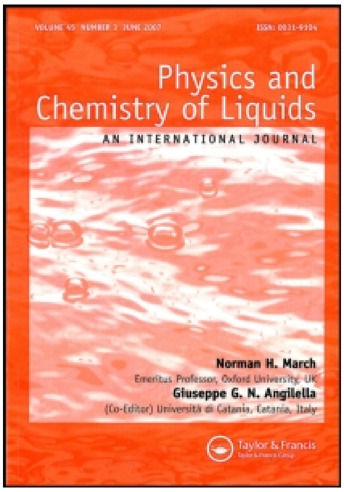

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An Equation for Viscosity and Isothermal Compressibility of Simple Liquids from a Closed-Form Expression for the Effective Viscosity of a Dispersed System

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AN EQUATION FOR VISCOSITY AND ISOTHERMAL COMPRESSIBILITY OF SIMPLE LIQUIDS FROM A CLOSED-FORM EXPRESSION FOR THE EFFECTIVE VISCOSITY OF A DISPERSED SYSTEM

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Viscosity and isothermal compressibility of a simple liquid have been related by means of a closed-form equation for the low-shear viscosity of a liquid dispersion of solid particles. It involves macroscopic density, total correlation function and free volume. The equation achieved, which does not have an explicit solution, was approximated and applied to two sets of experimental data, where the free volume contribution was evaluated on the basis of experimental values of either volumes at zero fluidity or force constants for second virial coefficients and pair interaction potentials.

Keywords: Compressibility; Viscosity; Simple liquid; Liquid dispersion

INTRODUCTION

Isothermal compressibility (κ_T) and shear viscosity (η) are among the fundamental properties of matter [1,2]. Particularly, their importance is still remarkable in the wide field represented by chemical physics of liquids, liquid metals and amorphous media [3-6]. We only recall that, basically, the first can be derived from the state equation of a substance, and expresses how much the volume decreases as an external pressure is applied at constant temperature [7]. The second is a

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measure of the extent to which forces in a fluid can be carried up to neighbouring positions, and identifies the phenomenological coefficient in the balance equation for momentum transport, as stated by thermodynamics of irreversible processes [8].

Calculating compressibility and viscosity in liquid media has a long history in both cases. Briefly, to determine κ_T, one can use the Ornstein-Zernike relation (see next Eq. (4)), which involves the total correlation function (h) [1]. On the other hand, although modelling viscous features of a liquid-like medium has been dealt with extensively, it still represents a challenging task, particularly when dispersions of solid particles and/or macromolecules are considered (see, for instance, Ref. [9]). In simple liquids, one can start from the state equation or taking advantage of several semiexact laws (for an excellent summary, see Ref. [10]). It is worth recalling that viscosity (or fluidity) of compressed gases and liquids is always depending upon the crowding degree of molecules, their capability to absorb the vector momentum applied to produce flow (due to softness, flexibility and rotational inertia), and on the resistance to the vector momentum offered by the randomly oriented thermal momenta [11].

In a recent work [12], the specific low-shear viscosity (η_{SP}) of a liquid suspension of solid particles was described in terms of a closed form relation for the total correlation function (see next Eq. (1)). It provides with the solid fraction contribution (ϕ) to the actual viscosity (η) of a dispersion in a liquid that is intrinsically viscous (η_0). Such a theory returns the well-known Einstein formula [13], Saito and Bruggeman equations for the effective viscosity [9, 14], and was satisfactorily applied to concentrated suspensions of either hard-spheres or interacting units.

In the present paper, viscosity and compressibility of a simple liquid are related through a comparison between state equation and the expression previously derived. As the current literature does not report systematic experimental investigations on the compressibility behaviour of suspensions (except from a limited number of cases, see for instance Ref. [15]), we will concentrate ourselves on simple liquids. Conceptually, we compare κ_T and η through free volume variations, and derive a phenomenological law which fits quite satisfactorily experimental data belonging to a wide class of liquid systems.

