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On the pressure dependence of the thermodynamical scaling exponent γ

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Since its initial discovery more than fifteen years ago, the thermodynamical scaling of the dynamics of supercooled liquids has been used to provide many new important insights in the physics of liquids, particularly on the link between dynamics and intermolecular potential. A question that has long been discussed is whether the scaling exponent γ_S is a constant or does it depends on pressure. An alternative definition of the scaling parameter, $\gamma_1 = \partial \ln T / \partial \ln \rho|_X$ has been presented in the literature, and has been erroneously considered equivalent to γ_S . Here we offer a simple method to determine the pressure dependence of γ_1 using only the pressure dependence of the glass transition and the equation of state. Using this new method we find that for the six nonassociated liquids investigated, γ_1 always decreases with increasing pressure. Importantly in all cases the value of γ_1 remains always larger than 4. Liquids having γ_1 closer to 4 at low pressure show a smaller change in γ_1 with pressure. We argue that this result has very important consequences for the experimental determination of the functional form of the repulsive part of the potential in liquids. Comparing the pressure and temperature dependence of γ_S and γ_1 we find, contrary to what has been assumed in the literature to date, that these two parameters are not equivalent and have very different pressure and temperature dependences.

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Introduction

The density and temperature dependence of dynamic properties of liquids and polymers (*i.e.* viscosity, relaxation and diffusion time) has been found to be well described by the thermodynamical scaling (TDS) behavior^{1–5}

$$\log(X) = \mathfrak{F}(T\rho^{-\gamma_S}), \quad (1)$$

where X is a dynamic property (relaxation time, viscosity, *etc.*), \mathfrak{F} is an unknown function, T the temperature, ρ the density, and γ_S the thermodynamical scaling exponent. This scaling behavior is sometimes referred in other publications also as “density scaling”.

The scaling condition can also be rewritten as

$$T_X \rho_X^{-\gamma_S} = \text{const} \quad \text{or} \quad \ln(T_X) - \gamma_S \ln(\rho_X) = \text{const}, \quad (2)$$

where T_X and ρ_X are the temperature and density at $X = \text{const}$.

An alternative definition of the scaling exponent has been derived from the Isomorph theory^{6,7}

$$\gamma_1 = \left(\frac{\partial \ln T}{\partial \ln \rho} \right)_{S_{\text{exc}}}, \quad (3)$$

where S_{exc} is the excess entropy. Constant excess entropy correspond to an isomorph, this corresponds to the condition for the dynamic properties $X = \text{const}$. The two definitions of γ have been used in the literature as equivalent, however if we differentiate eqn (2) we find

$$\gamma_S = \gamma_1 - \frac{\partial \gamma_S}{\partial \ln \rho} \ln \rho. \quad (4)$$

Thus, the two definition of γ are equivalent only in the case in which γ_S is a constant, and the determination of γ_S from γ_1 is clearly not straightforward. Consequently the pressure dependence of γ_1 cannot substituted in eqn (1) to find a new scaling function as

$$\log(X) \neq \mathfrak{F}(T\rho^{-\gamma_1(T,\rho)}). \quad (5)$$

Indeed, as we show in this paper referring to γ_1 as a “scaling” exponent it is not correct, since in general a master curve cannot be obtained using this parameter apart for special cases.

In the literature it has been debated at length whether the exponent of the thermodynamical scaling, γ_S , for nonassociated liquids is constant or state-point dependent.^{8–15} It has been shown for many materials that a constant γ_S gives a very good superposition of various dynamic properties over a broad range of density and temperature. However, in a recent investigation we have found unequivocal evidence that dielectric relaxation data for a nonassociated liquid (DC704) cannot be scaled according to eqn (1) with $\gamma_S = \text{const}$ and found that the exponent

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γ_1 is state-point dependent, decreasing with increasing pressure.¹⁴ The state-point dependence of γ_1 is in agreement with the predictions of the isomorph theory.^{16,17} Thus, it is of interest to re-analyze past results on other nonassociated liquids to investigate if a similar dependence can be found. It is worth mentioning that for nonassociated liquids we include liquids without strong directional bonds (*i.e.* covalent or hydrogen bonds), thus we are excluding systems such as polymers and liquids forming hydrogen bond networks. It is important to notice that in our previous analysis of the high pressure dielectric relaxation data of DC704, we have actually not determined the pressure dependence of γ_s , but only assumed that it was equivalent to that of γ_1 . Here we consider that, according to eqn (4), the two parameters are not the same, and we want to determine how different are the two behaviors of $\gamma_s(P)$ and $\gamma_1(P)$.

