$

We will first evaluate $\Psi_1(\phi)$:

$$\Psi_1(\phi) = \int_{v_1(\phi)}^{v_2(\phi)} dv\left[\frac{2}{v}-\frac{1}{v^3}-v\cos^2 2\phi\right]$$

$$= 2\ln\left|\frac{v_2}{v_1}\right| - \frac{1}{2}\left[\frac{1}{v_1^2}-\frac{1}{v_2^2}\right] - \frac{1}{2}\left[v_2^2-v_1^2\right]\cos^2 2\phi$$

$$= 2\ln\left|\frac{\cos\phi + \sin\phi}{\cos\phi - \sin\phi}\right| - \frac{1}{2}\left[(\cos\phi + \sin\phi)^2 - (\cos\phi - \sin\phi)^2\right]$$

$$-\frac{1}{2}\left[\frac{(\cos\phi + \sin\phi)^2 - (\cos\phi - \sin\phi)^2}{(\cos\phi + \sin\phi)^2(\cos\phi - \sin\phi)^2}\right](\cos^2\phi - \sin^2\phi)^2$$

$$= 2\ln\left|\frac{\cos\phi + \sin\phi}{\cos\phi - \sin\phi}\right| - 4\cos\phi\,\sin\phi$$

$$= 2\left[\ln\left|\tan\left(\frac{\pi}{4} + \phi\right)\right| - \sin 2\phi\right] . \qquad (64)$$

To evaluate $\Psi_2(\phi)$, we will first establish a few integral identities, namely:

$$\int_{v_1}^{v_2} v^n \ln v\,dv = \int_{\ln v_1}^{\ln v_2} x e^{(n+1)x}\,dx = \left[\frac{x e^{(n+1)x}}{(n+1)} - \frac{e^{(n+1)x}}{(n+1)^2}\right]_{\ln v_1}^{\ln v_2}$$

$$= \frac{1}{(n+1)}\left[v_2^{(n+1)}\ln v_2 - v_1^{(n+1)}\ln v_1\right] - \frac{1}{(n+1)^2}\left[v_2^{(n+1)} - v_1^{(n+1)}\right] , \qquad (65)$$

which is true for $n \neq -1$, and

$$\int_{v_1}^{v_2} \frac{dv}{v}\ln v = \int_{\ln v_1}^{\ln v_2} x\,dx = \frac{1}{2}\left[\ln^2 v_2 - \ln^2 v_1\right]$$

$$= \frac{1}{2}\ln(v_1 v_2)\ln\left(\frac{v_2}{v_1}\right) . \qquad (66)$$

Therefore:

$$\Psi_2(\phi) \equiv \int_{V_1(\phi)}^{V_2(\phi)} \left[\frac{2}{V} - \frac{1}{V^3} - V\cos^2 2\phi\right] \ln V \, dV$$

$$= \ln(V_2 V_1)\ln\left(\frac{V_2}{V_1}\right) + \frac{1}{2}\left[\frac{\ln V_2}{V_2^2} - \frac{\ln V_1}{V_1^2}\right] + \frac{1}{4}\left[\frac{1}{V_2^2} - \frac{1}{V_1^2}\right]$$

$$- \frac{1}{2}\left[V_2^2 \ln V_2 - V_1^2 \ln V_2\right]\cos^2 2\phi + \frac{1}{4}\left[V_2^2 - V_1^2\right]\cos^2 2\phi$$

$$= -\ln|\cos^2\phi - \sin^2\phi| \ln\left|\frac{\cos\phi + \sin\phi}{\cos\phi - \sin\phi}\right|$$

$$-\frac{1}{2}\left\{(\cos\phi - \sin\phi)^2 \ln|\cos\phi - \sin\phi| - (\cos\phi + \sin\phi)^2 \ln|\cos\phi + \sin\phi|\right\}$$

$$-\frac{1}{4}\left\{(\cos\phi + \sin\phi)^2 - (\cos\phi - \sin\phi)^2\right\}$$

$$+\frac{1}{2}\left\{\frac{\ln|\cos\phi - \sin\phi|}{(\cos\phi - \sin\phi)^2} - \frac{\ln|\cos\phi + \sin\phi|}{(\cos\phi + \sin\phi)^2}\right\}(\cos\phi - \sin\phi)^2(\cos\phi + \sin\phi)^2$$

$$+\frac{1}{4}\left\{\frac{1}{(\cos\phi - \sin\phi)^2} - \frac{1}{(\cos\phi + \sin\phi)^2}\right\}(\cos\phi - \sin\phi)^2(\cos\phi + \sin\phi)^2$$

$$= -\ln|\cos^2\phi - \sin^2\phi| \ln\left|\frac{\cos\phi + \sin\phi}{\cos\phi - \sin\phi}\right|$$

$$+ 2\sin\phi\cos\phi \ln|\cos\phi + \sin\phi| + 2\sin\phi\cos\phi \ln|\cos\phi - \sin\phi|$$

$$= \left\{-\ln\left|\tan\left(\frac{\pi}{4} + \phi\right)\right| + \sin 2\phi\right\} \ln|\cos 2\phi| \, . \tag{67}$$

We note that the integrand in Eq. (61) has a logarithmic singularity at $\phi = \frac{\pi}{4}$. Therefore, we will subtract out the singular part of the function, and integrate the remainder numerically, while the singular part can be integrated analytically. In other words, if we write

$$C_\lambda = \int_0^{\pi/2} \Phi(\phi)\, d\phi \tag{68}$$

where

$$\Phi(\phi) = \frac{1}{\pi^2} (\sin\phi \cos^3\phi)^{-1} \left\{ \Psi_1(\phi) \left[\sigma_\eta(4\tan^3\phi) - \frac{1}{3} \ln(\cos^3\phi + 4\sin^3\phi) \right] - \Psi_2(\phi) \right\} , \tag{69}$$

and let $\bar{\Phi}(\phi)$ be some function that can be analytically integrated such that

$$\Phi(\tfrac{\pi}{4}) - \bar{\Phi}(\tfrac{\pi}{4}) = 0 , \tag{70}$$

then we write

$$C_\lambda = \int_0^{\pi/2} [\Phi(\phi) - \bar{\Phi}(\phi)]\, d\phi + \int_0^{\pi/2} \bar{\Phi}(\phi)\, d\phi , \tag{71}$$

where the first integration is performed numerically, and the second analytically.

To construct $\bar{\Phi}(\phi)$, we expand the singular parts of $\Phi(\phi)$ about the singular point, $\phi = \frac{\pi}{4}$, and evaluate the non-singular terms at $\phi = \frac{\pi}{4}$. Thus using Eq. (69), we can write

$$\bar{\Phi}(\phi) = \frac{4}{\pi^2} \left\{ \bar{\Psi}_1(\phi) \left[\sigma_\eta(4) - \frac{1}{3} \ln(\tfrac{5}{4}\sqrt{2}) \right] - \bar{\Psi}_2(\phi) \right\} . \tag{72}$$

Around $\phi = \frac{\pi}{4}$, we can write

$$|\cos\phi - \sin\phi| = \frac{|\cos 2\phi|}{(\cos\phi + \sin\phi)} \approx \frac{1}{\sqrt{2}} \sin\left[2|\phi - \tfrac{\pi}{4}|\right] \approx \sqrt{2}\,|\phi - \tfrac{\pi}{4}| \ . \tag{73}$$

Therefore,

$$\Psi_1(\phi) = 2\left[\ln\left|\frac{\cos\phi + \sin\phi}{\cos\phi - \sin\phi}\right| - \sin 2\phi\right] \tag{64}$$

becomes

$$\bar{\Psi}_1(\phi) = 2\left[\ln\frac{1}{|\phi - \frac{\pi}{4}|} - 1\right] = -2\left[1 + \ln|\phi - \tfrac{\pi}{4}|\right] \quad , \tag{74}$$

and

$$\Psi_2(\phi) = \left[-\ln\left|\frac{\cos\phi + \sin\phi}{\cos\phi - \sin\phi}\right| + \sin 2\phi\right]\ln|\cos 2\phi| \tag{67}$$

becomes

$$\bar{\Psi}_2(\phi) = \left[-\ln\frac{1}{|\phi - \frac{\pi}{4}|} + 1\right]\ln 2|\phi - \tfrac{\pi}{4}|$$

$$= \ln 2 + (1 + \ln 2)\ln|\phi - \tfrac{\pi}{4}| + \ln^2|\phi - \tfrac{\pi}{4}| \ . \tag{75}$$

Noting that

$$\sigma(4) - \tfrac{1}{3}\ln\left(\tfrac{5}{4}\sqrt{2}\right) \approx -.4895 \quad , \tag{76}$$

we can insert Eqs. (76), (74) and (75) into (72) to obtain

$$\bar{\Phi}(\phi) = \frac{4}{\pi^2}\left\{2(.4895)\left[1 + \ln|\phi - \tfrac{\pi}{4}|\right] - \left[.6931 + 1.6931\ln|\phi - \tfrac{\pi}{4}| + \ln^2|\phi - \tfrac{\pi}{4}|\right]\right\}$$

$$= \frac{4}{\pi^2}\left\{(.9790 - .6931) + (.9790 - 1.6931)\ln|\phi - \tfrac{\pi}{4}| - \ln^2|\phi - \tfrac{\pi}{4}|\right\}$$

$$= \frac{4}{\pi^2}\left\{.2859 - .7141\,\ln\left|\phi - \frac{\pi}{4}\right| - \ln^2\left|\phi - \frac{\pi}{4}\right|\right\} . \tag{77}$$

To integrate $\bar{\Phi}(\phi)$, we note that

$$\int_0^{\pi/2} d\phi = \frac{\pi}{2} \quad , \tag{78}$$

$$\int_0^{\pi/2} \ln\left|\phi - \frac{\pi}{4}\right| d\phi = 2\int_0^{\pi/4} \ln x\, dx = 2\Big[x \ln x - x\Big]_0^{\pi/4}$$

$$= \left(\ln\frac{\pi}{4} - 1\right)\frac{\pi}{2} \approx -(1.2416)\frac{\pi}{2} \quad , \tag{79}$$

$$\int_0^{\pi/2} \ln^2\left|\phi - \frac{\pi}{4}\right| d\phi = 2\int_0^{\pi/4} \ln^2 x\, dx = 2\Big[x\ln^2 x - 2x\ln x + 2x\Big]_0^{\pi/4}$$

$$= \left(\ln^2\frac{\pi}{4} - 2\ln\frac{\pi}{4} + 2\right)\frac{\pi}{2} = (2.5416)\frac{\pi}{2} \quad . \tag{80}$$

Therefore, by Eq. (77)

$$\int_0^{\pi/2} \bar{\Phi}(\phi)\,d\phi = \frac{2}{\pi}\left\{.2859 + (.7141)(1.2416) - 2.5416\right\}$$

$$= \frac{2}{\pi}\left\{-1.3691\right\} = -0.8716 \quad , \tag{81}$$

A graph of $\Phi(\phi) - \bar{\Phi}(\phi)$ vs ϕ is shown in Fig. 8.

Numerical integration gives (see Appendix)

$$\int_0^{\pi/2}[\Phi(\phi) - \bar{\Phi}(\phi)]d\phi = -0.3747. \tag{82}$$

Therefore,

$$C_\lambda \approx -1.25\ , \tag{83}$$

and

$$\Delta\lambda_{\vec{q}} = -\frac{ZT}{16\eta_0 q}\cdot\frac{\bar{\eta}}{\eta_0}\cdot\frac{8}{15\pi^2}\left[\ln\frac{2k_D}{q} - 1.25\right]. \tag{84}$$

Thus, to first order, this is equivalent to writing

$$\lambda_{\vec{q}} = \frac{ZT}{16\eta_{\vec{q}}^{eff}q}\ , \tag{85}$$

where

$$\eta_{\vec{q}}^{eff} = \eta_0 + \frac{8\bar{\eta}}{15\pi^2}\left[\ln\frac{2k_D}{q} - 1.25\right] \tag{86}$$

Experimentally, it has been found that Eq. (85) is well satisfied if

$$\eta_{\vec{q}}^{eff} = \bar{\eta}\ , \tag{87}$$

where

$$\frac{\bar{\eta}}{\eta_0} = 1.29\ . \tag{88}$$

Thus, if we replace $\eta_{\vec{q}}^{eff}$ by $\bar{\eta}$ in Eq. (86) and solve for $\bar{\eta}$, we find that

$$\frac{\bar{\eta}}{\eta_0} = \left[1 - \frac{8}{15\pi^2}\left(\ln\frac{2k_D}{q} - 1.25\right)\right]^{-1}. \tag{89}$$

To check the above result with the linewidth measurements of Chang, Sengers, Keyes, and Alley[20], it is first necessary to determine the value of the parameter k_D, the high wavenumber cutoff. This is done by using the measurements of the temperature dependent viscosity of Stein, Allegra and Allen[17]. Both investigated the binary mixture 3-methylpentane-nitroethane. The critical viscosity was found to have a temperature dependence of the form

$$\Delta\eta = a \ln \varepsilon + b \quad , \tag{90}$$

where

$$\varepsilon \equiv \frac{T - T_c}{T_c} \quad , \tag{91}$$

and the best values of a and b were

$$\left.\begin{aligned} a &= -1.84 \times 10^{-4} \ \mathrm{gm/cm\text{-}sec} \\ b &= -4.7 \times 10^{-4} \ \mathrm{gm/cm\text{-}sec} \end{aligned}\right\} \quad , \tag{92}$$

with a background viscosity

$$\eta_0 = 3.8 \times 10^{-3} \ \mathrm{gm/cm\text{-}sec} \, . \tag{93}$$

The linewidth measurements produced a fitted effective value for the viscosity

$$\bar{\eta} = 4.8 \times 10^{-3} \ \mathrm{gm/cm\text{-}sec} \, . \tag{94}$$

Assuming that the correlation length obeys a power law of the form

$$\xi = \xi_o \left| \frac{T - T_c}{T_c} \right|^{-\nu} , \tag{95}$$

then we predict a temperature dependence for the critical viscosity as follows:

$$\Delta\eta = \frac{8\bar{\eta}}{15\pi^2}\left[\ln(2k_D\xi) - 1.333\right]$$

$$= -\left(\frac{8\nu\bar{\eta}}{15\pi^2}\right)\ln\varepsilon + \frac{8\bar{\eta}}{15\pi^2}\left[\ln(2k_D\xi_o) - 1.333\right]$$

$$= a'\ln\varepsilon + b' , \tag{96}$$

where

$$a' = -\frac{8\nu\bar{\eta}}{15\pi^2}$$

$$b' = \frac{8\bar{\eta}}{15\pi^2}\left[\ln(2k_D\xi_o) - 1.333\right] \tag{97}$$

The linewidth measurements were best fitted by the values

$$\left.\begin{aligned} \xi_o &= 2.56\ \text{Å} \\ \nu &= .616 \end{aligned}\right\} . \tag{98}$$

Using these values we get

$$a' = -1.63 \times 10^{-4}\ \text{gm/cm-sec} , \tag{99}$$

or an 11% difference from the value given by Stein, Allegra and Allen.

