

How Free Volume *Does* Influence the Dynamics of Glass Forming Liquids

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Abstract

In this article we show that inverse free volume is a natural variable for analyzing relaxation data on glass-forming liquids, and that systems obey the general form, $\log(\tau/\tau_{\text{ref}}) = (1/V_{\text{free}}) \times f(T)$, where $f(T)$ is a function of temperature. We demonstrate for eight glass-forming liquids that when experimental relaxation times ($\log \tau$), captured over a broad pressure-volume-temperature (PVT) space, are plotted as a function of inverse free volume ($1/V_{\text{free}}$) a fan-like set of straight line isotherms with T -dependent slopes ensues. The free volume is predicted independently of the dynamic results for each state point using PVT data and the Locally Correlated Lattice (LCL) equation of state. Taking $f(T) \propto 1/T^b$, we show that for each of the systems studied only the single, system-dependent parameter, b , is required to collapse the fan of linear isotherms into a straight line. We conclude that $\log \tau$ is a function of the combined variable, $1/(V_{\text{free}}T^b)$, and because it is linear, it allows us to write an explicit analytic expression for $\log \tau$ that covers a broad PVT space.

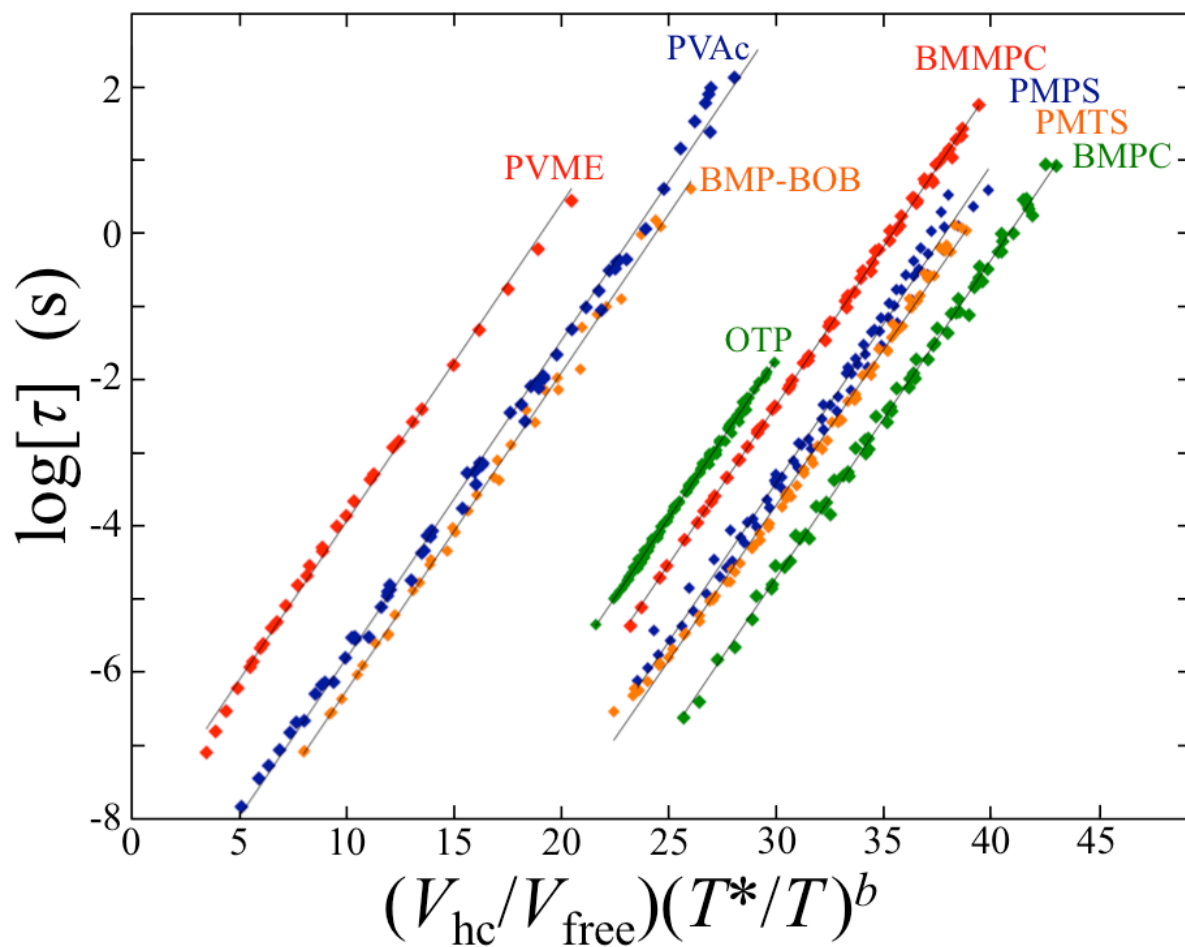
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How Free Volume *Does* Influence the Dynamics of Glass Forming Liquids

