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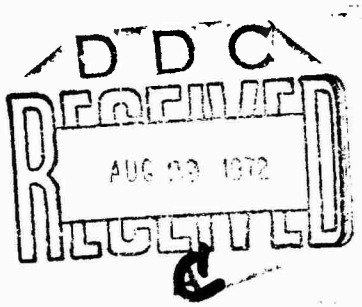

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ABSTRACT

The fluctuation-dissipation formula for the viscosity in terms of the stress tensor fluctuations reproduces the experimental logarithmic temperature dependence of the hydrodynamic viscosity. Using the theoretical wave number and frequency dependent viscosity in the problem of critical diffusion, we find that the effects of non-locality and retardation practically cancel, resulting in satisfactory agreement with a recent light scattering determination of the effective viscosity.

Kawasaki[1] has shown that the critical variation of the diffusion coefficient in a binary liquid near its critical point can be represented by the Einstein relation $D = T\,\mu_\xi$, where T is the temperature (we use natural units such that Boltzmann's constant is unity), ξ is the correlation length for the concentration fluctuations, and $\mu_\xi = (6\pi\eta\xi)^{-1}$ is Stokes' formula for the mobility of a sphere of radius ξ moving through a liquid of viscosity η. This result has also been established by one of the present authors[2] by a different method, and gives the rate of relaxation of a concentration fluctuation of wave number q as

$$\Gamma_q = D\,q^2 = \frac{Tq^2}{6\pi\eta\xi} \quad , \tag{1}$$

provided $\xi \ll q^{-1}$; i.e., the wavelength should be much greater than the correlation length. But as the critical point is approached, $T \to T_c$ and $\xi \to \infty$. The above inequality is then no longer satisfied and D becomes a function of q, corresponding to "non-local" diffusion. This change is carried out in Eq. (1) by substitution of an effective value for ξ^{-1} according to

$$(\xi^{-1})_{eff} = a_{eff} q, \tag{2}$$

where a_{eff} is some numerical constant of order of magnitude unity. Eq. (2) expresses in a quantitative form the qualitative rule of dynamical scaling[3,4] that all temperature dependence is to be expressed in terms of ξ and that as $T \to T_c$ all factors of ξ become

replaced by the wavelength. Actual computation yields $a_{eff} = 3\pi/8$ so that in the limit $T \to T_c$ we obtain

$$\Gamma_q^c = \frac{Tq^3}{16\eta_{eff}(q)} \tag{3}$$

In Eq. (3) we have allowed for the fact that recent experiments[5,6] have clearly established a critical temperature dependence in the hydrodynamic viscosity η. It, therefore, as well as the explicit factor ξ^{-1}, has to assume a q-dependent effective value, which we denote by $\eta_{eff}(q)$. The purpose of the present note is to compare our calculation of this function with some measurements of Γ_q^c recently carried out in this laboratory.[7] As the theory is rather involved, we prefer to present our results in a semiphenomenological fashion, touching only the main points of the calculation at the end. Proceeding in this spirit we first take note of the separation[8] of the hydrodynamical viscosity into an "ideal," non-critical background η_{id} and a residual critical portion $\Delta\eta$. An accurate empirical fit[8] to the ratio of the critical portion to the total as a function of ξ^{-1} for the binary liquid 3-methylpentane-nitroethane is

$$\frac{\Delta\eta(\xi^{-1})}{\eta(\xi^{-1})} = A \ln (q_D \xi), \tag{4}$$

where $A = 0.051$. The correlation length is known from light scattering intensity measurements[7] to have the temperature dependence

$(\xi/\xi_o) = (T-T_c/T_c)^{-\nu}$ with $\xi_o = 2.56\mathring{A}$ and $\nu = 0.616$. Now substituting from Eq. (2) and denoting the numerical factor by a_{eff}^{visc}, we obtain at the critical point

$$\frac{\eta_{eff}(q)-\eta_{id}}{\eta_{eff}(q)} = A(\ln \frac{q_D}{q} - \ln a_{eff}^{visc}) \qquad (5)$$

