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LETTER

Basic theory and some applications concerning the ratio of shear viscosity to entropy density in dense fluids

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Much interest continues relating to the conjecture from string theory of an inequality satisfied by the ratio η/s in dense fluids, where η is the shear viscosity and s the entropy density. First, we summarise the models which have prompted the proposal of the inequality. Second, we consider a model equation of state which may be appropriate for the dense fluids NH_3 and H_2O , both of which satisfy the inequality.

Keywords: dense fluids; equation of state; string theory

1. Background and outlines

In a recent study, the present authors have discussed, with examples of monatomic insulating liquids like argon, and metallic fluids, in particular the alkali metals [1] and the proposed lower bound for the ratio η/s [2,3]. Here, η denotes the shear viscosity, while s is the entropy density.

Because of the continuing fundamental interest in this ratio, the present Letter begins by summarising recent fundamental theoretical predictions beyond those referred to in [1]. Then, following this, we shall consider a model equation of state going back to a proposal by Chapman and March [4], which we shall bring into contact with [1] in relation to results presented there for the number density ρ versus temperature T under isobaric conditions for the dense fluids H_2O and NH_3 .

2. Fundamental examples on ratio η/s : mainly from relativistic quantum field string theory methods

In [1], we gave special attention to the theoretical study of Kovtun *et al.* [2] and also to that of Schäfer [3]. A very recent contribution by Evans and Threlfall [5] has provided some motivation for this further contribution on the ratio η/s discussed at some length in [1]. Their work studies the thermal phase transition in a quantum-chromodynamics (QCD)

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like holographic model. Near the conclusion of their article [5], they refer specifically to the study of Policastro et al. [6] in relation to the proposed lower bound result

$$
\frac{\eta}{s} \ge \frac{\hbar}{4\pi k_{\rm B}},\tag{1}
$$

where h and k_B denote the constants of Planck and Boltzmann, respectively. Policastro et al. [6] (see also the review by Son and Starinets [7]) refer to cases where the equality sign in Equation (1) applies, and note especially that such strict equality applies to certain nonsupersymmetric theories in their deconfined phase.

In this same context, Son [8] has very recently discussed hydrodynamics and gau ge/gravity duality. In particular, Son [8] reviews recent applications of this duality to finitetemperature quantum field theory. In this review, the authors set out the way the shear viscosity η can be calculated from gravity duals. Son asserts, from the results in [7] that Equation (1) is true for all theories with Einstein gravity duals. Son [8] then notes that within kinetic theory, the ratio η/s is proportional to the ratio of the mean free path and the de Broglie wavelength of the quasiparticles. Thus it then follows that in theories with gravity duals the mean free path is of the same order as the de Broglie wavelength. A further relevant reference relating to the equality sign in Equation (1) is the study of Janik [9].

It is also relevant here to emphasize two further fairly recent basic contributions in relation to Equation (1) [10,11,12]. There, results are given which bear on the inequality in Equation (1). These results have some relation to Figure 2(a) in [1] including dense liquids H2O and NH3, and prompt us to pass to the second part of this Letter, which proposes a model equation of state for these two fluids.

We note, to conclude this part of the present Letter, that very recently Kovtun and Nickel [13] have proved, in treating black holes and non-relativistic quantum systems, that the ratio of shear viscosity to entropy density is $\hbar/4\pi k_B$ in the dual theory they present for a whole range of dimensionality.

3. Model equation of state in relation to number density *versus* temperature in H_2O and $NH₃$

Whereas there are fundamental examples now, as cited above, for the equality sign in Equation (1), for H₂O and NH₃ it is the inequality for η/s that is appropriate, as is evident from Figure 2(a) in [1]. Our focus below will be on the shape of the entropy density versus T curves for H₂O and NH₃ depicted in Figure 2(b) in [1]. We shall argue below that the shape of these curves is critically dependent on the form of the number density ρ versus temperature T, under isobaric conditions. While these curves are known from experiment, our purpose below is to attempt to construct a model equation of state, which can be parametrised to give at least a semiquantitative fit of the experimental ρ -T curves for the dense fluids H_2O and NH_3 . To do so, we appeal to a proposal made some time ago by Chapman and March [4]. In their study, it was emphasised that flexibility in the so-called critical compressibility ratio Z_c , defined by

$$
Z_c = \frac{p_c V_c}{RT_c},\tag{2}
$$

was important in monatomic liquids. Therefore Chapman and March [4] studied the so-called pressure co-efficent v_V defined by

$$
\gamma_V = \left(\frac{\partial P}{\partial T}\right)_V.
$$
\n(3)

This they proposed to write in the form

$$
\frac{1}{\gamma_V} = \left(\frac{V - \alpha V_c}{R}\right) g(T^*, V^*),\tag{4}
$$

where $T^* = T/T_c$, $V^* = V/V_c$. In particular, it was stressed in [4] that $g = 1$ for the original van der Waals equation.