THEORY

The equation proposed to get the specific low-shear viscosity ($\eta_{SP} = (\eta/\eta_0) - 1$) of a suspension reads [12]:

$$\eta_{SP} = [\eta]\left(\bar{\rho}\int h(\underline{\varrho})\frac{\phi^{|\varrho|}}{1-\bar{\phi}^{|\varrho|}}d\underline{\varrho} + \frac{\phi}{1-\bar{\phi}}\right) \tag{1}$$

where the integral on the right sums over the spatial position, *i.e.*, $\underline{\varrho} = (r, \vartheta, \varphi)$, $[\eta]$ is the intrinsic viscosity, $\bar{\rho}$ is the macroscopic density, $h = h(\underline{\varrho})$ is the total correlation function, $\bar{\phi} = (\phi/\phi_M)$ denotes the ratio between actual and maximum solid volume fractions, and $|\varrho| = (\varrho/a)$ the radial coordinate in a unit of correlation length a. The physical meaning of Eq. (1) was exhaustively illustrated in Ref. [12].

In this paper, by relating ϕ to the volume occupied by the molecules themselves, Eq. (1) is applied to a simple liquid. To proceed, let us to consider the relative viscosity concept ($\eta_r = \eta_{SP} + 1$), accounting also for the bulk phase contribution:

$$\eta^* = 1 + \bar{\rho}\int h(\underline{\varrho})\Phi_v(\underline{\varrho})d\underline{\varrho} + \Phi_v(1) \tag{2}$$

with $\eta^* = (\eta_r/[\eta])$ and $\Phi_v(\underline{\varrho}) = (\phi^{|\varrho|}/1 - \bar{\phi}^{|\varrho|})$. It is interesting to note that Eq. (2) resembles the structure of an analytical state equation recently obtained from statistical mechanics [16]:

$$\frac{P}{\bar{\rho}k_BT} = 1 + B\bar{\rho} + \alpha\bar{\rho}h(d) \tag{3}$$

where P is the pressure, B is the second virial coefficient, α is a scaling factor that takes into account the softness of the particle repulsion, and $h(d)$ is the total correlation function at contact for hard spheres of diameter d (in our case, see $\Phi_v(1)$, when $a = d$). Letting k_BT be the usual thermal Boltzmann energy, the compressibility equation is [1]:

$$\bar{\rho}k_BT\kappa_T = 1 + \bar{\rho}\int h(\underline{\varrho})d\underline{\varrho} \tag{4}$$

so that, adding and subtracting h to the integrand in Eq. (2) leads to the following non-dimensional relation:

$$\eta^* = \bar{\rho}\left(k_B T \kappa_T + \int h(\varrho)(\Phi_v(\varrho) - 1)d\underline{\varrho}\right) + \Phi_v(1) \tag{5}$$

When a perfect gas system is considered, $\bar{\rho} \to 0$, the second ($h \to 0$) [3] and the third ($\phi \to 0$) contributions on the right vanishes, whereas one has $P \to \bar{\rho} k_B T$, $\kappa_T \to (1/P)$ [7]. Consistently, it turns out $\eta^* \simeq 1$, provided $[\eta]\eta_0$ identifies the contribution of the gaseous phase. In the following section, Eq. (5) will be applied in the form of a heuristic law to several simple liquid systems.

RESULTS AND DISCUSSION

Equation (5) gives a relation for the viscosity of a simple liquid, depending on compressibility and two additional contributions, coming from the first and all other peaks of the total correlation function. An interesting comparison can be done with the law due to Hildebrand [17]. He investigated the relation among fluidity φ, intrinsic volume V_0 (*i.e.*, the volume at zero fluidity) and free volume $V_F = V - V_0$, obtaining that:

$$\varphi \propto \frac{V_F}{V_0} \tag{6}$$

Therefore, since $\eta = (1/\varphi)$, setting the volume fraction to $\phi = (V_0/V)$ enables us to rewrite Eq. (6) as:

$$\eta \propto \frac{\phi}{1 - \phi} \tag{7}$$

namely, the volume fraction contribution associated with particles at contact, (*i.e.*, see the right side of Eqs. (1), (5)). Unfortunately, the integral to work out in Eq. (5), does not admit a primitive solution. In Ref. [12], we took advantage of a linear combination of Dirac distributions, each of them accounting for a corresponding correlation peak. Here, to reduce the number of phenomenological coefficients, it is convenient instead applying the average value theorem for integrals