The fact that the functional dependence is logarithmic permits us to consider the case that the logarithm is very large. The constant term can then be neglected. To this "logarithmic accuracy," we expect the fractional critical viscosity which is effective in the diffusion process to be precisely the same function of q that the hydrodynamic viscosity is of ξ^{-1}. This function is plotted as the solid line in Fig. 1. The values of $\eta_{eff}(q)$ determined experimentally from line widths are shown as circles. The parallel dashed line illustrates better-than-logarithmic accuracy for $a_{eff}^{visc} = 2^{-1}$, which would follow from an incomplete theoretical treatment, as explained below. This line serves to indicate the sensitivity of the logarithmic approximation to a_{eff}^{visc}. It is evident in Fig. 1 that for the theory to agree with the data the computed value of a_{eff}^{visc} should not be significantly smaller than unity. The remainder of this note is devoted to establishing that this is, indeed, the outcome. In fact, we find from a complete theoretical treatment (i.e., one taking into account both the wave number and the frequency dependence of the viscosity) $a_{eff}^{visc} = 0.92$. This is so close to unity that there is no

need to draw an additional line. We can regard the hydrodynamic function (a = 1.00) as a sufficiently accurate representation of the theoretical effective viscosity and we see from Fig. 1 that it is consistent with the experimental finding $a_{eff}^{visc}(EXP) = 2\pm1$.

In order to achieve better-than-logarithmic accuracy, we need a theory of critical viscosity for calculating a_{eff}^{visc}. Such a theory has been proposed by Kawasaki[9] and by Deutch and Zwanzig[10]. We have followed the latter approach, which is based on the fluctuation-dissipation theorem[11,12] connecting the viscosity with fluctuations in the off-diagonal components of the stress tensor. In this way we have obtained an expression[13] of precisely the form of Eq. (4) with a theoretical value for the coefficient[14] A equal to $8/15\pi^2 = 0.054$, in close agreement with the experimental value 0.051. (The Debye cutoff q_D is a free parameter in the theory and is to be fixed by taking it equal to the experimental value.) The fluctuation-dissipation theorem expresses the wave number and frequency-dependent viscosity as a four-dimensional space-time Fourier integral over the correlation function of fluctuations in the off-diagonal component T_{xy} of the stress tensor. (x and y are particular Cartesian coordinates.) It is more convenient, however, to treat the time dependence by the Laplace transform, in which we write the "frequency" as Γ_q^c times the dimensionless variable γ^3. Thus the generalized viscosity is

$$\eta(q,\gamma) = \frac{1}{2T} \int d^4 21 \, e^{i\, q\cdot x_{21} - \Gamma_q^c \gamma^3 |t_{21}|} \langle T_{xy}(2)\, T_{xy}(1)\rangle, \qquad (6)$$

where the integration is over all of space-time, $\underset{\sim}{q}$ is in the y-direction, and the angular brackets denote the thermal equilibrium average. We are interested in the critical fluctuations in T_{xy}, which are given by the canonical expression[15]

$$T_{xy} = s_x \frac{\partial F}{\partial s_y} = Z^{-1} s_x s_y, \tag{7}$$

where the Landau-Ginzburg free energy density depends quadratically on the partial derivations of the concentration $s_{x,y}$ thrcugh the gradient term $(\nabla s)^2/2Z$. Inserting Eq. (7) into Eq. (6) and factoring the ensemble average in terms of the concentration correlation function

$$G(21) = \langle s(2)\, s(1) \rangle = (2\pi)^{-3} \int d^3q\, e^{i\, \underset{\sim}{q}\cdot\underset{\sim}{x}_{21} - \Gamma_q^c |t_{21}|} g(q) \tag{8}$$

enables us to carry out the integration in terms of the Fourier transform

$$g(q) = \frac{ZT}{q^2} \quad . \tag{9}$$

Substituting Eq. (7) into Eq. (6) and factoring the fluctuating concentration variables into pairs we find for the critical viscosity, after a certain amount of manipulation,

$$\Delta\eta(q,\gamma) = \frac{(Z^2T)^{-1}}{64\pi^2 q^5} \quad X$$

$$\iint dq_1 dq_2 q_1 q_2 \frac{g(q_1)g(q_2)(q_1^2-q_2^2)^2}{\Gamma^c_{q_1}+\Gamma^c_{q_2}+\Gamma^c_q\gamma^3}[2q^2(q_1^2+q_2^2)-q^4-(q_1^2-q_2^2)^2]$$

$$q_1+q_2\geq q$$
$$|q_1-q_2|\leq q$$
$$q_{1,2}\leq q_c$$

$$= \frac{Tq^3}{64\pi^2\Gamma^c_q} \iint \frac{du_1 du_2}{u_1 u_2} \frac{(u_1^2-u_2^2)^2}{u_1^3+u_2^3+\gamma^3}[2(u_1^2+u_2^2)-1-(u_1^2-u_2^2)^2]$$

$$u_1+u_2\geq 1$$
$$|u_1-u_2|\leq 1$$
$$u_{1,2}\leq q_c/q \qquad (10)$$

The cutoff q_c is proportional to the Debye cutoff q_D. The static case $\gamma = 0$ can be integrated analytically and yields

$$\frac{\Delta\eta(q,o)}{\eta_{eff}(q)} = \frac{8}{15\pi^2}\left(\ln\frac{q_c}{q} + \frac{13}{15} - \frac{4\pi}{9\sqrt{3}}\right) = \frac{8}{15\pi^2}\left(\ln\frac{q_c}{q} + 0.062\right). \qquad (11)$$