In [4], the focus was on the alkali metals, for which it was found that Equation (4) was useful, with $g(T^*, V^*)$ a slowly varying function of its arguments. In particular for these liquid metals it was found in [4] that $g = 1.2$, whereas values of α in Equation (4) were found to range from 0.12 to 0.16 through the alkali series.

However, when these findings for the alkali metals are compared with, say, the insulating liquid argon, significantly more curvature of γ_V^{-1} versus molar volume was revealed as well as a larger departure of g from unity.

Further, as already mentioned, we shall explore the usefulness of the form given in Equation (4) for the dense insulating molecular liquids H_2O and NH_3 , which are isoelectronic with the insulating liquid Ne. For these liquids H_2O and NH_3 , we reproduce the results in [1] in Figure 1(a) for the number density $\rho_N = N/V$ as a function of temperature for a constant pressure $P = 100 \text{ MPa}$.

We next return to the derivative γ_V above and note that for a quite general equation of state we can write

$$
\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1\tag{5}
$$

or

$$
\gamma_V^{-1} = -\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T.
$$
\n(6)

We are interested, as stressed above, in $(\partial V/\partial T)_P$, which in turn is related to the isothermal compressibility κ_T defined by

$$
\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T.
$$
\n(7)

Substituting Equation (7) into Equation (6), we immediately find

$$
\left(\frac{\partial V}{\partial T}\right)_P = \gamma_V \kappa_T V. \tag{8}
$$

Using Equation (4) for γ_V in Equation (8) evidently yields the result

$$
\left(\frac{\partial V}{\partial T}\right)_P = \frac{R\kappa_T V}{(V - \alpha V_c)g(T^*, V^*)}.
$$
\n(9)

Figure 1. (a) Scaled number density $V_c\rho_N$ vs. scaled temperature T/T_c under isobaric conditions $(P = 100 \text{ MPa})$ for H₂O and NH₃ (redrawn after [1].) (b) Scaled function g for H₂O and NH₃, constructed using Equation (9) and data in Figure 1(a); different curves refer to $\alpha = 0.1 - 0.2$. (c) Unscaled function g for H₂O, with $\kappa_T \approx 3.5 \cdot 10^{10}$ Pa⁻¹ [16].

Table 1. Critical constants for fluid H_2O and NH_3 (taken from [14]).

Fluid	T_c (K)	P_c (atm)	V_c (cm ³ mol ⁻¹)
H_2O	647	218	55.4
NH ₃	406	112	72.0
Ne	44.7	26.9	44.3

Returning to the experimental data for $\rho_N(T)$ versus T in Figure 1(a), we extract the way the function g entering Equations (4) and (9) depends on the choice of the parameter α . This dependence is exhibited in Figure 1(b). We remind the reader that in the van der Waals model equation of state, $g = 1$. We have collected what is known about the critical constants T_c , P_c and V_c for fluid H₂O and NH₃ in Table 1, Ne being included for purposes of comparison.

We note from Figure 1(b) that certainly the dimensionless function g for H_2O , for which the isothermal compressibility κ_T is insensitive to temperature at 100 MPa, varies rather strongly with T/T_c . Figure 1(c) shows g versus T/T_c over the same temperature range. The (van der Waals) value $g = 1$ occurs around $T/T_c \sim 1$, with some spread due to the variation of $\alpha = 0.1 \div 0.2$. Unfortunately, for NH₃, the isothermal compressibility is only measured [15] at pressures up to $17 MPa$, so we cannot presently add $NH₃$ to Figure 1(c).

In summary, we have discussed basic theory of the ratio η/s . For a wide range of models related to relativistic quantum field string theory, the quantity in Equation (1) is by now established. Applications to H_2O and NH_3 show that the inequality sign is validated. In Equation (9), g is exhibited for H₂O as a function of T/T_c and varies appreciably. With this variation, the general shape of the number density of H_2O as a function of temperature required to correctly lead to the entropy density s in [1] is reproduced by the Chapman– March equation of state.

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