[18] to the second term on the right, *i.e.*:

$$\int h(\varrho)\Phi_v(\varrho)d\underline{\varrho} = \Phi_v^* \int h(\varrho)d\underline{\varrho} \tag{8}$$

where it is meant $\Phi_v^* = \Phi_v(\varrho^*), \varrho = \varrho^*$ standing for a finite position value. Thus, combining Eq. (8) with Eq. (4) yields in the end the following phenomenological law:

$$\eta = A\chi + A^* \tag{9}$$

with $\chi \equiv \bar{\rho}\Phi_v^*\kappa_T$, $(A/[\eta]) = k_BT$ and $(A^*/[\eta]) = \Phi_v(1) - \Phi_v^* + 1$. Recall that the average approximation maken in Eq. (8) is strong enough not to allow us to deal with thermal, for instance, or other specific effects. What can be done is taking a reasonable approximation for ϕ and verifying the linearity in Eq. (9) between χ and η at constant (room) temperature. To this end, we can regard ϕ as depending on the space occupied by the liquid units themselves and, in the following, two sets of experimental data are employed. In the first case, we adopted the definition suggested by Eqs. (6), (7) and evaluated the quantities $\phi \propto \bar{\rho}V_0$ in several simple fluids. Afterwards, taking advantage of experimental force constants for second virial coefficients and pair interaction potentials, we concentrate on a second set of systems, using $\phi \propto \bar{\rho}b_0(b_0 = 1.2615\sigma^3, \sigma[\text{Å}]$ being the molecular size) [19]. The best fit form adopted for evaluating $\Phi_v = \Phi_v(\rho)$ are reported in the captions to figures, together with the heuristic coefficients extrapolated. Tables I(a), I(b) collect the experimental quantities taken from literature

TABLE I(a) Two sets of simple liquid systems, with their values at the room temperature of molecular weight, mass density, isothermal compressibility, viscosity and volume at zero fluidity

Liquid	$V_0\,[cm^3/mole]$	$M\,[g]$	$\rho\,[g/cm^3]$	$\kappa_T\,[GPa^{-1}]$	$\eta\,[mPas]$
n-Pentane	94	72,15	0,62	2,13	0,21
n-Hexane	111	86,18	0,66	1,67	0,30
n-Heptane	129,1	100,20	0,68	1,44	0,38
n-Octane	146,4	114,23	0,70	1,28	0,49
n-Nonane	165	128,26	0,72	1,18	1,00
n-Decane	183	142,28	0,73	1,09	0,84
n-Undecane	201	156,31	0,74	1,08	1,09
n-Dodecane	217	170,34	0,75	0,99	1,38
n-Tetradecane	253	198,39	0,76	0,91	2,01
c-Pentane	83,3	70,13	0,75	1,36	0,41
2-Methylpentane	113,5	86,18	0,63	1,84	0,28

TABLE I(b) Two sets of simple liquid systems, with their values at the room temperature of molecular weight, mass density, isothermal compressibility, viscosity and volume evaluated from force constants for second virial coefficients and intermolecular potentials

Liquid	$b_0\,[cm^3/mole]$	$M\,[g]$	$\rho\,[g/cm^3]$	$\kappa_T\,[GPa^{-1}]$	$\eta\,[mPas]$
n-Pentane	33,38	72,15	0,62	2,13	0,21
n-Heptane	330,23	100,20	0,68	1,44	0,38
n-Octane	511,19	114,23	0,70	1,28	0,49
n-Nonane	721,31	128,26	0,72	1,18	0,71
Acetone	67,06	58,08	0,78	1,32	0,32
Methylacetate	162,47	74,08	0,93	1,13	0,36
Dichloromethane	136,06	84,90	1,32	1,03	0,36
Acetonotrile	81,95	41,05	0,78	1,07	0,36
Carbon Disulfide	110,42	76,14	1,26	0,95	0,36
n-Hexane	261,20	86,18	0,66	1,67	0,30

[10, 19–21] to apply Eq. (9). Molecular weight (M) and mass density (ρ_M) were used to calculate $\bar{\rho} = (\rho_M/M)$. Results are illustrated by Figures 1(a), 1(b), respectively, where χ is set in unit of Avogadro number ($= 6.02 \cdot 10^{23}$). As shown by the solid lines, the agreement is quite satisfactory in both cases here examined.