Eq. (10) has been written for the special case $\xi^{-1}=0$. Finite values of ξ require correction factors $[1+(q\xi)^{-2}]^{-1}$ and $[1+(q\xi)^{-2}]^{1/2}$ in $g(q)$ and Γ_q, respectively.[16] Comparison of the result for the $q = 0$, $\xi^{-1}>0$ hydrodynamic case with the $q>0$, $\xi^{-1}=0$ non-local case gives, in the language of Eq. (2)

$$a^{N.L.}_{eff} = 2\exp\left(\frac{4\pi}{9\sqrt{3}} - \frac{11}{5}\right) = 0.496. \qquad (12)$$

If we were to assume that the frequency dependence of the viscosity could be neglected in the critical diffusion process, we would have

the approximation $a_{eff}^{visc} \simeq a_{eff}^{N.L.}$. This approximation is depicted by the dashed line labelled "N.L." in Fig. 1. It is interesting to note that Eq. (12) confirms the general rule of thumb[17] that when the factorization brings in the correlation length twice (via the equal-time Green's function), $a_{eff} \simeq 1/2$.

But Eq. (12) cannot directly be applied to the diffusion problem because it is applicable only in the static limit. The approximation $a_{eff}^{visc} \simeq a_{eff}^{N.L.}$ is too crude, as the diffusion process depends upon the relaxation of current fluctuations, which are the product of concentration and velocity fluctuations. Because of the finite concentration relaxation rate we are forced to study viscuous damping of the velocity field at non-zero frequencies. This results in a kind of "retardation" correction to the critical viscosity which leads to a decrease in the effective viscosity. Our final task is the computation of this decrease, which entails the use of Eq. (10) at all frequencies γ[3]. We define a dynamical scaling function $\sigma(\gamma)$ by

$$\frac{\eta(q,\gamma)-\eta(q,o)}{\eta_{eff}(q)} = \frac{8}{15\pi^2}\,\sigma(\gamma). \tag{13}$$

For $0<\gamma<<1, \sigma(\gamma) = -0.316\gamma^3$, while for $\gamma>>1$ we have the high frequency approximation

$$\sigma(\gamma) = \ln\frac{2^{1/3}}{\gamma} - \frac{\pi/3}{\sin(\pi/3)}(2^{2/3}\gamma)^{-2} - \frac{13}{15} + \frac{2\pi/3}{3\sin(\pi/3)}$$

$$= 0.169 - \ln\gamma - 0.479\gamma^{-2} \tag{14}$$

We have confirmed by numerical computation that the above low and high frequency approximations are, in fact, very accurate for $\gamma<0.5$ and $\gamma>1.5$, respectively. Interpolation through the region $\gamma\simeq1$ yields a smooth negative-definite monotonic curve. Therefore, the effect of retardation is necessarily to decrease the logarithmic divergence by a weighted mean[15], $\sigma_{AVE}<0$. To determine σ_{AVE} we expanded the reciprocal of the viscosity, which appears in the time-dependent velocity correlation function, in powers of the critical portion $\Delta\eta$, and worked to first order in $\Delta\eta$. The resulting two-dimensional integral over the wave numbers of the concentration and velocity fluctuations can be reduced analytically to quadrature in terms of their ratio γ. Using the values of $\sigma(\gamma)$ obtained as described above, and carrying out this integration numerically, we have found $\sigma_{AVE} = -0.62$, corresponding to

$$a_{eff}^{visc} = a_{eff}^{N.L.}\, e^{-\sigma_{AVE}} = 0.92. \qquad (15)$$

As mentioned above, this is in satisfactory agreement with the experimental value a_{eff}^{visc} (EXP) = 2±1. The fact that this coefficient comes out so close to unity is a consequence of two competing physical effects, namely the non-locality and the retardation.

A further outcome of the theory, which we mention only in passing, is that the retardation produces some non-Lorentzian distortion[15] in the diffusion line shapes which may, however, be too weak an effect to detect experimentally. Finally, it is a pleasure to acknowledge a stimulating conversation with Professor L. Kadanoff and many helpful discussions with R.F. Chang, P.H. Keyes, J.V. Sengers, and C.O. Alley.