If we assume that our predicted value of b' is the same as the value by given by the viscosity data, then

$$\ln(k_D \xi_o) = \frac{15\pi^2}{8\eta} b + (1.333 - 0.693)$$

$$= -1.158$$

$$k_D = 0.123 \text{Å}^{-1} \quad . \tag{100}$$

The wavenumber used in the linewidth data was dependent on the scattering angle of the laser light, and was given by

$$q = \frac{4\pi n}{\lambda} \sin\frac{\theta}{2} \quad , \tag{101}$$

where $\lambda = 6328\text{Å}$ was the wavelength of the laser light used, and $n = 1.38$ was the index of refraction of the liquid. Thus

$$q = (2.74 \times 10^{-3} \text{Å}^{-1}) \sin\frac{\theta}{2} \quad , \tag{102}$$

and

$$\frac{2k_D}{q} = \frac{89.8}{\sin\frac{\theta}{2}} \quad . \tag{103}$$

Using the fact that

$$\ln 89.8 = 4.498 \tag{104}$$

and inserting it into Eq. (89) we obtain

$$\frac{\bar{\eta}}{\eta_0} = \left\{ 1 - \frac{8}{15\pi^2}\left[-1.25 + 4.50 - \ln\sin\frac{\theta}{2}\right]\right\}^{-1}$$

$$= \left\{.828 + .124 \log_{10} \sin\frac{\theta}{2}\right\}^{-1} \quad . \tag{105}$$

The scattering angle ranged from 30° to 130° leading to

$$\left(\frac{\bar{\eta}}{\eta_0}\right)_{max} = 1.32 \tag{106}$$

$$\left(\frac{\bar{\eta}}{\eta_0}\right)_{min} = 1.22 \quad , \tag{107}$$

whereas, the observed value is

$$\left(\frac{\bar{\eta}}{\eta_0}\right)_{obs} = 1.29 , \tag{108}$$

which, within experimental uncertainty, is in very good agreement with theory, considering that it is only a first order theory.

D. Viscosity-Diffusion Self Consistency

In this section we will demonstrate that self-consistency of the viscosity and the diffusion coefficient demands that no power law divergence occur in the critical viscosity. We will do this by examining the Fourier-Laplace transforms of both the viscosity and the diffusion coefficient. We can adequately express the Fourier-Laplace transform of the diffusion coefficient as

$$D^*_{\vec{q}}(p) = \frac{\lambda^*_{\vec{q}}(p)}{\chi_{\vec{q}}} \quad , \tag{109}$$

where we neglect the frequency dependence of the susceptibility. This is justified because we know that in the critical region the decay rate of the concentration fluctuations becomes vanishingly small, while the decay rate of the velocity fluctuations remains finite, and possibly diverges. To study the Laplace transform of the diffusion coefficient we put a factor of $e^{-pt_{21}}$ into Eq. (5) and change the limits of integration to (o,∞), and substitute it into Eq. (109), to obtain

$$D^*_{\vec q}(p) = \frac{1}{T\chi_{\vec q}}\int_0^\infty dt_{21}\, e^{-pt_{21}} \int d^3r_{21}\, e^{-i\vec q\cdot\vec r_{21}} \langle s(\vec r_2)s(\vec r_1)\rangle\langle \hat q\cdot\vec v(\vec r_2,t_2)\hat q\cdot\vec v(\vec r_1,t_1)\rangle , \tag{110}$$

where we neglect the time dependence of the concentration fluctuations. If we Fourier transform in space

$$s(\vec r) = \frac{1}{\Omega^{1/2}}\sum_{\vec k'} s_{\vec k'}\, e^{i\vec k'\cdot\vec r} \tag{111}$$

$$\vec v(\vec r,t) = \frac{1}{\Omega^{1/2}}\sum_{\vec k} \vec v_{\vec k}(t)\, e^{i\vec k\cdot\vec r} \quad , \tag{112}$$

then

$$D^*_{\vec q}(p) = \frac{1}{\Omega}\sum_{\vec k} \frac{\chi_{\vec q-\vec k}}{\chi_{\vec q}}\left[1-(\hat q\cdot\hat k)^2\right]\frac{T}{\rho}\,\frac{1}{p+\frac{1}{\rho}\eta^*_{\vec k}(p)k^2} \tag{113}$$

Similarly, by Eq. (39) of the previous chapter we have

$$\Delta\eta^*_{\vec q}(p) = -\frac{1}{2TZ^2\Omega}\sum_{\vec k'-\vec k''=\vec q} k_x k'_x (k'_z-k_z)^2\chi_{\vec k'}\chi_{\vec k''}\,\frac{1}{p+D^*_{\vec k'}(p)k'^2+D^*_{\vec k''}(p)k''^2} . \tag{114}$$

Let us now define two characteristic frequencies associated with the critical Rayleigh linewidth and viscosity, p_Γ and p_η, respectively. They are obtained by replacing all wavenumbers by κ, the reciprocal of the correlation length, as follows:

$$p_\Gamma \equiv D^*_\kappa(p_\Gamma)\,\kappa^2 \tag{115}$$

$$p_\eta \equiv \frac{\eta_\kappa^*(p_\eta)}{\rho}\kappa^2 \quad , \tag{116}$$

and we know that $p_\eta >> p_\Gamma$.

We assume that the critical behavior of the shear viscosity disappears at frequencies larger than p_η. Thus if we look at the frequency denominator in Eq. (113), we see that the most important contribution is from wavenumbers smaller than κ, so that we can replace all lengths by κ^{-1}, and the hydrodynamic value of D is of the order of magnitude

$$D\eta_\kappa^*(p_\eta) \sim \kappa \ . \tag{117}$$

However, from the frequency denominator of Eq. (114) we see that the critical frequency behavior of $\Delta\eta$ cuts off at p_Γ, a frequency much smaller than p_η. Thus $\eta_\kappa^*(p_\eta)$ can no longer have any critical behavior. Therefore, all the power law behavior on the left side of Eq. (117) is taken up by D, and as a result the shear viscosity cannot have any more drastic behavior than a logarithmic divergence, as was previously demonstrated by Swift[22], and Kawasaki[13].

Equation (117) is a general equation for all fluids. That is, it can be used to determine the critical variation of the transport coefficients D and η. The liquid-gas phase transition is very similar to the binary liquid phase transition, with the density difference between the liquid and gas phases replacing the concentration fluctuation as the order parameter. The transport equations are also similar, with the particle diffusion coefficient D, replaced by the quantity $\frac{\lambda}{\rho C_p}$ in the liquid-gas, where λ is the heat conductivity, ρ the density, and C_p the specific heat at constant pressure. However $\frac{\lambda}{\rho C_p}$, like D, vanishes proportionately to κ. In fact, it is possible to use the same arguments leading up to Eq. (117) to show that the shear viscosity cannot have a power law divergence, only a logarithmic divergence at worst, and that the decay rate of the order parameter varies as the third power of the wavenumber, a result previously found by Kadanoff and Swift[21].

The situation is more complex in the superfluid phase transition[18]. However, to the extent of the validity of mean field theory and dynamical scaling, it is still possible to use Eq. (117) to predict the behavior of the critical shear viscosity. In the superfluid we have a complex order parameter, with the superfluid density related to the square of the amplitude of the order parameter, and the superfluid velocity proportional to the gradient of the phase of the order parameter. The diffusion coefficient D of liquid helium in a porous medium leads to the anomalous increase in the thermal conductivity in the high temperature region, and describes the anomalous attenuation of second sound in the low temperature region. It can be shown the D diverges as $\kappa^{-1/2}$, so that Eq. (117) would predict that the shear viscosity vanishes as $\kappa^{3/2}$ in the hydrodynamic regime, and varies as the wavenumber k raised to the 3/2 power for $k \gg \kappa$, if we assume the validity of dynamical scaling.

In this chapter we have shown how the critical shear viscosity decreases the value of the relaxation rate of the order parameter predicted by the mode-coupling theory of Kawasaki. We have also explored the self consistent nature of the critical diffusion and viscosity, and its extension to other fluids.

IV. PERTURBATION THEORY

In this chapter we will explore the effect of higher order pertubations on the critical shear viscosity and Rayleigh linewidth. We will present an equal time justification for the decoupling approximation in the calculation of the anomalous shear viscosity. Finally we will examine "vertex corrections" resulting from time dependent perturbation theory, and show that they are very small effects in the critical Rayleigh linewidth and shear viscosity.

A. Static Perturbation Theory

In static perturbation theory we employ the fourth order term in the Ginzburg-Landau equation for the free energy density[5]. If $F_\Omega^{(o)}$ denotes the total free energy of the quadratic terms, then the partition function can be written

$$Z_\Omega = \sum_{\{s\}} \exp\left\{-\beta F_\Omega^{(o)} - \frac{\beta b}{4}\int S(\vec{r})^4 d^3r\right\}$$

$$= \sum_{\{s\}} \exp\left\{-\beta F_\Omega^{(o)}\right\} \sum_{n=0}^{\infty}\left(\frac{-\beta b}{4}\right)^n \frac{1}{n!}\int\cdots\int d^3r_1\cdots d^3r_n\, S(\vec{r}_1)^4\cdots S(\vec{r}_n)^4 . \qquad (1)$$

Because $F_\Omega^{(o)}$ is a diagonal quadratic form in wavenumber space, it does not induce any cross-correlations. Thus, to first order in b we can calculate correlation functions just as before, except that we must introduce, within the expectation values, a factor

$$-\frac{\beta b}{4}\int d^3r\, s(\vec r)^4 = -\frac{\beta b}{4\Omega}\sum\sum\sum_{\vec k_1+\vec k_2+\vec k_3+\vec k_4=\vec 0} s_{\vec k_1} s_{\vec k_2} s_{\vec k_3} s_{\vec k_4}\ . \qquad (2)$$

Proceeding in this spirit we will examine the effect of the above factor on the critical shear viscosity, which by Eq. (30) of Chap. II can be written as

$$\Delta\eta_{\vec q}(\omega) = -\frac{1}{2TZ^2\Omega}\sum_{\vec l}\sum_{\vec l'} l_x(q_z-l_z)\,l'_x(q_z+l'_z)\int_{-\infty}^{\infty} dt_{21}\, e^{i\omega t_{21}}$$

$$\times\langle s_{\vec l}(t_2)\, s_{\vec q-\vec l}(t_2)\, s_{\vec l'}(t_1)\, s_{-\vec q-\vec l'}(t_1)\rangle\ . \qquad (3)$$

If we insert Eq. (2) into the equal time value (t_{21}=o) of the time integrand in Eq. (3) then we obtain a term proportional to

$$\frac{1}{\Omega^2}\sum_{\vec l}\sum_{\vec l'} l_x(q_z-l_z)\,l'_x(q_z+l'_z)\langle|s_{\vec l}|^2\rangle\langle|s_{\vec q-\vec l}|^2\rangle\langle|s_{\vec l'}|^2\rangle\langle|s_{\vec q+\vec l'}|^2\rangle\ , \qquad (4)$$

which conveniently splits up into the product of two sums, one over wavenumber $\vec l$, and one over wavenumber $\vec l'$. However, because $\vec q$ is taken to be along the z-axis both sums turn out to be antisymmetric in the x-direction and as a result are zero as shown below:

$$\sum_{\vec l}\frac{l_x(q-l_z)}{l^2(\vec q-\vec l)^2} = \sum_{\vec l}\frac{l_x(q-l_z)}{l^2(q^2+l^2-2ql_z)} = 0 \qquad (5)$$

$$\sum_{\vec l'}\frac{l'_x(q+l'_z)}{l'^2(\vec q+\vec l')^2} = \sum_{\vec l'}\frac{l'_x(q+l'_z)}{l'^2(q^2+l'^2+2ql'_z)} = 0\ . \qquad (6)$$

Thus we see that from the standpoint of static perturbation theory, the decoupling approximation entering into critical shear viscosity is justified. It is worth noting that the decoupling approximation is valid to all orders of static perturbation theory, because to all orders the double sum in Eq. (4) will be split into a product of two sums, leading to the zero result of Eqs. (5) and (6).