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A central goal in the study of glass forming liquids has been to explain their complex dynamical behaviour (diffusion, relaxation times (τ), viscosity (η), etc.) in terms of the key physical driving forces, as reflected in thermodynamic properties.¹⁻¹⁵ In this Letter we propose that the natural variables for analyzing the relaxation data of liquids (polymeric and small molecule) are temperature (T) and *free volume* (V_{free}). We demonstrate that whenever temperature is fixed (i.e. on an isotherm), the log of relaxation times are linearly proportional to inverse free volume. In particular, we show that over a broad PVT space, systems obey $\log(\tau/\tau_{\text{ref}}) = (1/V_{\text{free}}) \times f(T)$, where $f(T)$ is a function of temperature. Going further, we demonstrate that data covering ten decades in relaxation time can be collapsed into a single straight line by introducing a new thermodynamic scaling relationship. Our free-volume based model requires only a single parameter to effect this collapse, and it leads to a *linear* form; the slope and intercept of the resulting line yield the remaining two system-dependent (but not adjustable) parameters. This simple analytic result reflects a fundamental connection between our characterization of a liquid's equilibrium *thermodynamic* properties and its *dynamic* relaxation.

In describing dynamics, the most widely-used simple form is the Arrhenius expression (for viscosity, also called the Andrade equation¹⁶) given by

$$\ln \eta, \text{ or, } \ln \tau = \ln A + B/T \quad [1]$$

where A and B are constants (B , being the activation energy). However, glass forming liquids deviate from simple Arrhenius behavior as T is lowered, becoming highly viscous and extremely sensitive to just small further decreases in T . An example is shown in the inset of Figure 1, which gives a plot of the log of the segmental relaxation times^{17,18} for poly vinyl acetate (PVAc) vs. $1/T$ at constant pressure, along the $P = 1$ atm isobar. The plot is not linear, the upward curvature indicating an increase in the apparent activation energy. This so-called "super Arrhenius behavior" is ubiquitous in glass forming systems. In order to fit the data an alternative phenomenological form is often used, such as the well known Vogel-Fulcher-Tammann (VFT) equation¹⁹⁻²¹

$$\ln \eta, \text{ or, } \ln \tau = \ln A + B/(T - T_0) \quad [2]$$

This introduces a third parameter, T_0 , often called the Vogel temperature. Note that in moving along an isobar the volume will change with T . The effect of having both V and T changing are not explicitly addressed in eq [2]; this is pursued in further detail below. In addition, each optimized VFT 3-parameter set will only apply over a single thermodynamic path/coordinate, i.e. a single particular isobar, or single isochore.

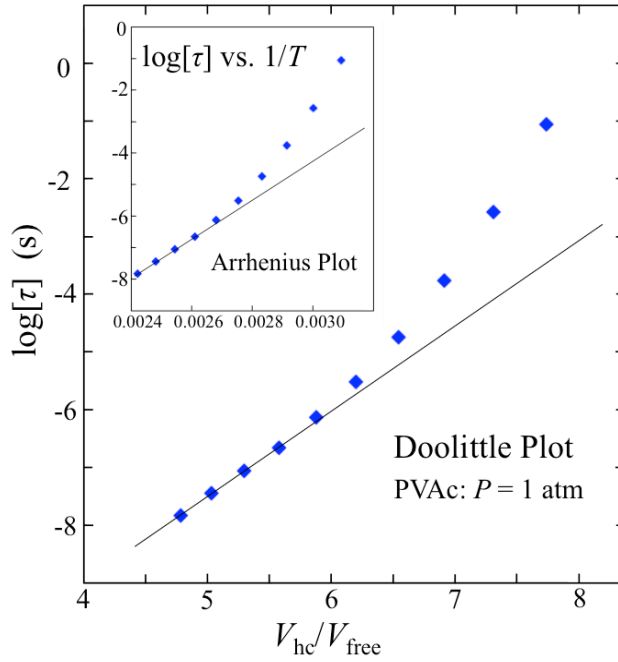


Figure 1. Inset: Arrhenius plot for PVAc showing log of the segmental relaxation times ($\log[\tau]$) plotted vs. $1/T$ (units K^{-1}) at ambient pressure ($P = 1 \text{ atm}$). Main plot: A "Doolittle plot" for PVAc where, for the same points in the Arrhenius plot (inset), $\log[\tau]$ is plotted vs. inverse *relative free volume*. The LCL EOS analysis of PVT data is used to determine the V_{hc}/V_{free} values. See Table 1 for parameters. Experimental relaxation times from refs 17 and 18.