A standard way to determine if the parameter γ_s is constant is to plot $\ln(T)$ versus $\ln(\rho)$ at constant X . It is generally found that γ_s determined from the average slope from a linear best fit to the data gives a good scaling of $\ln(X(T, \rho))$ (eqn (1)). When determining the state-point dependence of γ_1 , it is necessary to find the local slope of $\ln(T)$ versus $\ln(\rho)$ at constant X . Thus, γ_s is generally close to an average of γ_1 . The problem of determining the state-point dependence of γ_1 is reduced to the calculation of the local slope of the $\ln(T_X)$ versus $\ln(\rho_X)$ behavior from a limited number of points (typically 4). This is not trivial since the range of T and ρ are limited. An additional problem of using this method is that it is not clear what should be the function describing the state-point dependence of γ_1 .

To overcome this problem in here, we re-analyze existent data using a different approach. Recently it was proposed to determine the state-point dependence of γ_1 using the equation^{11,14,18}

$$\gamma_1 = \frac{\Delta V}{\kappa_T E_p - T \Delta V \alpha_p}, \quad (6)$$

where $\Delta V (= RT(\partial \ln(X)/\partial P)_T)$ is the activation volume, κ_T the isothermal compressibility, E_p the isobaric activation energy and α_p is the isobaric expansion coefficient. It is worth mentioning that the parameters κ_T and α_p are not constants but are functions calculated from the EOS at varying thermodynamic conditions in all equations herein. Using this method, we determined the variation of γ_1 with pressure for the liquid DC704, decreasing from $\gamma_1 \approx 7$ at atmospheric pressure to $\gamma_1 \approx 4$ at $P = 0.9$ GPa.¹⁴

Recently,²¹ we have also shown that, taking into consideration the available data for nonassociated liquids, out of fifty liquids only for two reported values of γ_s are smaller than 4, and both liquids are extremely polar, propylene carbonate ($\gamma_s = 3.7$, dipole moment $\mu \cong 3.9$ D) and acetonitrile ($\gamma_s = 3.5$, $\mu \cong 4.9$ D). A large value of $\gamma_s (= 7.6)$ has been reported for the very polar ($\mu \cong 2.33$ D) molecular crystal pentachloronitrobenzene (PCNB).¹⁹ However, PCNB is not an isotropic liquid and thus not included. Theoretically, the reduced dimensionality could be used to justify the large value of γ_s found for PCNB, but this is beyond the scope of this paper. Since molecular dynamic simulations have shown that a large dipole moment is expected

to cause a decrease of γ_s , the polarity of propylene carbonate and acetonitrile may explain their lower value of γ_s .²⁰ Thus, the value $\gamma_s \approx 4$ appears to be a limit behavior for nonassociated liquids.

Recently, we also showed²¹ that eqn (6) can be further simplified to

$$\gamma_1 = \frac{1}{T \left(\kappa_T \frac{\partial P}{\partial T} \Big|_X - \alpha_p \right)}. \quad (7)$$

Using this equation, the state-point dependence of γ_1 can be determined using just three quantities. With eqn (3) we also investigated three associated liquids: glycerol, dibutyl phthalate, and dipropylene glycol, and found that the exponent γ_1 increases (from $\gamma_1 < 4$) towards $\gamma_1 \approx 4$ at high pressure.²¹

Here we present a simple derivation obtaining an analytical function for the state dependence of γ_1 instead of determining γ_1 at discrete experimental points using eqn (7) or by determining the local slope of $\ln(T_X)$ versus $\ln(\rho_X)$ from few experimental points. We show how the pressure behavior of γ_1 can be deduced from the pressure behavior of the temperature at constant X , $T_X(P)$.

Using this new method we present new data on the pressure behavior of the thermodynamical scaling exponent γ_1 and we compare the difference in the behavior of γ_s expected from eqn (4).