Unfortunately, the above result does not show up in the calculation of the critical bulk viscosity. The bulk viscosity ζ is proportional to the space-time integral of the correlation function of the trace of the stress tensor[10]. If we employ the canonical formalism of Chap. II, then it is easy to see that the trace of the stress tensor has a term proportional to the square of the order parameter. Thus to calculate the temperature dependence of the hydrodynamic bulk viscosity it is necessary to cope with a term of the form

$$\zeta(\kappa) \sim \frac{1}{\Omega} \sum_{\vec{\ell}} \sum_{\vec{\ell}'} f(|\vec{\ell}|, |\vec{\ell}'|) \int_{-\infty}^{\infty} \langle S_{\vec{\ell}}(t_2) S_{-\vec{\ell}}(t_2) S_{\vec{\ell}'}(t_1) S_{-\vec{\ell}'}(t_1) \rangle \, dt_{21} \quad , \qquad (7)$$

where $f(|\vec{\ell}|, |\vec{\ell}'|)$ has no angular dependence, depending only on the magnitudes of the wavenumbers ℓ and ℓ'. We see that we no longer have any angular dependence in the integral to save us, as in the case of the shear viscosity. When we substitute Eq. (2) into (7), we find that the equal time value of the integrand in Eq. (7) becomes proportional to

$$-\frac{b}{T\Omega^2} \sum_{\vec{\ell}} \sum_{\vec{\ell}'} f(|\vec{\ell}|, |\vec{\ell}'|) \langle |S_{\vec{\ell}}|^2 \rangle^2 \langle |S_{\vec{\ell}'}|^2 \rangle^2$$

$$= -\frac{bZ^2T}{\Omega^2}\sum_{\vec{l}}\sum_{\vec{l}'} f(|\vec{l}|,|\vec{l}'|)(l^2+\xi^{-2})^2(l'^2+\xi^{-2})^2. \tag{8}$$

In other words, the equal time value of the integrand is multiplied by the product of two correlation functions. It is easy to estimate the relative values of Eqs. (8) and (7) by replacing all factors of wavenumber by ξ^{-1}, and the volume Ω by ξ^3; in this manner, we find that

$$\frac{\Delta\zeta(\kappa)}{\zeta^{(o)}(\kappa)} \propto \left(\frac{\xi}{\xi_o}\right) \tag{9}$$

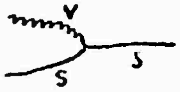
where ξ_o is the characteristic length defined in Chap. I, as

$$\xi_o = (bZ^2T)^{-1}, \tag{10}$$

and $\zeta_o(\kappa)$ is the zero frequency and wavenumber value of the critical viscosity using the decoupling approximation in Eq. (7), and $\Delta\zeta(\kappa)$ is the value obtained from Eq. (8). Therefore, as the critical point is approached the accuracy of mean field theory becomes considerably diminished. In fact, each order of perturbation theory will predict a larger divergence, so that mean field theory is obviously not applicable to the bulk viscosity.

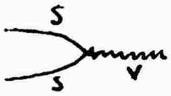
B. Time Dependent Perturbation Theory

To formulate the principles of time dependent perturbation theory it is necessary to consider relevant non-linear terms in the hydrodynamic equations, and how they effect the decay of concentration and velocity modes. We will only consider how a concentration and velocity mode yield another concentration mode, and how two concentration modes yield a velocity mode. These vertices are characterized by



(11a)

and



(11b)

The vertex (11a) is easily derived by considering the convective term $\vec{\nabla}\cdot(s\vec{v})$ as a perturbation to the time rate of change of the concentration fluctuation. In wavenumber space the hydrodynamic equation is

$$\left(\frac{d}{dt} + \Gamma_{\vec{q}}\right) s_{\vec{q}}(t) = -\frac{i}{\Omega^{1/2}} \sum_{\vec{\ell}'} \vec{q}\cdot\vec{v}_{\vec{q}-\vec{\ell}'}(t)\, s_{\vec{\ell}'}(t) , \qquad (12)$$

where we treat the right hand side as a perturbation. We can think of the zeroth order value $s_{\vec{q}}^{(o)}(t)$ as the solution to the homogeneous equation, and $s_{\vec{q}}^{(1)}(t)$ as the first iteration of Eq. (12), that is for t>o:

$$s_{\vec{q}}^{(o)}(t) = s_{\vec{q}}(o)\, e^{-\Gamma_{\vec{q}} t} \qquad (13)$$

and

$$s_{\vec{q}}^{(1)}(t) = -\frac{i}{\Omega^{1/2}} \sum_{\vec{\ell}'} \int_{o}^{t} dt'' e^{-\Gamma_{\vec{q}}(t-t'')}\, s_{\vec{\ell}'}^{(o)}(t'')\, \vec{q}\cdot v_{\vec{q}-\vec{\ell}'}^{(o)}(t'') . \qquad (14)$$

To derive the vertex (11b), we must consider the canonical form of the stress tensor. If $\mathcal{T}(\vec{r},t)$ is the part of the stress tensor at space time point $(\vec{r},t)$ due to concentration fluctuations, then we can write the hydrodynamic equation for the transverse velocity as follows:

$$\rho \frac{\partial}{\partial t}\vec{v}(\vec{r},t) - \eta \nabla^2 \vec{v}(\vec{r},t) = \vec{\nabla}\cdot \overleftrightarrow{\mathcal{T}}(\vec{r},t) \, , \tag{15}$$

where in Chapter II we showed that

$$\mathcal{T}_{ij} = s_i \frac{\partial \mathcal{F}}{\partial s_j} - \delta_{ij}\,\mathcal{F} \tag{16}$$

and

$$\mathcal{F}[s, s_i] = \frac{a}{2} s^2 + \frac{Z^{-1}}{2} \sum_{k=1}^{3} s_k^{\,2} \tag{17}$$

with

$$s_k \equiv \frac{\partial s}{\partial x_k} = (\vec{\nabla} s)_k \, . \tag{18}$$

In Eq. (17) we neglect fourth order terms, and also assume that $\mu = 0$. Then

$$\mathcal{T}_{ij} = Z^{-1} s_i s_j - \delta_{ij}\left[\frac{a}{2} s^2 + \frac{Z^{-1}}{2}\sum_{k=1}^{3} s_k^{\,2}\right] \, , \tag{19}$$

and

$$\sum_{i=1}^{3} \frac{\partial}{\partial x_i}\mathcal{T}_{ij} = \sum_{i=1}^{3} Z^{-1}\left[s_{ii} s_j + s_i s_{ij}\right] - a s s_j - \sum_{k=1}^{3} Z^{-1} s_k s_{kj} \tag{20}$$

so that

$$\vec{\nabla}\cdot\overleftrightarrow{\mathcal{T}} = \frac{1}{Z}\left(\nabla^2 s - \kappa^2 s\right)\vec{\nabla} s \, , \tag{21}$$

where

$$\kappa \equiv (aZ)^{1/2}. \qquad (22)$$

Transforming to wavenumber space, we find that the $\vec{q}$ component of $\vec{\nabla}\cdot\overleftrightarrow{\mathfrak{T}}$ is

$$(\vec{\nabla}\cdot\vec{\mathfrak{T}})_{\vec{q}} = -\frac{i}{Z\Omega^{1/2}}\sum_{\vec{\ell}}\vec{\ell}\left[(\vec{q}-\vec{\ell})^2+\kappa^2\right]S_{\vec{q}-\vec{\ell}}S_{\vec{\ell}}$$

$$= -\frac{i}{\Omega^{1/2}}\sum_{\vec{\ell}}\frac{1}{\chi_{\vec{q}-\vec{\ell}}}\vec{\ell}\,S_{\vec{q}-\vec{\ell}}S_{\vec{\ell}} = \frac{i}{\Omega^{1/2}}\sum_{\vec{\ell}}\frac{1}{\chi_{\vec{\ell}}}(\vec{q}-\vec{\ell})S_{\vec{\ell}}S_{\vec{q}-\vec{\ell}}$$

$$= -\frac{i}{2\Omega^{1/2}}\sum_{\vec{\ell}}\left\{\vec{\ell}\left(\frac{1}{\chi_{\vec{q}-\vec{\ell}}}-\frac{1}{\chi_{\vec{\ell}}}\right)+\vec{q}\,\frac{1}{\chi_{\vec{\ell}}}\right\}S_{\vec{\ell}}S_{\vec{q}-\vec{\ell}}\ . \qquad (23)$$

Since we are only dealing with transverse velocity components, it is necessary to subtract out the longitudinal components, that is the components of $(\vec{\nabla}\cdot\overleftrightarrow{\mathfrak{T}})$ along the direction of the wavevector $\vec{q}$, so that

$$(\vec{\nabla}\cdot\vec{\mathfrak{T}})^{\perp}_{\vec{q}} = \frac{i}{2\Omega^{1/2}}\sum_{\vec{\ell}}\left(\vec{\ell}-\frac{\vec{q}\cdot\vec{\ell}}{q^2}\vec{q}\right)\left(\frac{1}{\chi_{\vec{\ell}}}-\frac{1}{\chi_{\vec{q}-\vec{\ell}}}\right)S_{\vec{\ell}}(t)S_{\vec{q}-\vec{\ell}}(t). \qquad (24)$$

Using Eqs. (15) and (24) we can write the hydrodynamic equation for the transverse velocity modes as

$$\left(\frac{d}{dt}+\frac{\eta}{\rho}q^2\right)\vec{v}_{\vec{q}}(t) = \frac{i}{2\rho\Omega^{1/2}}\sum_{\vec{\ell}}\left(\vec{\ell}-\frac{\vec{q}\cdot\vec{\ell}}{q^2}\vec{q}\right)\left(\chi^{-1}_{\vec{\ell}}-\chi^{-1}_{\vec{q}-\vec{\ell}}\right)S_{\vec{\ell}}(t)S_{\vec{q}-\vec{\ell}}(t) \qquad (25)$$

The solution to the homogeneous equation is just

$$\vec{V}^{(0)}_{\vec{q}}(t) = \vec{V}^{(0)}_{\vec{q}}(0)\, e^{-\frac{\eta}{\rho} q^2 t} \quad , \tag{26}$$

for t>o, and the first iteration is

$$\vec{V}^{(1)}_{\vec{q}}(t) = \frac{i}{2\rho\Omega^{1/2}} \sum_{\vec{\ell}} \left(\vec{\ell} - \frac{\vec{q}\cdot\vec{\ell}}{q^2}\vec{q}\right)\left(\frac{1}{\chi_{\vec{\ell}}} - \frac{1}{\chi_{\vec{q}-\vec{\ell}}}\right)$$

$$\times \int_0^t dt'\, e^{-\frac{\eta}{\rho} q^2 (t-t')}\, S^{(0)}_{\vec{\ell}}(t')\, S^{(0)}_{\vec{q}-\vec{\ell}}(t') . \tag{27}$$

Having evaluated the vertices (11a) and (11b) we are in a position to examine the vertex corrections to the critical Rayleigh linewidth and shear viscosity.

C. Vertex Corrections

To examine the wavenumber and frequency dependence of the critical Rayleigh linewidth, we write the fluctuation dissipation formula

$$\Gamma_{\vec{q}}(\omega) = \frac{1}{T\chi_{\vec{q}}} \int_0^\infty dt\, e^{i\omega t} \langle \vec{q}\cdot\vec{J}_{\vec{q}}(t)\,(-\vec{q})\cdot\vec{J}_{-\vec{q}}(0)\rangle \quad , \tag{28}$$

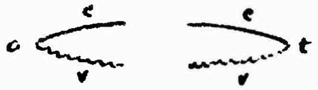
where

$$\vec{q}\cdot\vec{J}_{\vec{q}}(t) = \frac{1}{\Omega^{1/2}} \sum_{\vec{k}} S_{\vec{k}}(t)\, \vec{q}\cdot\vec{V}_{\vec{q}-\vec{k}}(t) \quad , \tag{29}$$

so that

$$\Gamma_{\vec{q}}(\omega) = \frac{1}{T\chi_{\vec{q}}\Omega} \sum_{\vec{k}} \sum_{\vec{k}'} \int_0^\infty dt\, e^{i\omega t} \langle S_{\vec{k}}(t)\,\vec{q}\cdot\vec{V}_{\vec{q}-\vec{k}}(t)\, S_{\vec{k}'}(0)(-\vec{q})\cdot\vec{V}_{-\vec{q}-\vec{k}'}(0)\rangle . \tag{30}$$

Thus we must correlate a concentration and a velocity mode at time t with a concentration and velocity mode at time 0, as shown below:

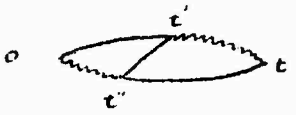
 (31)

Just connecting the lines to form the bubble

 (32)

corresponds to the decoupling mode approximation of Ferrell[14], discussed in Chapter III, Section B, and yields the Kawasaki[13] result.