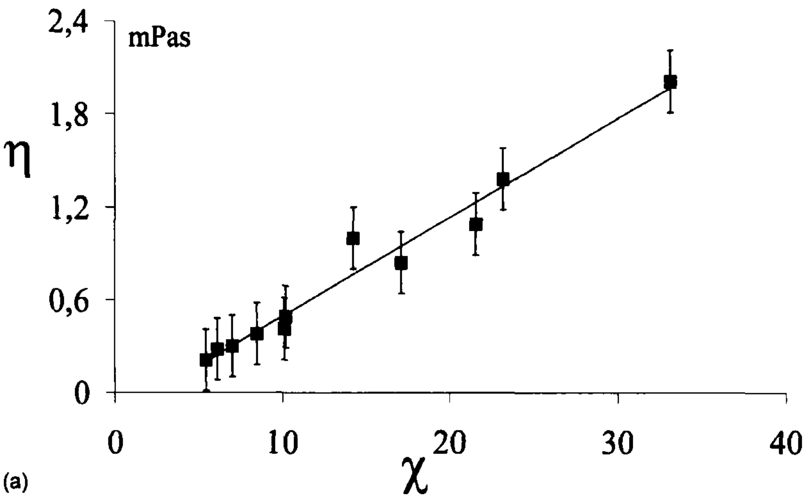

FIGURE 1 (a), (b) Behaviour of η^* *vs.* χ for the systems reported respectively in Tables I(a), I(b). The best fit function for $\Phi_\upsilon = \Phi_\upsilon(\varrho)$ was fixed to $\Phi_\upsilon^* = (\phi^{\rho^*}/1 - k\phi^{\rho^*})$. Phenomenological coefficients turned out to be (a) $k \simeq 1.0$, $\rho^* \simeq 15.7$ and (b) $k \simeq 0.95$, $\rho^* \simeq 0.19$.

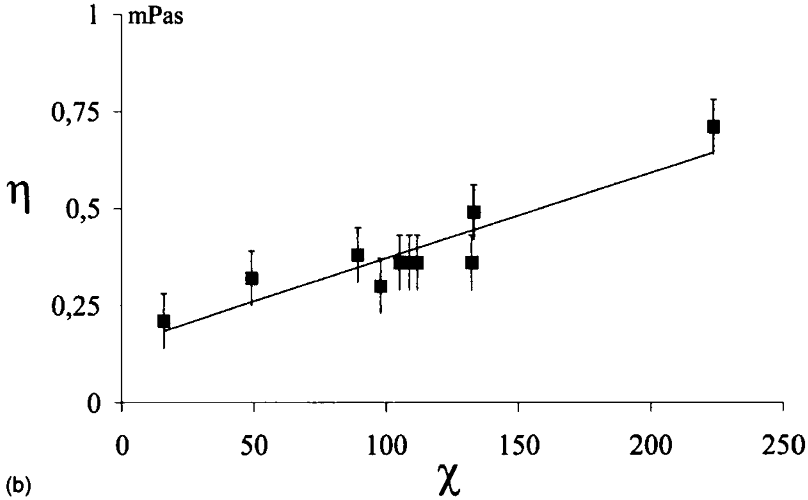

FIGURE 1 (Continued).

CONCLUSIONS

(1) Viscosity and isothermal compressibility of a simple liquid have been related by a closed-form equation for the total correlation function, which describes the low-shear viscosity of a liquid dispersion of solid particles. It contains viscosity, compressibility, macroscopic density, total correlation function and a quantity taking into account the free volume concentration.

(2) A liquid is imagined as a dispersion in a free volume which, in order to perform calculations, has been evaluated first according to the volume at zero fluidity and then by molecular force constants determined experimentally.

(3) An useful approximation for the equation achieved allowed us to describe two sets of experimental measurements, interpreted in terms of a linear form for viscosity against the product among compressibility, density and a factor accounting for the effect resulting from free volume variations.

(4) The same calculation is obviously expected to be valid for a suspension of solid units in a liquid medium.

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