Methods

Derivation of $\gamma_1(P)$ equation

The pressure dependence of the temperature at a fixed value of X , $T_X(P)$, has been found for several systems to be non-linear, and its behavior can be described by the empirical equation of Andersson and Andersson (AA)²²

$$T_X(P) = T_0 \left(1 + \frac{P}{P_0} \right)^{\frac{1}{a}}, \quad (8)$$

where T_0 , a and P_0 are constants. The derivative of the AA equation is $\partial T_X / \partial P = T_0 / a P_0 (P/P_0 + 1)^{\frac{1}{a} - 1}$. This equation has been verified for a large number of materials by many different experimental groups.²³⁻²⁹ Although the AA equation was originally introduced empirically, it has been also derived from theoretical models.^{30,31}

The dependence of the density from pressure and temperature is well described by the Tait equation of state (EoS).³²

$$\rho(T, P) = \rho_0(T) \left\{ 1 - C \ln \left[1 + \frac{P}{b_0 \exp(-b_1 T)} \right] \right\}, \quad (9)$$

where $\rho_0(T)$ is the temperature dependent density at zero pressure (described either as a polynomial or exponential) and C , b_0 and b_1 are constants.

By combining eqn (8) and (9) we can describe the pressure dependence of the density at constant X , $\rho_X(P)$ as

$$\rho_X(P) = \rho_0(T_X(P)) \left\{ 1 - C \ln \left[1 + \frac{P_0 \left[\left(\frac{T_X(P)}{T_0} - 1 \right)^a \right]}{b_0 \exp(-b_1 T_X(P))} \right] \right\} \quad (10)$$

Rewriting the isomorph condition as

$$\gamma_I(P) = \frac{\partial \ln(T_X)}{\partial \ln(\rho_X)} \quad (11)$$

we can determine the pressure dependence of the exponent γ_I as

$$\gamma_I(P) = \frac{\rho_X}{T_X} \frac{\partial T_X}{\partial \rho_X} \quad (12)$$

Therefore, from the behavior of the pressure dependence of T_X (eqn (8)) together with an EoS, it is possible to determine the pressure dependence of the exponent γ_I without the need to directly analyze the deviation from the linear behavior of $\ln(\rho_X)$ versus $\ln(T_X)$.

Substituting eqn (10) into eqn (12), it is possible to determine the analytical function of $\gamma_I(P)$,

$$\gamma_I(P) = \left\{ T_X(P) \left[-\alpha_P + \frac{C}{1 + \ln \left(1 + \frac{P}{B(P)} \right)} \frac{\left(\frac{a(P+P_0)}{T_X(P)} + b_1 P \right)}{P+B(P)} \right] \right\}^{-1} \quad (13)$$

where

$$B(P) = b_0 \exp[-b_1 T_X(P)]. \quad (14)$$

It is interesting to note that considering the typical values of the parameters for nonassociated liquids in eqn (13), the term due to α_P in eqn (13) (and eqn (7)) varies much less than the second term related to the compressibility; the latter increases with pressure, causing the decrease of γ_I . It is important to notice that an extrapolation to much higher pressure than the EoS data or the $T_X(P)$ data is likely to give unreasonable results, since the high pressure validity (*i.e.* out of the measured range) of the two starting equations is unknown.

Below we use this method for six nonassociated liquids for which the high pressure behavior of the dielectric relaxation time has been previously investigated. For these liquids a constant γ_S was found to give a good superposition of dynamic data, and the plots of $\ln(\rho_X)$ versus $\ln(T_X)$ are nearly linear.

Results

The dielectric relaxation and EoS data along with the scaling exponent γ_S were previously published for six non-associated liquids: *o*-terphenyl (OTP), $\gamma_S = 5.3$,^{33,34} 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC), $\gamma_S = 8.5$,^{35,36} phenylphthalein-dimethylether (PDE), $\gamma_S = 4.5$,^{37,38} and three polychlorinated biphenyls (PCB42, PCB54 and PCB62), found to