To calculate the vertex correction we trace back the velocity mode at time t and presume it was caused by two concentration modes, and trace back the concentration mode at time t and presume it was caused by a velocity and a concentration mode. We will also assume that the concentration mode was formed first, so that the intermediate state consists of three concentration modes, and no velocity modes, otherwise we obtain a correction of a smaller order of magnitude, as we will later show. Therefore, we need to calculate the following diagram:

 , $t' > t''$. (33)

We insert Eqs. (14) and (27) into (30) and obtain

$$\Gamma_{\vec q}^{(1)'}(\omega) = \frac{1}{2\rho T \chi_{\vec q} \Omega^2} \sum_{\vec k} \sum_{\vec l} \sum_{\vec k'} \sum_{\vec l'} \left[\vec l \cdot \vec q - \frac{\vec l \cdot (\vec q - \vec k)\, \vec q \cdot (\vec q - \vec k)}{(\vec q - \vec k)^2} \right] \left[\frac{1}{\chi_{\vec l}} - \frac{1}{\chi_{\vec q - \vec k - \vec l}} \right] \times$$

$$\times \int_0^\infty dt\, e^{i\omega t} \int_0^t dt'\, e^{-\frac{\eta}{\rho}(\vec{q}-\vec{k})^2(t-t')} \int_0^{t} dt''\, e^{-\Gamma_{\vec{k}}(t-t'')} \langle S_{\vec{\ell}}(t') S_{\vec{q}-\vec{k}-\vec{\ell}}(t') S_{\vec{\ell}'}(t'') S_{\vec{k}'}(0)\rangle \times$$

$$\times \langle \vec{k}\cdot\vec{v}_{\vec{k}-\vec{\ell}'}(t'')(-\vec{q})\cdot\vec{v}_{-\vec{q}-\vec{k}'}(0)\rangle . \qquad (34)$$

To evaluate the above equation we take the coupling of the concentration modes shown by the lines above the equation and double it, since by symmetry it must give a contribution equal to the coupling denoted by the lines underneath the equation. Therefore, we presume that as far as Eq. (34) is concerned

$$\langle S_{\vec{\ell}}(t') S_{\vec{q}-\vec{k}-\vec{\ell}}(t') S_{\vec{\ell}'}(t'') S_{\vec{k}'}(0)\rangle = 2T^2 \chi_{\vec{\ell}} \chi_{\vec{q}-\vec{k}-\vec{\ell}}\, e^{-\Gamma_{\vec{\ell}}(t'-t'')}\, e^{-\Gamma_{\vec{q}-\vec{k}-\vec{\ell}}t'} \times$$

$$\times \delta_{\vec{\ell}',-\vec{\ell}}\, \delta_{\vec{k}',-\vec{q}+\vec{k}+\vec{\ell}} \quad , \qquad (35)$$

and

$$\langle \vec{k}\cdot\vec{v}_{\vec{k}-\vec{\ell}'}(t'')(-\vec{q})\cdot\vec{v}_{-\vec{q}-\vec{k}'}(0)\rangle = \left[\vec{k}\cdot\vec{q} - \frac{\vec{k}\cdot(\vec{k}+\vec{\ell})\,\vec{q}\cdot(\vec{k}+\vec{\ell})}{(\vec{k}+\vec{\ell})^2}\right] \times$$

$$\times \frac{T}{\rho}\, e^{-\frac{\eta}{\rho}(\vec{k}+\vec{\ell})^2 t''}\, \delta_{\vec{\ell}',-\vec{q}+\vec{k}-\vec{k}'} \; . \qquad (36)$$

Note that

$$\vec{k}\cdot\vec{q} - \frac{\vec{k}\cdot(\vec{k}+\vec{\ell})\,\vec{q}\cdot(\vec{k}+\vec{\ell})}{(\vec{k}+\vec{\ell})^2} = \frac{(\vec{k}+\vec{\ell})}{(\vec{k}+\vec{\ell})^2}\cdot\left[\vec{\ell}(\vec{k}\cdot\vec{q}) - \vec{k}(\vec{\ell}\cdot\vec{q})\right] . \qquad (37)$$

The time integrals then become

$$\int_0^\infty dt\, e^{i\omega t} \int_0^t dt'\, e^{-\frac{\eta}{\rho}(\vec{q}-\vec{k})^2(t-t')} \int_0^t dt''\, e^{-\Gamma_{\vec{k}}(t-t')}\, e^{-\Gamma_{\vec{r}}(t'-t'')}\, e^{-\Gamma_{\vec{q}-\vec{k}-\vec{r}}\, t'} \times$$

$$\times\, e^{-\frac{\eta}{\rho}(\vec{k}+\vec{r})^2 t''}$$

$$= \int_0^\infty d(t-t')\, e^{[i\omega - \frac{\eta}{\rho}(\vec{q}-\vec{k})^2](t-t')} \int_0^\infty d(t'-t'')\, e^{[i\omega - \Gamma_{\vec{k}} - \Gamma_{\vec{r}} - \Gamma_{\vec{q}-\vec{k}-\vec{r}}](t'-t'')} \times$$

$$\times \int_0^\infty d(t'')\, e^{[i\omega - \frac{\eta}{\rho}(\vec{k}+\vec{r})^2]t''}$$

$$= \left[-i\omega + \frac{\eta}{\rho}(\vec{q}-\vec{k})^2\right]^{-1} \left[-i\omega + \Gamma_{\vec{k}} + \Gamma_{\vec{r}} + \Gamma_{\vec{q}-\vec{k}-\vec{r}}\right]^{-1} \left[-i\omega + \frac{\eta}{\rho}(\vec{k}+\vec{r})^2\right]^{-1}. \qquad (38)$$

In the above integrals we neglected concentration decay rates with respect to velocity decay rates. Therefore, if there had been any velocity modes propagating in the intermediate interval, then all three frequency denominators would contain velocity decay rates, and since the velocity decay rate is proportional to the square of the wavenumber, while the concentration decay rate is proportional to the cube of the wavenumber, the sum in Eq. (34) would have an extra wavenumber factor, thus reducing the order of magnitude. If we substitute Eqs. (35)-(38) into (34), we obtain

$$\Gamma_{\vec{q}}^{(1)'}(\omega) = -\left(\frac{T}{\rho\Omega}\right)^2 \sum_{\vec{k}} \sum_{\vec{l}} \left[\vec{q}\cdot\vec{l} - \frac{\vec{q}\cdot(\vec{q}-\vec{k})\,\vec{l}\cdot(\vec{q}-\vec{k})}{(\vec{q}-\vec{k})^2}\right]\left[1 - \frac{\chi_{\vec{q}-\vec{k}-\vec{l}}}{\chi_{\vec{l}}}\right]\frac{\chi_{\vec{l}}}{\chi_{\vec{q}}} \times$$

$$\times \frac{(\vec{k}+\vec{l})}{(\vec{k}+\vec{l})^2}\cdot\left[\vec{l}(\vec{q}\cdot\vec{k}) - \vec{k}(\vec{q}\cdot\vec{l})\right]\left[i\omega + \frac{\eta}{\rho}(\vec{q}-\vec{k})^2\right]^{-1}\left[i\omega + \Gamma_{\vec{k}} + \Gamma_{\vec{l}} + \Gamma_{\vec{q}-\vec{k}-\vec{l}}\right]^{-1}\left[i\omega + \frac{\eta}{\rho}(\vec{k}+\vec{l})^2\right]^{-1}. \quad (39)$$

There is another contribution to the vertex correction. It is derived by tracing back the velocity mode at time t, and assuming it was formed by two concentration modes at time t', and further assuming that one of the concentration modes was formed by a concentration and a velocity mode at time t". That is, if

$$\vec{q}\cdot\vec{v}_{\vec{q}-\vec{k}}(t) = \frac{i}{2\rho\Omega^{1/2}} \sum_{\vec{l}} \left[\vec{l}\cdot\vec{q} - \frac{\vec{l}\cdot(\vec{q}-\vec{k})\,\vec{q}\cdot(\vec{q}-\vec{k})}{(\vec{q}-\vec{k})^2}\right]\left[\chi_{\vec{l}}^{-1} - \chi_{\vec{q}-\vec{k}-\vec{l}}^{-1}\right] \times$$

$$\times \int_0^t dt' e^{-\frac{\eta}{\rho}(\vec{q}-\vec{k})^2(t-t')} s_{\vec{l}}(t')\, s_{\vec{q}-\vec{k}-\vec{l}}(t'), \quad (40)$$

then we split up one of the concentration modes at t':

$$s_{\vec{l}}(t') = -\frac{i}{\Omega^{1/2}} \sum_{\vec{l}'} \int_0^{t'} dt'' e^{-\Gamma_{\vec{l}'}(t'-t'')} s_{\vec{l}'}(t'')\, \vec{l}\cdot\vec{v}_{\vec{l}-\vec{l}'}(t''). \quad (41)$$

If we substitute Eqs. (40) and (41) into (30) we obtain

$$\Gamma_{\vec{q}}^{(1)''}(\omega) = \frac{1}{2\rho T\chi_{\vec{q}}\Omega^2} \sum_{\vec{k}} \sum_{\vec{l}} \sum_{\vec{k}'} \sum_{\vec{l}'} \left[\vec{q}\cdot\vec{l} - \frac{\vec{q}\cdot(\vec{q}-\vec{k})\,\vec{l}\cdot(\vec{q}-\vec{k})}{(\vec{q}-\vec{k})^2}\right]\left[\chi_{\vec{l}}^{-1} - \chi_{\vec{q}-\vec{k}-\vec{l}}^{-1}\right] \times$$

$$\times \int_0^\infty dt\, e^{i\omega t} \int_0^t dt' e^{-\frac{\eta}{\rho}(\vec{q}-\vec{k})^2(t-t')} \int_0^{t'} dt'' e^{-\Gamma_{\vec{l}}(t'-t'')} \left\langle s_{\vec{k}}(t)\, s_{\vec{q}-\vec{k}-\vec{l}}(t')\, s_{\vec{l}'}(t'')\, s_{\vec{k}'}(0)\right\rangle \times$$

$$\times \frac{(\vec{k}+\vec{\ell})}{(\vec{k}+\vec{\ell})^2}\cdot\left[\vec{\ell}(\vec{q}\cdot\vec{k})-\vec{k}(\vec{q}\cdot\vec{\ell})\right]\left[-i\omega+\frac{\eta}{\rho}(\vec{q}-\vec{k})^2\right]^{-1}\left[-i\omega+\Gamma_{\vec{k}}+\Gamma_{\vec{\ell}}+\Gamma_{\vec{q}-\vec{k}-\vec{\ell}}\right]^{-1}\left[-i\omega+\frac{\eta}{\rho}(\vec{k}+\vec{\ell})^2\right]^{-1}. \tag{46}$$

Therefore the total vertex correction to the decay rate of the concentration modes is given by

$$\Gamma^{(1)}_{\vec{q}}(\omega) = \Gamma^{(1)'}_{\vec{q}}(\omega) + \Gamma^{(1)''}_{\vec{q}}(\omega)$$

$$= -\left(\frac{T}{\rho\Omega}\right)^2 \sum_{\vec{k}}\sum_{\vec{\ell}}\left[1-\frac{\chi_{\vec{q}-\vec{k}-\vec{\ell}}}{\chi_{\vec{\ell}}}\right]\left[\frac{\chi_{\vec{\ell}}-\chi_{\vec{k}}}{\chi_{\vec{q}}}\right]\left[\vec{q}\cdot\vec{\ell}-\frac{\vec{q}\cdot(\vec{q}-\vec{k})\,\vec{\ell}\cdot(\vec{q}-\vec{k})}{(\vec{q}-\vec{k})^2}\right]\times$$

$$\times\frac{(\vec{k}+\vec{\ell})}{(\vec{k}+\vec{\ell})^2}\cdot\left[\vec{\ell}(\vec{q}\cdot\vec{k})-\vec{k}(\vec{q}\cdot\vec{\ell})\right]\left[i\omega+\frac{\eta}{\rho}(\vec{q}-\vec{k})^2\right]^{-1}\times$$

$$\times\left[-i\omega+\Gamma_{\vec{k}}+\Gamma_{\vec{\ell}}+\Gamma_{\vec{q}-\vec{k}-\vec{\ell}}\right]^{-1}\left[-i\omega+\frac{\eta}{\rho}(\vec{k}+\vec{\ell})^2\right]^{-1}. \tag{47}$$

The above result is the same as that found by Kawasaki[23]. According to him the above amounts only to a 2.4% correction if $q \gg \kappa$, and 0.4% if $q \ll \kappa$, both in the zero frequency limit. Actually, it is fairly simple to see that the vertex correction to the Rayleigh linewidth is very small compared to the zeroth order value

$$\Gamma^{(0)}_{\vec{q}}(\omega) = \frac{T}{\rho\Omega}\sum_{\vec{k}}\frac{\chi_{\vec{q}-\vec{k}}}{\chi_{\vec{q}}}\left[q^2-\frac{(\vec{q}\cdot\vec{k})^2}{k^2}\right]\left[-i\omega+\frac{\eta}{\rho}k^2\right]^{-1}, \tag{48}$$

because we can write

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$$\Gamma^{(1)}_{\vec{q}}(\omega) = \frac{T}{\rho\Omega}\sum_{\vec{k}} \frac{\chi_{\vec{q}-\vec{k}}}{\chi_{\vec{q}}}\left[q^2 - \frac{(\vec{q}\cdot\vec{k})^2}{k^2}\right]\left[-i\omega + \frac{\eta}{\rho}k^2\right]^{-1} V_{\vec{q},\vec{k}}(\omega) \, , \qquad (49)$$

where we have multiplied the integrand of Eq. (48) by the correction function $V_{\vec{q},\vec{k}}(\omega)$, which by Eq. (47) is given by

$$V_{\vec{q},\vec{k}}(\omega) = -\frac{T}{\rho\Omega}\sum_{\vec{r}}\left[1 - \frac{\chi_{\vec{q}-\vec{k}-\vec{r}}}{\chi_{\vec{r}}}\right]\left[\frac{\chi_{\vec{r}}-\chi_{\vec{k}}}{\chi_{\vec{q}}}\right]\left[\frac{\vec{q}\cdot\vec{r} - \frac{1}{(\vec{q}-\vec{k})^2}\,\vec{q}\cdot(\vec{q}-\vec{k})\,\vec{r}\cdot(\vec{q}-\vec{k})}{q^2 - \frac{1}{k^2}(\vec{q}\cdot\vec{k})^2}\right]\times$$

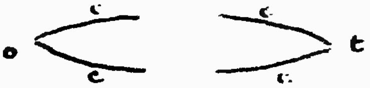
$$\times\frac{(\vec{k}+\vec{r})}{(\vec{k}+\vec{r})^2}\cdot\left[\vec{r}(\vec{q}\cdot\vec{k}) - \vec{k}(\vec{q}\cdot\vec{r})\right]\left[\frac{-i\omega + \frac{\eta}{\rho}k^2}{-i\omega + \frac{\eta}{\rho}(\vec{q}-\vec{k})^2}\right]\left[-i\omega + \Gamma_{\vec{k}} + \Gamma_{\vec{r}} + \Gamma_{\vec{q}-\vec{k}-\vec{r}}\right]^{-1}\left[-i\omega + \frac{\eta}{\rho}(\vec{k}+\vec{r})^2\right]^{-1}. \qquad (50)$$

$V_{\vec{q},\vec{k}}(\omega)$ is a completely dimensionless quantity. It is also not very difficult to see that it is very small for all ranges of k and q. If we examine the integrand we see that it varies as k/ℓ^4 if $\ell \gg k$, in both the very small and very large region of q. If ℓ is very small, then the integrand varies as the inverse cube of the greater of q and k. If ℓ and k have the same magnitude or the same direction, the integrand is zero. As a result we expect $\Gamma^{(1)}_{\vec{q}}(\omega)$ to be of smaller order of magnitude than $\Gamma^{(0)}_{\vec{q}}(\omega)$, although it has essentially the same wavenumber and frequency dependence.