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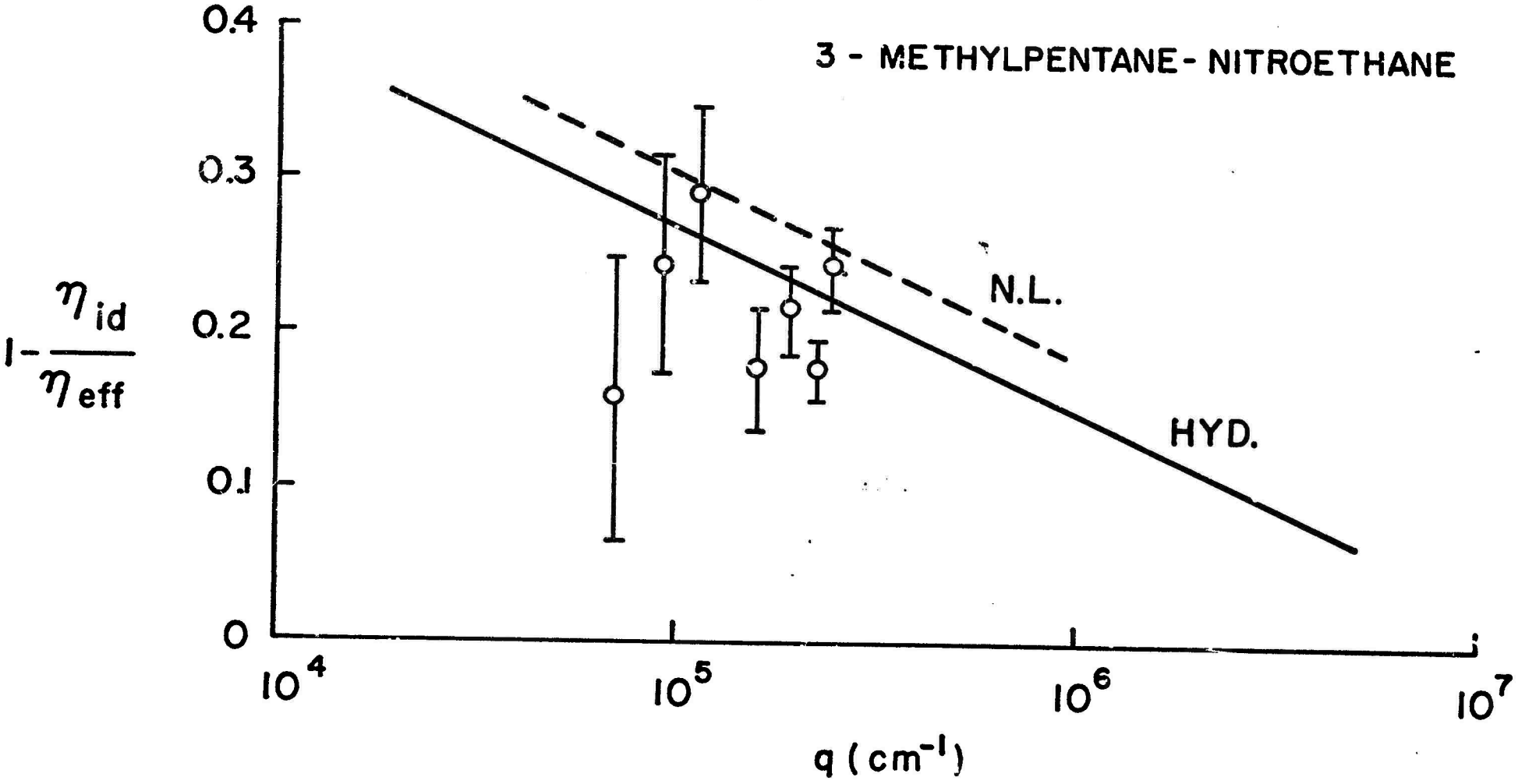
CAPTIONS FOR THE FIGURES

Fig. 1 Fractional critical viscosity vs. wave number. The solid line labelled "HYD." represents the experimental logarithmic dependence of the hydrodynamic viscosity upon the inverse correlation length (references 5 and 6). The dashed line labelled "N.L." shows the static non-local correction for the theoretically computed value of $a_{N.L.} = 0.496$. This would be the result for a crude theory which did not include retardation. In the complete theory the correction for retardation cancels the effect of static non-locality and brings the theory back down to the solid line. Thus the solid line represents both the hydrodynamic viscosity and the theoretically expected effective viscosity. This line is in satisfactory agreement with the circles, which show the light scattering line widths measured by Chang, Keyes, Sengers, and Alley (reference 7).


3 - METHYLPENTANE - NITROETHANE
N.L.
HYD.
0.4
0.3
0.2
0.1
0
$1-\frac{\eta_{id}}{\eta_{eff}}$
10^4
10^5
10^6
10^7
q (cm^{-1})