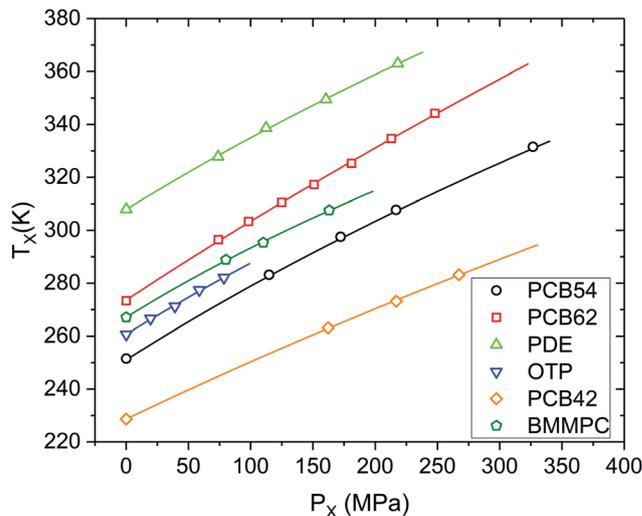


Fig. 1 Temperature T_X versus pressure P_X at constant relaxation time for six nonassociated liquids. The points are experimental data and the line are the best fit to the AA equation (eqn (8)). The best-fit parameters are reported in Table 1.

have very different values of γ_S (PCB42 $\gamma_S = 5.5$, PCB54 $\gamma_S = 6.7$ and PCB62 $\gamma_S = 8.5$).³⁹ In particular, between these materials BMMPC and PCB62 have some of the largest values of γ_S reported in the literature for dielectric relaxation data. Dielectric relaxation spectroscopy data were used in this study because they have the advantage of a larger frequency range compared with other experimental techniques used to study the dynamics of supercooled liquids.⁴⁰ Although in the literature there are more data, these samples mostly cover the entire range of γ_S values found for nonassociated liquids.

For each material, we extracted from the data the pressure dependence of the temperature T_X where X was the dielectric relaxation time τ . Since the change of T_X with pressure increases with increasing τ , for each data set the value of τ chosen was the longest (*i.e.* closest to the glass transition) for which the largest number of data points was available; for most liquids considered in this study was typically $\tau = 10$ s. The pressure dependence of T_X for the six liquids is reported in Fig. 1 (symbols), together with the best fit (solid lines) to the AA equation (eqn (8)). The best-fit parameters are reported in the Table 1.

In Fig. 2 are reported the experimental data (open symbols) of temperature T_X versus the density ρ_X at constant relaxation time on a log-log plot. The solid lines in Fig. 2 are not a best fit,

Table 1 Best-fit parameters of the data in Fig. 1 to the AA equation (eqn (8)) displayed as solid lines in Fig. 1

	T_0 [K]	P_0 [MPa]	a
PCB54	251.5 ± 0.1	350.9 ± 9	2.38 ± 0.04
OTP	260.7 ± 0.5	366 ± 100	2.4 ± 1
PCB62	273.6 ± 0.5	499 ± 87	1.77 ± 0.25
PDE	307.8 ± 0.6	399 ± 95	2.6 ± 0.5
PCB42	224.55 ± 0.04	362 ± 6	2.60 ± 0.03
BMMPC	267 ± 0.5	274 ± 76	3.3 ± 0.7

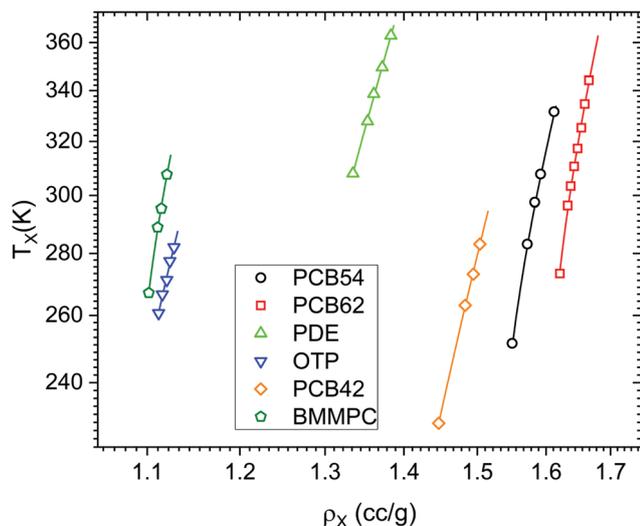


Fig. 2 log–log plot of temperature, T_x , versus density, ρ_x , at a constant relaxation time for 6 non-associated liquids. The symbols are experimental data and the solid lines are the data calculated using eqn (10) using the best fit to the AA equation (eqn (8)) and the Tait EOS (eqn (9)).