We can use the same techniques to examine the vertex corrections to the critical shear viscosity. By Eq. (30) of Chap. II, the critical part of the shear viscosity can be written as

$$\Delta\eta_{\vec{q}}(\omega) = -\frac{1}{Z^2 T\Omega}\sum_{\vec{k}}\sum_{\vec{k}'} k_x(q_z - k_z)\,k'_x(q_z + k'_z)\int_0^{\infty} dt\, e^{i\omega t}\langle S_{\vec{k}}(t)\,S_{\vec{q}-\vec{k}}(t)\,S_{\vec{k}'}(0)\,S_{-\vec{q}-\vec{k}'}(0)\rangle . \qquad (51)$$

Here we have two concentration modes at time t correlated with two concentration modes at time 0, as shown below



(52)

Joining the lines to form the bubble

(53)

corresponds to the decoupled mode approximation of Chapter II. We will examine the vertex correction caused by a velocity mode propagating in an intermediate state, as illustrated by the diagram:

(54)

To calculate the above diagram, we assume that both concentration modes at time t were produced by a concentration and velocity mode at some previous time. Therefore, we let

$$S_{\vec{k}}(t) = -\frac{i}{\Omega^{1/2}}\sum_{\vec{p}}\int_0^t dt'\, e^{-\Gamma_{\vec{k}}(t-t')} S_{\vec{p}}(t')\,\vec{k}\cdot\vec{v}_{\vec{k}-\vec{p}}(t') \quad , \tag{55}$$

and

$$S_{\vec{q}-\vec{k}}(t) = -\frac{i}{\Omega^{1/2}}\sum_{\vec{p}'}\int_0^t dt''\, e^{-\Gamma_{\vec{q}-\vec{k}}(t-t'')} S_{\vec{p}'}(t'')\,(\vec{q}-\vec{k})\cdot\vec{v}_{\vec{q}-\vec{k}-\vec{p}'}(t'') \, , \tag{56}$$

and substitute into Eq. (51) to obtain the vertex correction

$$\Delta\eta^{(1)}_{\vec{q}}(\omega) = \frac{1}{TZ^2\Omega^2}\sum_{\vec{k}}\sum_{\vec{p}}\sum_{\vec{k}'}\sum_{\vec{p}'} k_x(q_z-k_z)k'_x(q_z+k'_z)\int_0^\infty dt\, e^{i\omega t}\int_0^t dt'\, e^{-\Gamma_{\vec{k}}(t-t')} \times$$

$$\times\int_0^t dt''\, e^{-\Gamma_{\vec{q}-\vec{k}}(t-t'')}\left\langle S_{\vec{p}}(t' \;\; S_{\vec{p}'}(t'')S_{\vec{k}'}(0)S_{-\vec{q}-\vec{k}'}(0)\right\rangle\left\langle \vec{k}\cdot\vec{v}_{\vec{k}-\vec{p}}(t')(\vec{q}-\vec{k})\cdot\vec{v}_{\vec{q}-\vec{k}-\vec{p}'}(t'')\right\rangle$$

$$= -\frac{1}{\rho Z^2\Omega^2}\sum_{\vec{k}}\sum_{\vec{\ell}}\sum_{\vec{k}'} k_x(q_z-k_z)k'_x(q_z+k'_z)\left[\vec{k}\cdot(\vec{q}-\vec{k})-\frac{\vec{k}\cdot(\vec{k}-\vec{\ell})(\vec{q}-\vec{k})\cdot(\vec{k}-\vec{\ell})}{(\vec{k}-\vec{\ell})^2}\right]\times$$

$$\times\int_0^\infty dt\, e^{i\omega t}\int_0^t dt'\, e^{-\Gamma_{\vec{k}}(t-t')}\int_0^t dt''\, e^{-\Gamma_{\vec{q}-\vec{k}}(t-t'')}\, e^{-\frac{\eta}{\rho}(\vec{k}-\vec{\ell})^2(t-t'')}\left\langle S_{\vec{\ell}}(t')S_{\vec{q}-\vec{\ell}}(t'')S_{\vec{k}'}(0)S_{\vec{q}-\vec{k}'}(0)\right\rangle. \tag{57}$$

Using the decoupling approximation, and setting $\vec{q}$ along the z-axis as in Chapter II, we obtain

$$\Delta\eta^{(1)}_{\vec{q}}(\omega)=\frac{T^2}{\rho Z^2\Omega^2}\sum_{\vec{k}}\sum_{\vec{\ell}} k_x(q-k_z)\ell_x(q-2\ell_z)\chi_{\vec{\ell}}\chi_{\vec{q}-\vec{\ell}}\left[\vec{k}\cdot(\vec{q}-\vec{k})-\frac{\vec{k}\cdot(\vec{k}-\vec{\ell})(\vec{q}-\vec{k})\cdot(\vec{k}-\vec{\ell})}{(\vec{k}-\vec{\ell})^2}\right]\times$$

$$\times\left[-i\omega+\Gamma_{\vec{k}}+\Gamma_{\vec{q}-\vec{k}}\right]^{-1}\left[-i\omega+\frac{\eta}{\rho}(\vec{k}-\vec{\ell})^2\right]^{-1}\left[-i\omega+\Gamma_{\vec{\ell}}+\Gamma_{\vec{q}-\vec{\ell}}\right]^{-1}. \tag{58}$$

Recalling that the uncorrected critical shear viscosity can be written as

$$\Delta\eta^{(0)}_{\vec{q}}(\omega)=\frac{T}{Z^2\Omega}\sum_{\vec{k}} k_x(q-k_z)k_x(q-2k_z)\chi_{\vec{k}}\chi_{\vec{q}-\vec{k}}\left[-i\omega+\Gamma_{\vec{k}}+\Gamma_{\vec{q}-\vec{k}}\right]^{-1}, \tag{59}$$

we rewrite Eq. (58) in the form of Eq. (59) with a vertex factor in the summand as we did with the Rayleigh linewidth, as follows:

$$\Delta\eta^{(1)}_{\vec{q}}(\omega)=\frac{T}{Z^2\Omega}\sum_{\vec{k}} k_x(q-k_z)k_x(q-2k_z)\chi_{\vec{k}}\chi_{\vec{q}-\vec{k}}\left[-i\omega+\Gamma_{\vec{k}}+\Gamma_{\vec{q}-\vec{k}}\right]W_{\vec{q},\vec{k}}(\omega), \tag{60}$$

where $W_{\vec{q},\vec{k}}(\omega)$ is the dimensionless quantity given by

$$W_{\vec{q},\vec{k}}(\omega)=\frac{T}{\rho\Omega}\sum_{\vec{\ell}}\frac{\ell_x}{k_x}\frac{(q-2\ell_z)}{(q-2k_z)}\left[-i\omega+\Gamma_{\vec{\ell}}+\Gamma_{\vec{q}-\vec{\ell}}\right]^{-1}\times$$

$$\times\left[\vec{k}\cdot(\vec{q}-\vec{k})-\frac{\vec{k}\cdot(\vec{k}-\vec{\ell})(\vec{q}-\vec{k})\cdot(\vec{k}-\vec{\ell})}{(\vec{k}-\vec{\ell})^2}\right]\left[-i\omega+\frac{\eta}{\rho}(\vec{k}-\vec{\ell})^2\right]^{-1}. \qquad (61)$$

Because of the proliferation of angular factors we expect that the above term should be very small, although, it may introduce a $\ln(k_D/q)$ term, since it is necessary to cut off the integration over ℓ in order to insure convergence. As in the case of the critical Rayleigh linewidth, the vertex correction to the shear viscosity has essentially the same wave-number and frequency dependence as the uncorrected value, but reduced greatly enough, so that its effect is negligible.

In this chapter, we have justified the use of the decoupling approximation for the shear viscosity and diffusion coefficient. We have found that static perturbation theory has absolutely no effect on the critical shear viscosity, even though it produces a divergent series for the bulk viscosity. After formulating the relevant techniques for time dependent perturbation theory, we examined the effect of vertex corrections on the shear viscosity and Rayleigh linewidth, and showed it to be negligible.

V. CONCLUSION

A. Summary and Discussion

The fluctuation-dissipation theorem was a very useful tool in obtaining the results of this paper. It related transport coefficients, quantities which are proportional to the dissipation rate of fluctuating internal modes of the system, to the correlation function of the strengths of those fluctuations. It is intuitively clear that since a fluctuation of any internal quantity is a deviation from the equilibrium configuration of the system, the stability criterion, or the principle of minimization of free energy, demands a return to equilibrium. Therefore, the larger the fluctuation, the greater the restoring force. One manifestation of the fluctuation dissipation theorem is the Kubo formula[8,9,24], which equates the transport coefficient to the time and space integral of the correlation function of the relevant flux. In both the shear viscosity and diffusion coefficient, the flux was found to be the second order product of two fluctuating quantities. Therefore, in the calculation of the correlation functions it was necessary to use a decoupling, or factoring, approximation[14], which transformed a correlation function involving four fluctuating quantities into the product of two correlation functions, each involving two fluctuating quantities. The explicit equations for the correlation functions were derived from mean field theory and linear hydrodynamics.

These methods were first used by Ferrell[14] in calculating the critical temperature dependence of the diffusion coefficient. He verified the result of Kawasaki[13], namely

$$D = T\mu_\xi \quad , \tag{1}$$

where

$$\mu_\xi = (6\pi\eta\xi)^{-1} \quad , \tag{2}$$

is Stokes' formula for the mobility of a sphere of radius ξ moving through a liquid of viscosity η. This result suggests an intuitive picture of the phase transition, as consisting of a binary liquid with regions of large concentrations of solute. These regions can be thought of as rigid spheres having radii equal to the correlation length. As the critical temperature is approached, the correlation length grows; that is the size of the inhomogeneities grows larger, corresponding to a decrease in the mobility of these regions, thus accounting for the sluggishness of the system, and its lack of haste in returning to equilibrium. When the correlation length grows larger than the wavelength of the concentration fluctuations, i.e. when $q >> \xi^{-1}$, the above formulae are no longer valid, because D becomes a function of q corresponding to "non local" diffusion. This change is carried out by the substitution

$$\xi^{-1} \rightarrow aq \quad , \tag{3}$$

where a is some numerical constant of the order of unity. Eq. (3) illustrates the principle of dynamical scaling[18,19], that all temperature dependence be expressed in terms of the correlation length ξ, and as $T \to T_c$ all factors of ξ be replaced by the wavelength of the fluctuations. In the case of the diffusion coefficient $a = 3\pi/8$, so that in the limit $T \to T_c$ we obtain

$$\Gamma_q = D_q q^2 = \frac{Tq^3}{16\eta} . \tag{4}$$

All of the above equations assume a constant value of the shear viscosity. However, recent experiments have clearly established a critical temperature dependence in the hydrodynamic shear viscosity η. It was the purpose of this paper to theoretically derive the temperature, wavenumber, and frequency dependence of the excess shear viscosity, and determine how it affects the critical diffusion in coefficient. In other words, what value of η should be used in Eq. (4)?

A Kubo type formula relating the shear viscosity to the correlation function of the off-diagonal component of the stress tensor[10] was employed. A canonical formalism identifying the Ginzburg-Landau free energy density with a Lagrangian density established that the off-diagonal component of the stress tensor due to concentration fluctuations is proportional to the product of two orthogonal components of the gradient of the concentration. To evaluate the correlation function, it was necessary to employ a decoupling approximation, whose validity was later confirmed by perturbation theory. The rest of the calculation was rather straightforward and produced a logarithmic temperature divergence[15]. By the principle of dynamical scaling a logarithmic wavenumber and frequency dependence was predicted and actually calculated, and for the shear viscosity the factor a in Eq. (3) was found to be .497, confirming the general rule of thumb[25], that when factorization introduces the correlation length twice (via the equal time correlation function), a is close to $\frac{1}{2}$.

The above scaling factor is not directly valid in the diffusion problem because it is only applicable in the static limit. Therefore, it is not correct to blindly insert the wavenumber dependent viscosity into Eq. (4) in determining the critical Rayleigh linewidth. The diffusion process depends upon the relaxation of current fluctuations, which are the product of concentration and velocity fluctuations. The finite concentration relaxation rate forces us to study the viscous damping of velocity fluctuations at non-zero frequencies. This results in a kind of "retardation" correction to the effective critical viscosity used in the calculation of the critical diffusion coefficient. It is manifested by the increase in the scaling constant a_{eff} to be used in the shear viscosity which is to be inserted into Eq. (4). The result is

$$a_{eff} = e^{-(1.33-1.25)} = e^{-0.08} = 0.92. \tag{5}$$

The self-consistent nature of the viscosity and diffusion was then studied. It was found that the product of the diffusion coefficient and excess shear viscosity should have the same temperature behavior as the inverse of the correlation length. Making use of the fact that the characteristic frequency associated with viscous damping is much larger than the characteristic frequency associated with diffusion, it was deduced that the critical shear viscosity cannot have a temperature divergence more drastic than a logarithmic one[21,22]. The self-consistency was then applied to other fluids, namely the gas, and the superfluid.