they are obtained using eqn (10), with the parameters determined from the best fit of the AA equation (eqn (8)) to $T_x(P)$ and the Tait EoS (eqn (9)). It is important to notice that both axes in Fig. 2 are presented on a logarithmic scale, consequently in this plot the scaling behavior described by eqn (1) with $\gamma_s = \text{constant}$ would correspond to a linear behavior with a slope equal to γ_1 . Evidently, the behaviors reported in Fig. 2 do not show a strong deviation from linearity and a precise determination of the pressure dependence of γ_1 is rather difficult, especially without an *a priori* model describing the nonlinear behavior of $\ln(T_x)$ versus $\ln(\rho_x)$. Instead of determining the pressure dependence of the exponent γ_1 from the deviation from linearity of $\ln(T_x)$ versus $\ln(\rho_x)$ data, we use the newly derived equation for $\gamma_1(P)$ (eqn (13)) which does not require any additional data fitting apart from the best-fit parameters obtained from the fit of $\rho(T,P)$ to the Tait EoS and the $T_x(P)$ to the AA equation.

The pressure behavior of the exponent $\gamma_1(P)$ (obtained using eqn (13)) is reported in Fig. 3. The results in Fig. 3 clearly show that for all six liquids the exponent γ_1 decreases with pressure. The decrease of γ_1 with pressure is more dramatic for liquids having a larger value of γ_s , while for materials with γ_s closer to 4, the change of γ_1 is much smaller. It is important to notice that in all cases, even at the highest pressure, the parameter γ_1 remains always larger than 4. This behavior is consistent with that recently observed for DC704, for which γ_1 was found to decrease from ~ 7 to a value close to 4, although over a much larger pressure range (up to $P = 0.9$ GPa).¹⁴ It is important to notice that the parameter γ_1 is dependent also on temperature (inset to Fig. 3), with a similar behavior to that observed versus pressure, γ_1 decreases with increasing temperature tending at high temperature to what appears to be a limit value close to 4. We compare the results in Fig. 3 with previous values reported for γ_s from either (method 1) calculations of γ_s from a master curve superpositioning dynamic data as a function of $T\rho^{-\gamma_s}$ or

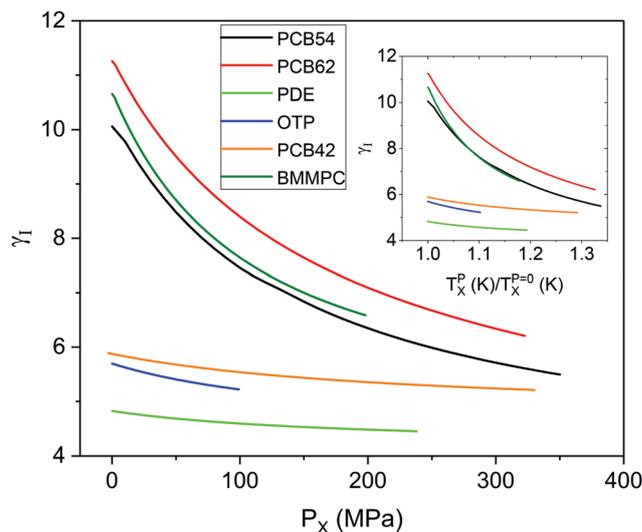


Fig. 3 Main: pressure dependence of the parameter γ_1 for six non-associated liquids calculated using eqn (13) with the parameters from the EoS and the best-fit of the AA equation to the $T_x(P)$ data (Table 1). Inset: Temperature dependence of the parameter γ_1 for six non-associated liquids calculated as described above. The temperature T_x was normalized by its value at atmospheric pressure.

(method 2) slope values of a linear fit to the data in Fig. 2. Both methods give determinations of γ_s close to the average value of γ_1 over the entire pressure range.

Discussion

A limit of the method described above is that the $T_x(P)$ behavior may be better described with different equations than the AA equation. In principle, it could be possible to obtain a different $\gamma_1(P)$ behavior. For this reason we analyzed the $T_x(P)$ behavior for the case of PCB62 (since it has the largest number of points) using two nonlinear equations alternative to the AA equation: a quadratic equation $T_x(P) = d_0 + d_1P + d_2P^2$ and logarithmic equation $T_x(P) = a_0[1 + a_1 \ln(1 + P/a_2)]$ (where d_n and a_n are constants).

The best fit to the $T_x(P)$ data using these two equations (best-fit parameters are in the Fig. 4 caption) are reported in Fig. 4 together with the best fit obtained with the AA equation. From an analysis of the best-fit residuals (lower inset to Fig. 4) it is evident that all equations give a good description of the $T_x(P)$ behavior, while larger deviations are observed fitting the data with a linear behavior of $T_x(P)$ with pressure.

The top inset to Fig. 4 shows the parameter γ_1 determined by calculating numerically using eqn (12) for the four different best-fit equations to $T_x(P)$. We find that as long as the best fit had a similar deviation from the $T_x(P)$ data (residuals are shown in the bottom inset to Fig. 4), a similar behavior of γ_1 was found within a deviation of about 0.2. Interestingly, if we analyzed the $T_x(P)$ data using a linear behavior (which has a larger deviation from the data, especially at low pressure, as shown in the bottom inset to Fig. 4), the resulting pressure dependence of γ_1 is strongly reduced (top inset to Fig. 4).

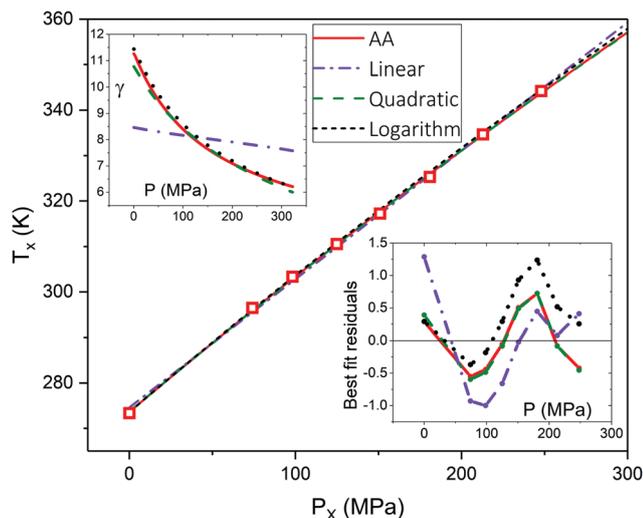


Fig. 4 Pressure dependence of T_x for PCB62 (same as in Fig. 1) with the best fit to the data using the AA equation and three other equations. A linear equation $T_x(P) = l_0 + l_1P$ (best-fit parameters $l_0 = 274.6 \pm 0.6$, $l_1 = 0.282 \pm 0.004$), a quadratic equation $T_x(P) = d_0 + d_1P + d_2P^2$ (best-fit parameters $d_0 = 273.7 \pm 0.5$, $d_1 = 0.306 \pm 0.009$, $d_2 = (-9.5 \pm 3.4) \times 10^{-5}$) and a logarithmic equation $T_x(P) = a_0[1 + a_1 \ln(1 + P/a_2)]$ (best-fit parameters $a_0 = 273.6 \pm 0.5$, $a_1 = 1316 \pm 485$, $a_2 = 1.5 \pm 0.5$). Lower inset: Best fit residuals, versus pressure, for the best fit to the four equations used for the description of $T_x(P)$. Upper inset: γ_1 parameter versus pressure, obtained calculating numerically eqn (12) for the four different equations used to describe the behavior of $T_x(P)$.

The difference between the pressure dependence of γ_1 obtained fitting the $T_x(P)$ data with a linear versus non-linear behavior, is indicative that most of the observed change in γ_1 is related to the non-linear behavior of $T_x(P)$. The observation that other equations alternative the AA equation can give a satisfactory description of $T_x(P)$ evidently imposes a limit to the use of eqn (13) for determining the behavior of γ_1 beyond the range of the experimental data. Following the same procedure described above, but substituting the AA equation with a quadratic or logarithmic equation, different equations for the pressure dependence of γ_1 can be obtained and these will certainly have a different behavior at pressures beyond the experimental range of the measurements. It is worth mentioning that the same analysis for PCB62 repeated at different τ (up to $\tau = 10^{-6}$ s) gives the same behavior reported above (for $\tau = 1$ s) with same deviations at high frequency (< 0.3) within the error determined by propagation of the error of the best fit to the AA equation.