Finally, we applied the results of perturbation theory to test the reliability of the previous results on the critical shear viscosity and diffusion coefficients. The fourth order term of the Ginzburg-Landau equation serves as the perturbation in the static case; it is found to have no effect on the shear viscosity, even though it produces a divergent perturbation series in the case of the bulk viscosity. Non-linear hydrodynamics serves as the basis for time dependent perturbation theory, which was used to study the effect of vertex corrections on the critical diffusion and shear viscosity. Although, the vertex corrections had similar temperature, wavenumber and frequency behavior as the uncorrected quantities, their sizes were diminished by at least an order of magnitude.

B. Areas of Further Study

At first glance, it seems that the techniques developed here would be suitable for studying the critical bulk viscosity and sound attenuation in the binary liquid phase transition. Unfortunately, it is difficult to treat the correlation function of four concentration fluctuations because of the failure of the decoupling approximation. Therefore, it will be important to learn how to treat higher order correlation functions, and apply the results to the bulk viscosity.

A more promising area of research is the non-Lorentzian behavior of the frequency spectrum of the concentration modes. This behavior will be manifested in the frequency dependence of the diffusion coefficient. The most important contribution to the frequency dependence will probably arise from the frequency dependence of the excess shear viscosity, which we have already derived here.

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APPENDIX

In this appendix, the computer programs that were used for numerical calculations are presented. They were run on the INTERCOM system of the CDC 6400 computer at the U.S. Naval Ordnance Laboratory.

Program FLV283 determined the value of the viscosity scaling function at zero frequency, given by Eq. (109) in Chap. II.

Program SLP283 determined the initial slope (minus 1/3) of the viscosity scaling function, given by Eq. (110) in Chap. II.

Program SCL283 was used to plot the viscosity scaling function for various values of P, given by Eq. (100) in Chap. II. Simpson's Rule was used in the numerical integration.

Program DIF283 was used to plot $\Phi(\phi) - \bar{\Phi}(\phi)$ for various ϕ. $\Phi(\phi)$ is defined by Eq. (69) and $\bar{\Phi}(\phi)$ by Eq. (77) of Chap. III. This program used the results of SCL283, and employed linear interpolation to calculate intermediate values of the scaling function. By integrating $\Phi(\phi)-\bar{\Phi}(\phi)$ by Simpson's Rule, the program was able to calculate C_{λ}.

```
LIST

FLV253    13.41.14. 03/07/72
10 PRØGRAM FLV253 (INPUT,ØUTPUT)
20 ATANH(Y) = .5*ALØG((1.+Y)/(1.-Y))
30 GH(X) = 1. - X*X
40 GJ1(X) = GH(X)*(X*ATANH(1./X)-1.)
50 GC(X) = 1. + X*X/3.
60 SQ3(X) = SQRT(3.)/X
70 GJ2(X) = GC(X)*(1.-ATAN(SQ3(X))/SQ3(X))
80 F(X) = -(15./(8.*X))*(GH(X)*(GJ1(X)+GJ2(X))+(8./15.))
90 G(A) = F(TAN(A))/CØS(A)**2
100 N2 = 50
105 PI = 3.1415926536
110 H = .25/FLØAT(N2)
120 N = N2/2
130 N1 = N - 1
140 PRINT 40
150 A1 = .25 + H
160 G1 = G(PI*A1)
170 PRINT 50, A1,G1
180 S = 4.*G1 - 2.
190 DØ 20 I = 1, N1
200 A1 = .25 + H*FLØAT(2*I)
210 G1 = G(PI*A1)
220 PRINT 50, A1, G1
230 A2 = A1 + H
240 G2 = G(A2*PI)
250 PRINT 50, A2,G2
260 S = 2.*G1 + 4.*G2 + S
270 20 CØNTINUE
300 S = PI*H*S/3.
310 PRINT 60, H,S
320 40 FØRMAT(/12X,*A*,18X,*G(A)*/)
330 50 FØRMAT(5X,F10.3,10X,E15.8)
340 60 FØRMAT(/* WITH H = *,F10.3,*, C = *,E15.8)
350 STØP
360 END
            A                   G(A)

          .255           -.18723280E+01
          .260           -.18018852E+01
          .265           -.17217608E+01
          .270           -.16491373E+01
          .275           -.15823742E+01
          .280           -.15203807E+01
          .285           -.14623735E+01
          .290           -.14077605E+01
          .295           -.13560775E+01
          .300           -.13069505E+01
          .305           -.12600709E+01
          .310           -.12151800E+01
          .315           -.11720574E+01
          .320           -.11305133E+01
          .325           -.10903920E+01
          .330           -.10515181E+01
          .335           -.10137926E+01
          .340           -.97709037E+00
          .345           -.94130832E+00
          .350           -.90635336E+00
          .355           -.87214120E+00
          .360           -.83859527E+00
          .365           -.80564576E+00
          .370           -.77322892E+00
          .375           -.74128645E+00
          .380           -.70976492E+00
          .385           -.67861542E+00
          .390           -.64779314E+00
          .395           -.61725708E+00
          .400           -.58696979E+00
          .405           -.55689717E+00
          .410           -.52700820E+00
          .415           -.49727486E+00
          .420           -.46767192E+00
          .425           -.43817680E+00
          .430           -.40876948E+00
          .435           -.37943233E+00
          .440           -.35015001E+00
          .445           -.32090933E+00
          .450           -.29169917E+00
          .455           -.26251028E+00
          .460           -.23333521E+00
          .465           -.20416813E+00
          .470           -.17500467E+00
          .475           -.14584181E+00
          .480           -.11667763E+00
          .485           -.87511123E-01
          .490           -.58335250E-01
          .495           -.28657729E-01

WITH H =        .005, C =  -.63260654E+00
13.39.20.STØP
**READY.
```

```
SLP283    14.44.56. 04/12/72
10 PRØGRAM SLP283(INPUT,ØUTPUT)
15 DIMENSIØN G(50)
20 DATA PI, S3/3.1415926536, 1.7320508076/
30 HYP(X) = 0.5*ALØG((1.+X)/(1.-X))/X
40 CIR(X) = (PI/2.-ATAN(1./(S3*X)))/(S3*X)
50 FH(X) = 1. - X*X
60 FC(X) = 1. + 3.*X*X
70 BR1(X) = FH(X)*(HYP(X)-CIR(X))/(16.*X*X)
80 BR2(X) = (FC(X)*CIR(X)-1.)/(24.*X*X)
90 F(X) = 7.5*FH(X)*(BR1(X)-BR2(X))
100 PRINT 100
110 N = 20
120 DØ 10 I = 1,N
130 Y = FLØAT(I)/FLØAT(N)
140 G(I) = F(Y)
150 PRINT 110, Y, G(I)
160 10 CØNTINUE
170 100 FØRMAT(15X,*X*,14X,*F(X)*)
180 110 FØRMAT(2(10X,F10.5))
190 S = 4.*G(1)
200 N1 = N/2 - 1
210 DØ 20 J = 1,N1
220 S = 2.*G(2*J)+4.*G(2*J+1)+S
230 20 CØNTINUE
240 XINT = (S+G(N))/(3.*FLØAT(N))
250 PRINT 120, XINT
260 120 FØRMAT(/5X,*INTEGRAL ØF F(X) = *,F10.5)
270 STØP
280 END
**READY.
FF-TN

SLP283    14.46.55. 04/12/72
               X              F(X)
            .05000            -.00248
            .10000            -.00969
            .15000            -.02099
            .20000            -.03540
            .25000            -.05178
            .30000            -.06895
            .35000            -.08577
            .40000            -.10125
            .45000            -.11458
            .50000            -.12512
            .55000            -.13236
            .60000            -.13595
            .65000            -.13561
            .70000            -.13113
            .75000            -.12231
            .80000            -.10895
            .85000            -.09075
            .90000            -.06729
            .95000            -.03774
           1.00000            0.00000

     INTEGRAL ØF F(X) =     -.07908
14.47.13.STØP
**READY.
```

```
SCL283    14.41.36. 04/12/72
10 PRØGRAM SCL283 (INPUT,ØUTPUT)
20 ATANH(Y) = 0.5*ALØG((1.+Y)/(1.-Y))
30 GH(X) = 1. - X*X
40 GJ1(X) = GH(X)*(X*ATANH(1./X)-1.)
50 A(X,P) = SQRY(X*X*X+P)
60 B(X) = SQRT(3.*X)
70 GC(X,P) = 1. + (A(X,P)/B(X))**2
80 GJ2(X,P) = GC(X,P)*(1.-(A(X,P)/B(X))*ATAN(B(X)/A(X,P)))
90 D(X,P) = A(X,P)**2 + (X*B(X))**2
100 BRC(X,P)=GH(X)*(GJ1(X)+GJ2(X,P))+2.*D(X,P)/(15.*A(X,P)**2)
110 F(X,P) = -7.5*X*X*BRC(X,P)/D(X,P)
120 G(T,P) = F(TAN(T),P)/CØS(T)**2
130 N2 = 50
140 PI = 3.1415926536
150 H = .25/FLØAT(N2)
160 N = N2/2
170 N1  =  N - 1
180 PRINT 100
190 DØ 30 I = 1,50
200 P = 10.**((I-20.)/10.)
210 T1 = .25 + H
220 G1 = G(PI*T1,P)
230 S = 4.*G1 -2./(1.+P)
240 DØ 20 J = 1,N1
250 T1 = .25 + H*FLØAT(2*J)
260 G1 = G(PI*T1,P)
270 T2 = .25 + H*FLØAT(2*J+1)
280 G2 = G(PI*T2,P)
290 S = 2.*G1 + 4.*G2 + S
300 20 CØNTINUE
310 SIG = PI*H*S/3.
320 PRINT 110, P, SIG
330 30 CØNTINUE
340 100 F3RMAT(/20X,*P*,28X,*SIG(P)*/)
350 110 FØRMAT(2(10X,E15.8))
360 STØP
370 END
**READY.
                    P                            SIG(P)

          .12589254E-01          -.62942[illegible]58E+00
          .15848932E-01          -.628614[illegible]1E+00
          .19952623E-01          -.627593[illegible]7E+00
          .25118864E-01          -.626314[illegible]0E+00
          .31622777E-01          -.62471582E+00
          .39810717E-01          -.62272017E+00
          .50118723E-01          -.62023444E+00
          .63095734E-01          -.61714676E+00
          .79432823E-01          -.61332375E+00
          .10000000E+00          -.60860916E+00
          .12589254E+00          -.60282379E+00
          .15848932E+00          -.59576615E+00
          .19952623E+00          -.58721[illegible]75E+00
          .25118864E+00          -.57695128E+00
          .31622777E+00          -.56474323E+00
          .39810717E+00          -.55039305E+00
          .50118723E+00          -.53374507E+00
          .63095734E+00          -.51471358E+00
          .79432823E+00          -.49330666E+00
          .10000000E+01          -.46964341E+00
          .12589254E+01          -.44396236E+00
          .15848932E+01          -.41661444E+00
          .19952623E+01          -.38804418E+00
          .25118864E+01          -.35875678E+00
          .31622777E+01          -.32928187E+00
          .39810717E+01          -.30013327E+00
          .50118723E+01          -.27177696E+00
          .63095734E+01          -.24460628E+00
          .79432823E+01          -.21892826E+00
          .10000000E+02          -.19495950E+00
          .12589254E+02          -.17283178E+00
          .15848932E+02          -.15260081E+00
          .19952623E+02          -.13426075E+00
          .25118864E+02          -.11775693E+00
          .31622777E+02          -.10300045E+00
          .39810717E+02          -.89878408E-01
          .50118723E+02          -.78265445E-01
          .63095734E+02          -.68029655E-01
          .79432823E+02          -.59039367E-01
          .10000000E+03          -.51166899E-01
          .12589254E+03          -.44290852E-01
          .15848932E+03          -.38298733E-01
          .19952623E+03          -.33086989E-01
          .25118864E+03          -.28561412E-01
          .31622777E+03          -.24637326E-01
          .39810717E+03          -.21239211E-01
          .50118723E+03          -.18299635E-01
          .63095734E+03          -.15759154E-01
          .79432823E+03          -.13565504E-01
          .10000000E+04          -.11672572E-01
 14.39.41.STØP
 **READY.
 LIST
```

```
DIF283    17.31.23. 03/13/72
10     DIM X(100), Y(100), S4(100)
20     LET N = 51
30     FOR I = 1 TO N
40     READ X(I), Y(I)
50     NEXT I
60     LET PI = 3.1415926536
70     PRINT
80     PRINT "ANGLE(RAD/PI)", "INTEGRAND"
90     PRINT
95     LET L = 0
96     LET P4 = LOG(PI/4.)
97     LET S4(0) = -4.*(.2859-.7141*P4-P4↑2)/PI↑2
98     PRINT L, S4(0)
100    F2R M = 0.01 TO 0.50 STEP 0.01
102    LET L = L + 1
104    IF L = 25 GO TO 230
106    IF L = 50 GO TO 240
111    LET A = M* PI
120    LET X0 = 4*(TAN(A))↑3
130    GOSUB 650
140    LET T1 = COS(A) + SIN(A)
150    LFT T2 = ABS(COS(A)-SIN(A))
160    LET T3 = ABS(TAN(A+0.25*PI))
165    LET T4 = ABS(COS(2.*A))
170    LFT J1 = 2.*(LOG(T3) - SIN(2.*A))
180    LET J2 = LOG(T2)↑2-LOG(T1)↑2+SIN(2.*A)*LOG(T4)
190    LFT D = SIN(A)*COS(A)↑3
200    LET L1 = COS(A)↑3 + 4.*SIN(A)↑3
210    LET S1 = J1*(Y0-(1/3)*LOG(L1)) - J2
220    LFT S2 = S1/(D*PI↑2)
222    LET T5 = LOG(ABS(A-.25*PI))
225    LET S3 = 4.*(.2859-.7141*T5-T5*T5)/PI↑2
227    LFT S4(L) = S2 - S3
228    GO TO 250
230    LFT S4(L) = 0.0
235    GO TO 250
240    LFT S4(L) = 2.*S4(L-1) - S4(L-2)
245    GO TO 250
250    PRINT M, S4(L)
260    NEXT M
270    LET C = S4(0) + 4.*S4(1)
280    FOR J = 1 TO (L-2)/2
290    LET C = 2.*S4(2*J) + 4.*S4(2*J+1) + C
300    NFXT J
310    LET C = .01*PI*(C+S4(L))/3. - 0.8716
320    PRINT "C(LAMBDA) = "C
350    STOP
650    IF X0 >= X(1) GO TO 690
660    LET P = (X0-X(1))/(X(2)-X(1))
670    LET Y0 = (1-P)*Y(1) + P*Y(2)
680    GO TO 760
690    FOR K = 2 TO N
695    IF X0 >= X(K) GO TO 740
710    LET P = (X0-X(K-1))/(X(K)-X(K-1))
720    LET Y0 = (1-P)*Y(K-1) + P*Y(K)
730    GO TO 760
740    NEXT K
750    LET Y0 = -.9868*X0↑(-.642)
760    RETUPN
800    DATA 0.0, -.6326
805    DATA .01259,-.6294,.01585,-.6286,.01995,-.6276
810    DATA .02512,-.6263,.03162,-.6247,.03981,-.6227
815    DATA .05012,-.6202,.06310,-.6171,.07943,-.6133
820    DATA 0.10, -.6086
825    DATA .1259,-.6028,.1585,-.5958,.1995,-.5872
830    DATA .2512,-.5770,.3162,-.5647,.3981,-.5504
835    DATA .5012,-.5337,.6310,-.5147,.7943,-.4933
840    DATA 1.00, -.4696
845    DATA 1.2589,-.4440,1.5849,-.4166,1.9953,-.3880
850    DATA 2.5119,-.3588,3.1623,-.3293,3.9811,-.3001
855    DATA 5.0119,-.2718,6.3096,-.2446,7.9433,-.2189
860    DATA 10.000, -.1950
865    DATA 12.589,-.1728,15.849,-.1526,19.953,-.1343
870    DATA 25.119,-.1178,31.623,-.1030,39.811,-.08986
875    DATA 50.119,-.07827,63.096,-.06803,79.433,-.05904
880    DATA 100.000, -.05117
885    DATA 125.89,-.04429,158.49,-.03830,199.53,-.03309
890    DATA 251.19,-.02856,316.23,-.02464,398.11,-.02124
895    DATA 501.19,-.01830,630.96,-.01576,794.33,-.01167
900    DATA 1000.0, -.01167
999    END
**READY.
```

```
ANGLE(RAD/PI) INTEGRAND

 0             -.162133
 .01           -.165618
 .02           -.168486
 .03           -.170593
 .04           -.171789
 .05           -.171917
 .06           -.170812
 .07           -.168294
 .08           -.164173
 .09           -.158244
 .1            -.150283
 .11           -.140045
 .12           -.127275
 .13           -.1116[illegible]9
 .14           -9.30346E-2
 .15           -7.10009E-2
 .16           -4.53502E-2
 .17           -1.58554E-2
 .18            .01758
 .19            5.47647E-2
 .2             9.48846E-2
 .21            .136435
 .22            .175817
 .23            .204802
 .24            .200509
 .25            0
 .26           -.252907
 .27           -.331934
 .28           -.377598
 .29           -.407413
 .3            -.427891
 .31           -.442116
 .32           -.45243
 .33           -.459595
 .34           -.464047
 .35           -.466359
 .36           -.466996
 .37           -.466243
 .38           -.464514
 .39           -.461997
 .4            -.4586
 .41           -.45453
 .42           -.450147
 .43           -.445387
 .44           -.440381
 .45           -.435251
 .46           -.430174
 .47           -.42518
 .48           -.420376
 .49           -.415882
 .5            -.411388
C(LAMBDA) = -1.24804
**READY.
```