From the results shown above we see that, notwithstanding a constant γ_s was found to give a good superposition of dynamic data^{33–39} and that the plot of $\ln(\rho_x)$ versus $\ln(T_x)$ is nearly linear (Fig. 2), a significant dependence of γ_1 on pressure can still be found using eqn (13). These two results seems to be in contradiction with each other, especially if we intuitively think that γ_1 and γ_s should have a similar value. To check for this apparent discrepancy, we determined the pressure dependence of γ_s from the same data using a different approach. We rewrote eqn (2) as

$$\ln(T_x(P)) - \gamma_s(P)\ln(\rho_x(P)) = \ln(T_x(0)) - \gamma_s(0)\ln(\rho_x(0)). \quad (15)$$

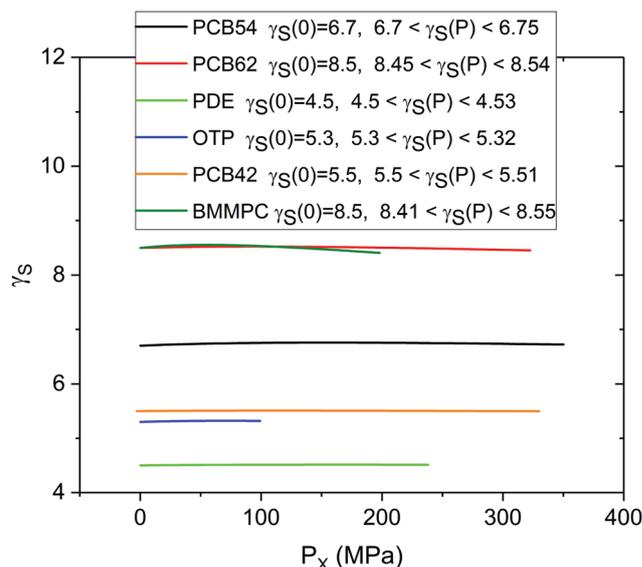


Fig. 5 Parameter $\gamma_s(P)$ as a function of pressure determined using eqn (16) with the value $\gamma_s(0)$ equal to the value found from superposition the $X(T, \rho)$ data.

From this follows the condition for the pressure dependence of $\gamma_s(P)$ necessary to have a “perfect” scaling,

$$\gamma_s(P) = \frac{\ln(T_x(P)) - \ln(T_x(0)) + \gamma_s(0)\ln(\rho_x(0))}{\ln(\rho_x(P))}. \quad (16)$$

Since the pressure dependence of $T_x(P)$ and $\rho_x(P)$ are known the only free parameter is $\gamma_s(0)$. Evidently, we don't have an *a priori* value of $\gamma_s(0)$, and different values will correspond to very different pressure dependences of $\gamma_s(P)$. However, we found that if we use an initial value of $\gamma_s(0)$ close to the γ_s determined before from the superposition of $X(T, \rho)$, then the behavior of $\gamma_s(P)$ is extremely different from that of $\gamma_1(P)$.

In Fig. 5 the pressure behavior of $\gamma_s(P)$ is reported on the same scale of the behavior of $\gamma_1(P)$ in Fig. 3. Since the behavior is very close to a constant, the interval of variation of $\gamma_s(P)$ is reported in the caption of Fig. 5, and we find that $\gamma_s(P)$ changes within 0.1 of the average value. This behavior is very different from that observed for $\gamma_1(P)$ in Fig. 3 where variations of more than a factor of 2 are shown.

These results clearly show that a good scaling plot (eqn (1)) can be found also in cases in which $\gamma_1(P)$ depends strongly on pressure.

This is because the superpositioning method and the log-log plot method are better suited at determining an average value of γ_1 rather than evaluating its state-point dependence. In particular, we find that such dependence is larger for materials having larger γ_s and at high pressure the value of γ_1 remains larger than 4 like in the case of DC704.¹⁴ This is in contrast with the behavior of associated liquids for which was found to increase with pressure approaching the value $\gamma_1 \sim 4$ at high pressure.²¹ Interestingly, in both cases of associated and non-associated liquids, even if the pressure behavior is opposite, the condition $\gamma_1 = 4$ appear to be same high pressure limit. As

discussed in ref. 21, the opposite behavior for associated liquids is attributed to the progressive reduction of the hydrogen bonded network with increasing pressure, which initially causes γ_1 to be smaller than 4.

Conclusions

In this study we report a new analytical method to describe the pressure dependence of the exponent γ_1 . To use this method it is only necessary to determine the pressure dependence of the temperature at constant X , $T_X(P)$ and the EoS.

Using this new method it is possible to determine the pressure dependence of the parameter γ_1 even for liquids for which a constant γ_S exponent gives a very good superposition of various dynamic properties and an almost linear behavior of $\ln(T_X)$ versus $\ln(\rho_X)$. In the past γ_S and γ_1 have been considered to be the same, but here we show that this is not true and that their behavior with pressure (and temperature) is very different. We find that the previously determined values of γ_S are close to an average value of the observed $\gamma_1(P)$, and its change with pressure is significantly smaller than that of $\gamma_1(P)$. In several papers these two parameters have been considered equivalent,^{6,7,11,14,16} which is clearly not correct in general. In particular, it is not correct to refer to the parameter γ_1 as a scaling exponent, since no superposition of the $X(T, \rho)$ data can be obtained using this parameter, unless for special cases in which $\gamma_1 \sim \text{const}$ (*i.e.* changes of less than 10% over the investigated range).

For all nonassociated liquids, the exponent $\gamma_1(P)$ is found to decrease with pressure. The change of $\gamma_1(P)$ is found to be smaller for liquids with $\gamma_1(0)$ (and γ_S) closer to 4, consistent with a high pressure limit of $\gamma_1(P) \sim 4$. This behavior is similar to that found in a recent report on the pressure dependence of the $\gamma_1(P)$ exponent for the nonassociated liquid DC704. While it is in contrast with that of associated liquids for which we found $\gamma_1(P)$ increases with pressure from $\gamma_1(0) < 4$ to $\gamma_1(P) \sim 4$ at high pressure.

From a theoretical point of view, it has been demonstrated that the TDS behavior (eqn (1)) is predicted in the case for which the intermolecular potential, $U(r)$, is dominated by the repulsive part of the potential and it can be described by an inverse power law behavior $U(r) \propto r^{-n}$. In this case the TDS follows with $\gamma_S = \frac{n}{3}$.^{41,42} Molecular dynamic simulations have shown that, in the case of Lennard Jones (LJ) type potentials in which the attractive part cannot be neglected, the TDS behavior is still verified but with $\gamma_S > \frac{n}{3}$ (where n is the exponent of the repulsive part at an average intermolecular distance), and $3\gamma_S$ represents an average slope of the intermolecular potential.^{43–45} Accordingly the parameter γ_1 can be considered as the local slope of the potential. Therefore, the variation of the exponent γ_1 with pressure for nonassociated liquids is consistent with a decrease of the effect of the attractive part of the potential with increasing pressure, so that at high pressure the intermolecular potential is dominated by its

repulsive part. In particular, since the data are consistent with $\gamma_1 \sim 4$ as the high pressure limit of the exponent γ_1 , then the high pressure limit of the potential corresponds to $U(r) \propto r^{-n}$ with $n \sim 12$.²¹ Therefore, current results are consistent with an exponent of the repulsive part of the potential, $n \sim 12$, for all seven nonassociated liquids in which a change of γ_1 has been found using eqn (7).

This form for the repulsive term of the potential is evidently consistent with a potential such as the Lennard-Jones 6-12 potential. However, it is not a proof of the validity of the LJ potential, since the high-pressure measurements are relevant for very small intermolecular distances. Our results only indicate that at very small intermolecular distances, the intermolecular potential can be described locally with a mathematical form that is close to an inverse power law with an exponent close to 12 in the limit of high pressure (high density and high temperature). This is very important since there is currently no other experimental determination of the repulsive part of the potential, and these results may offer an experimental approach to determine a functional form of the potential that can be used in molecular dynamics simulation.

Conflicts of interest

There are no conflicts to declare.

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