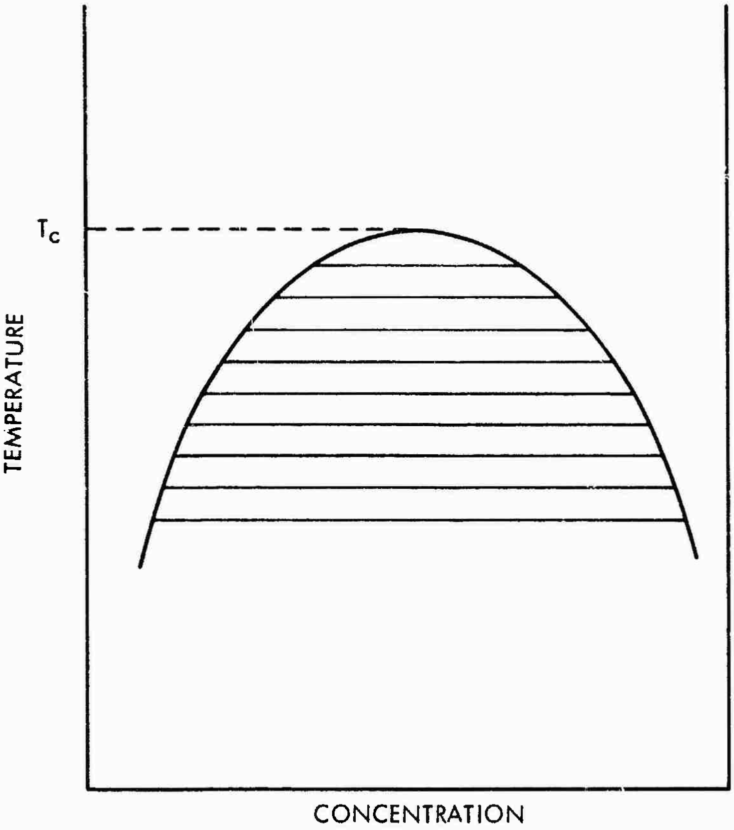

FIG. 1

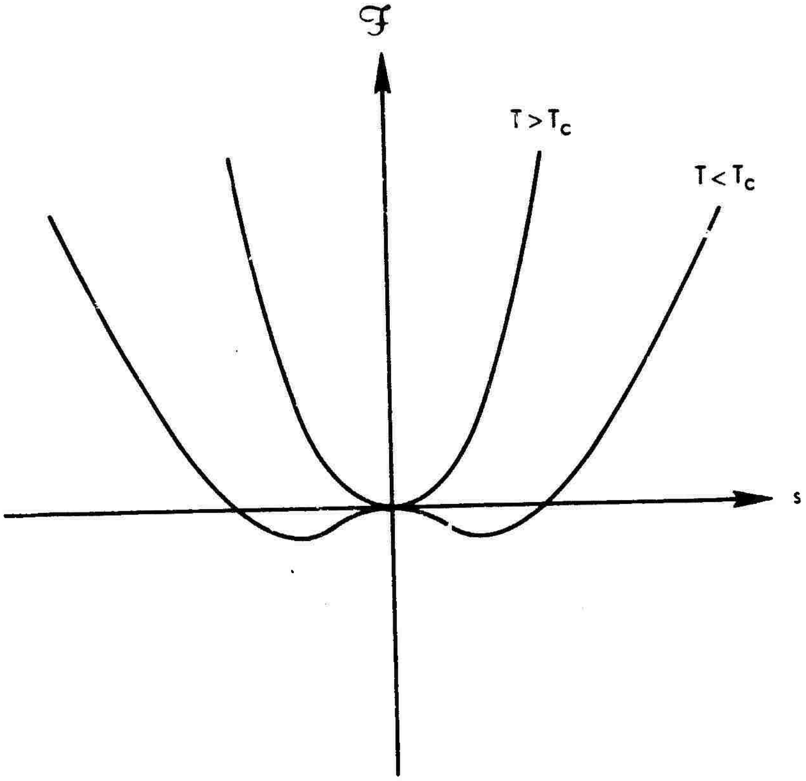

FIG. 2

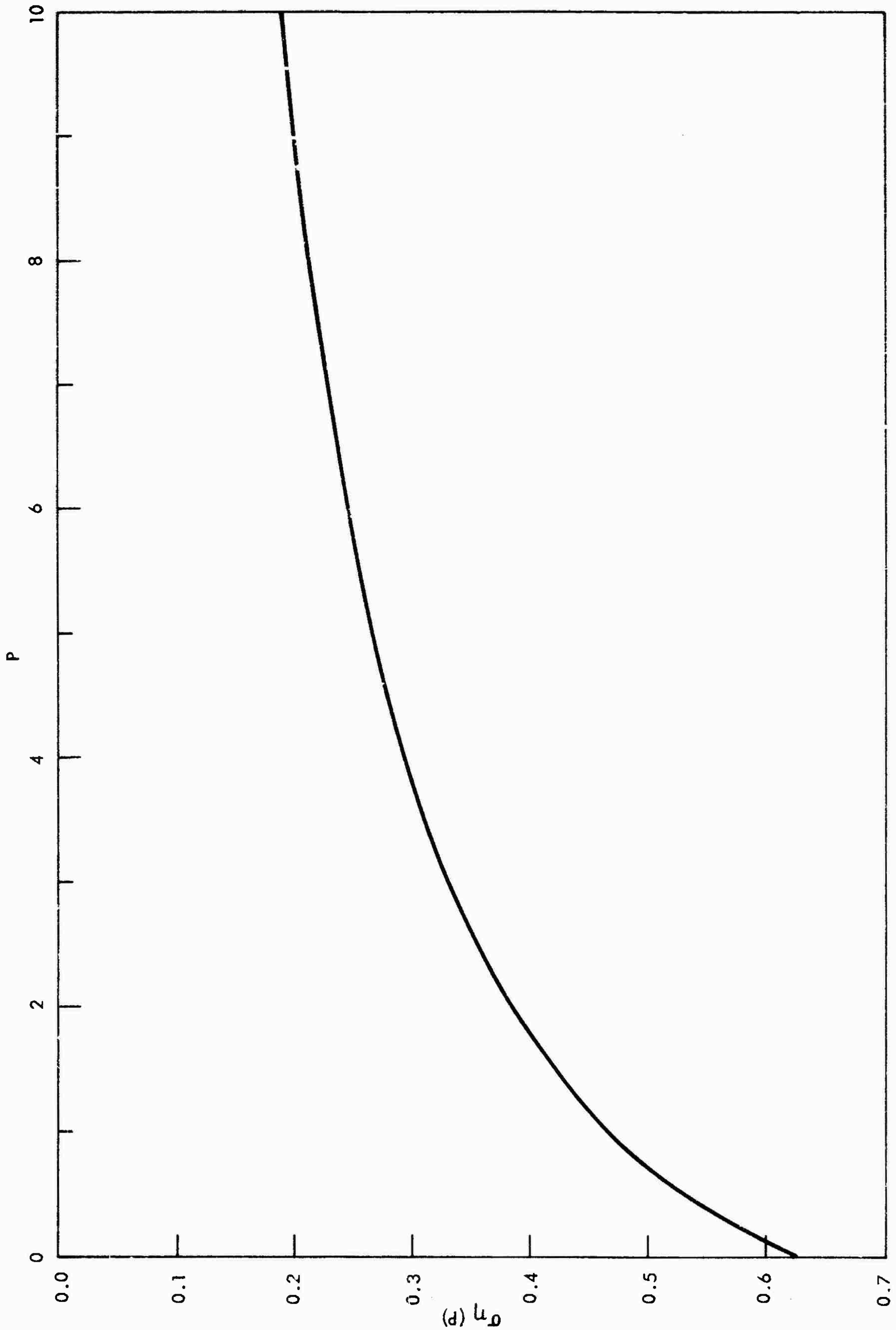

FIG. 3

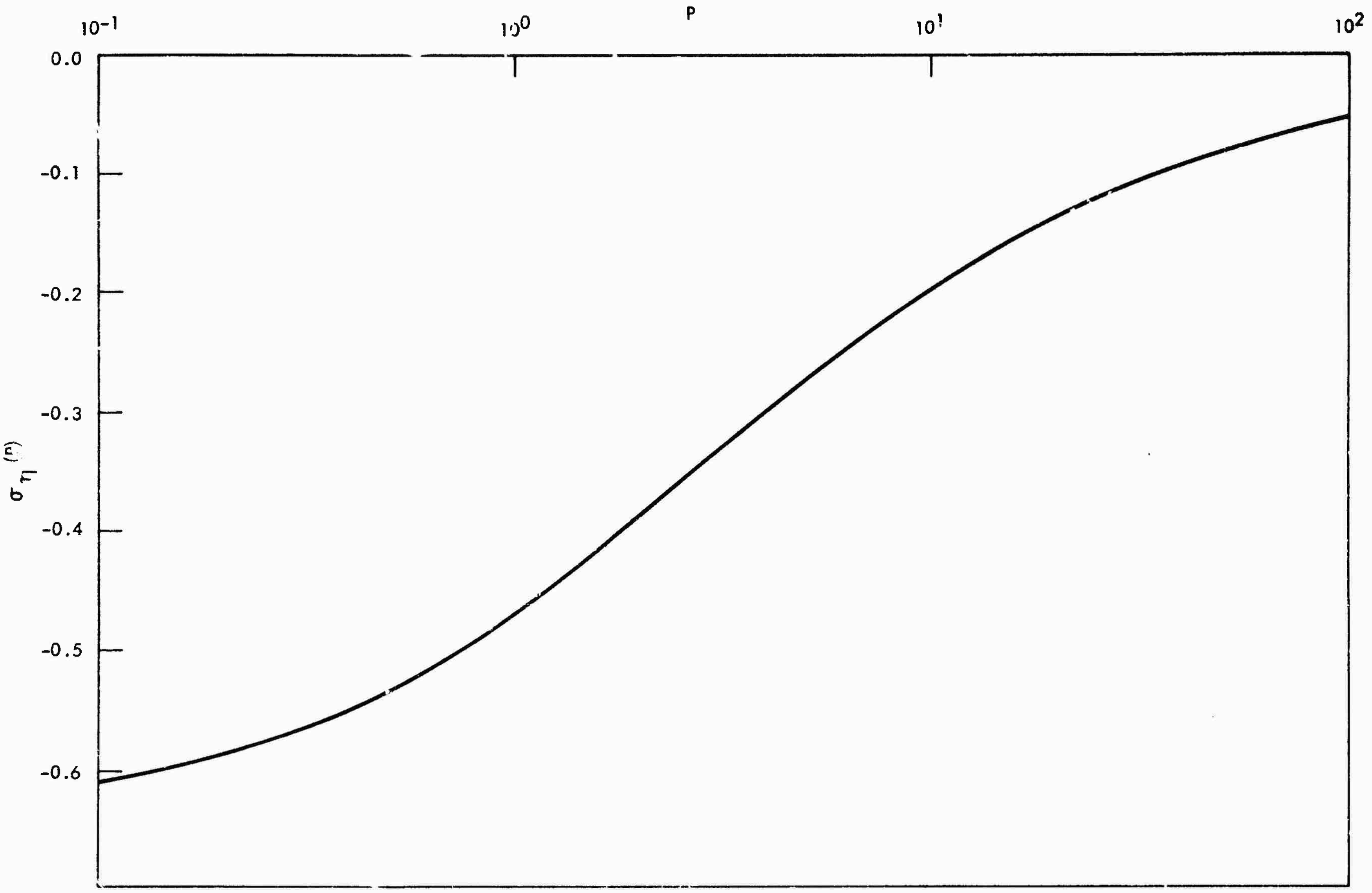

FIG. 4

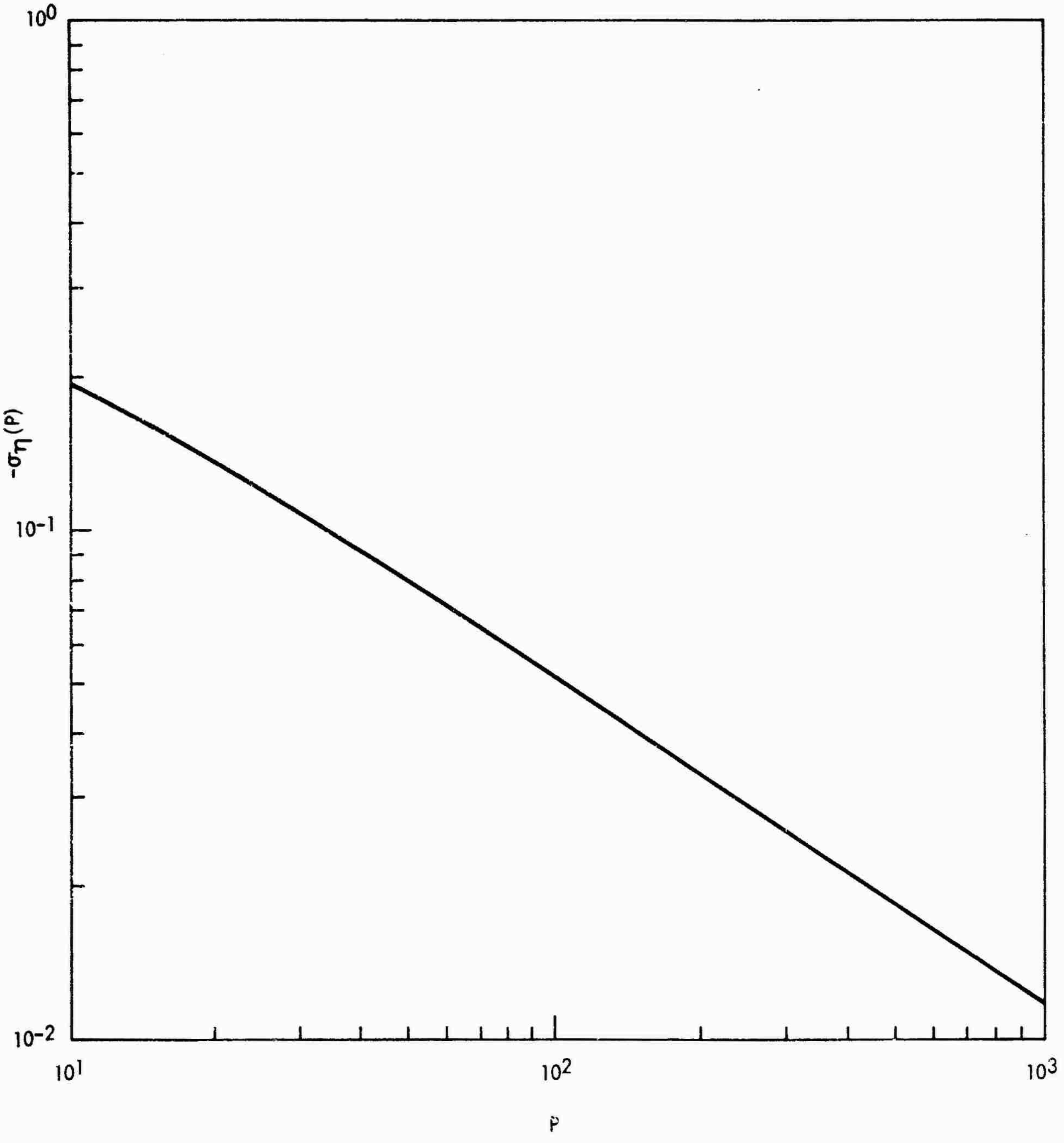

FIG. 5

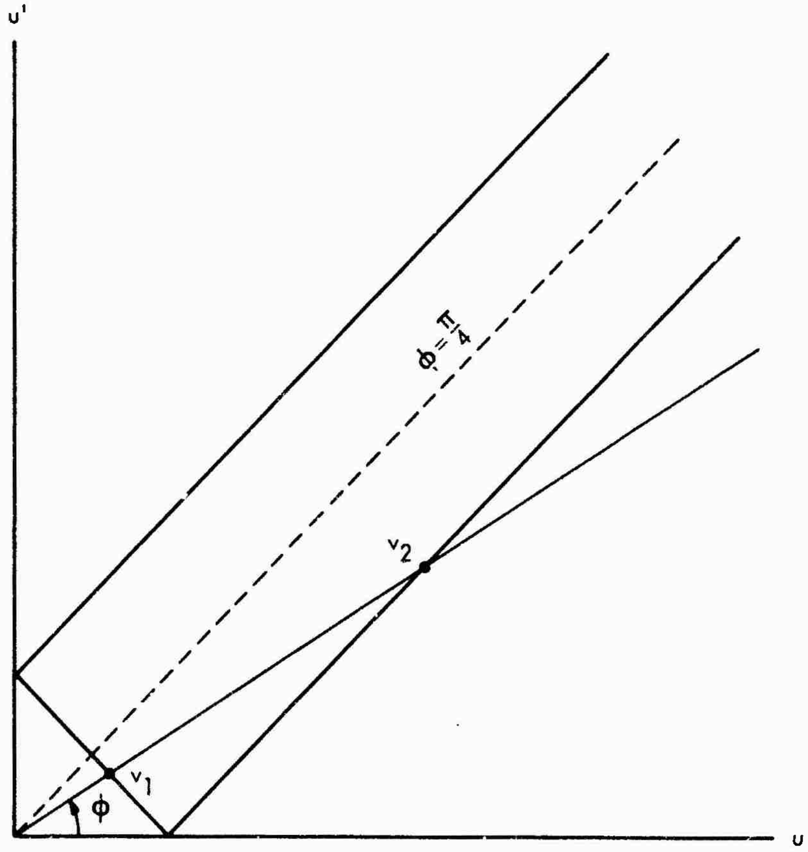

FIG. 6

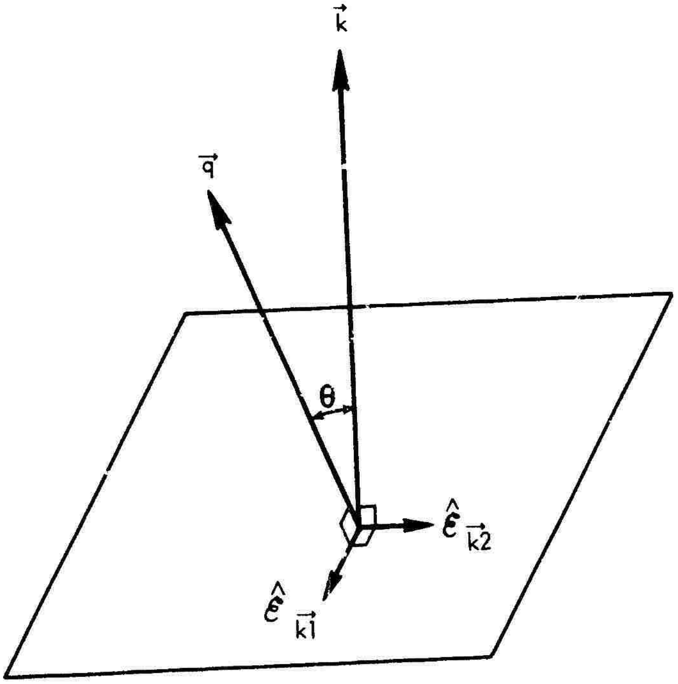

FIG. 7

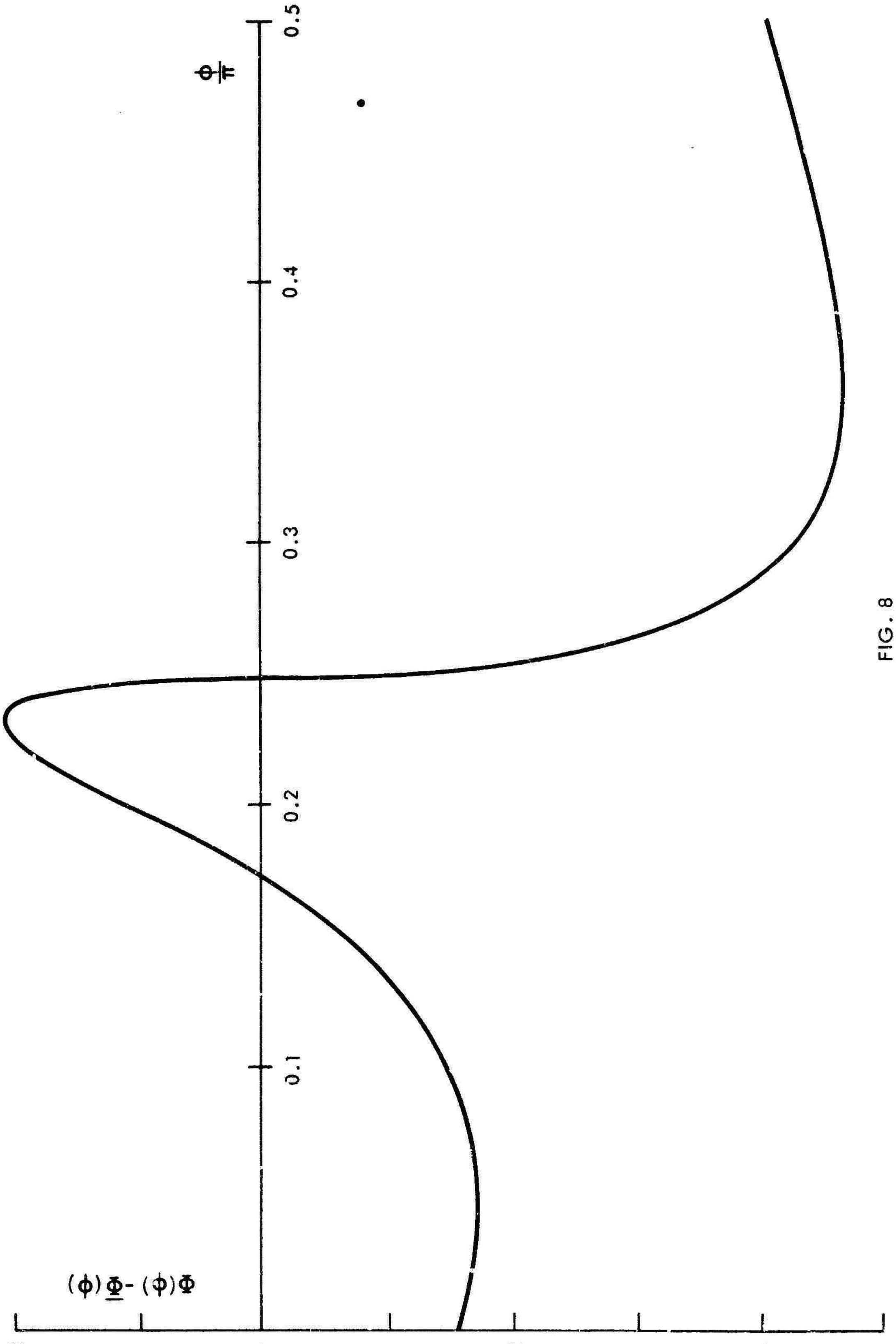

FIG. 8