The fact that simple inverse temperature dependence cannot explain the super-Arrhenius behavior has lead to free volume-based explanations. In its most focused form this involves asserting that free volume, alone as a single variable, accounts for all the trends. For example, the "Doolittle equation" connects the log of the viscosity ($\ln \eta$, or $\ln \tau$) to the inverse relative free volume as follows:²²

$$\begin{aligned} \ln \eta, \text{ or, } \ln \tau &= \ln A + BV_{hc}/(V - V_{hc}) \\ &= \ln A + BV_{hc}/V_{free} \end{aligned} \quad [3]$$

where V_{hc} is the system's limiting hard-core volume and the free volume, $V_{\text{free}} = V - V_{\text{hc}}$ (again A and B are constants). The Doolittle equation links dynamic behaviour to a single variable: free volume.

The Doolittle equation has been most often applied by substituting a temperature-dependent expression for the input free volume.²³⁻²⁵ See for example, the work by Cohen and Turnbull²³ and Williams-Landel-Ferry²⁴ (WLF). Each involves using a linear form for V_{free} as a function of T at constant P in eq [3]. The result is an equation equivalent in form to the phenomenological VFT expression. That form does indeed fit super-Arrhenius behavior (e.g. as T changes along an isobar), however, it does not create a link to any reasonable measure of the "actual" free volume, nor can it account for the P -dependence of relaxation behavior.

In fact we can show that the Doolittle equation (eq [3]) *does not even correctly describe the ambient pressure dynamics* by direct input of PVT -based free volumes. We use our Locally Correlated Lattice (LCL) model^{26,27} to predict the free volume of a melt for all T values that match the experimental data points for τ , and thus the left and right sides of eq 3 can be compared. Using PVAc as an example, we applied the LCL equation of state to fit its experimental pressure-volume-temperature (PVT) surface²⁸. The resulting characteristic parameters (see Table 1) yield the limiting hard-core volume (V_{hc}), the value of which is independent of T and P . The free volume as a function of T at $P = 1$ atm is then obtained as $V_{\text{free}}(T) = V(T) - V_{\text{hc}}$. Figure 1 shows the experimental^{17,18} $\log \tau$ plotted vs. the LCL $V_{\text{hc}}/V_{\text{free}}$ at each state point for the ambient pressure isobar. If the Doolittle form were correct then the points would form a straight line, and clearly this is not the case for any more than about two decades. The straight line was drawn through the leftmost four points as a guide to the eye.

To our knowledge this is the first time such a test has been performed using PVT -based free volumes as direct input. It is also worth adding that, while the historical free volume models^{23-25,29} invoked the Doolittle equation to act as "the link" to tracking super Arrhenius behavior, the experimental data (on alkanes) that were analyzed in the original paper by Doolittle²² were not in a super Arrhenius regime, since T was not low enough. Furthermore, if one plots all of the data for the 10 systems in Table 1 of that paper, both in Doolittle form, i.e.

$\ln \eta$ vs. Doolittle's $V_{\text{hc}}/V_{\text{free}}$ values, and in Arrhenius form, $\ln \eta$ vs. $1/T$, it becomes clear that there are only marginal differences between the two forms.

A wealth of experimental evidence leads to the expectation that the dynamics will depend on both temperature and volume, bolstered by results from pressure dependent studies (where a full PVT space can be tested).^{1,4} For example, P -dependent results clearly show that if volume (and thus free volume) is fixed, and only the temperature is changed, the dynamics still change, and likewise there are changes in dynamics when T is fixed, and only V changes.

We have come to the conclusion that temperature and *free* volume are natural variables for analyzing relaxation data. The correlation is clearly revealed when P -dependent segmental relaxation times are tracked along an *isotherm*. In Figure 2 multiple isotherms for experimental $\log \tau$ results on PVAc^{17,18} are plotted as a function of inverse relative free volume ($V_{\text{hc}}/V_{\text{free}}$), calculated using the LCL equation of state at all the corresponding T, P points. Strikingly linear behavior is observed over a span of more than 10 decades. These results indicate just how intimately free volume is connected to the relevant underlying physics. This is the first time such a relationship has been shown to connect dynamic relaxation data over a considerable range of T and P with corresponding *independent predictions* for free volume (i.e. based on actual volumetric data).

The slopes of the isotherms in Figure 2 are T -dependent, which leads us to propose $\log(\tau/\tau_{\text{ref}}) = (1/V_{\text{free}}) \times f(T)$, where $f(T)$ is a function of temperature. Going further, we can collapse all data to a single line using just a single (system-dependent) parameter denoted by, b . This is illustrated in the inset of Figure 2, which shows a plot of $\log \tau$ vs. $(V_{\text{hc}}/V_{\text{free}})/T^b$, where a trial and error adjustment yields that a value of $b = 3.9$ produces a collapse of all the isotherms. More detail is provided below.

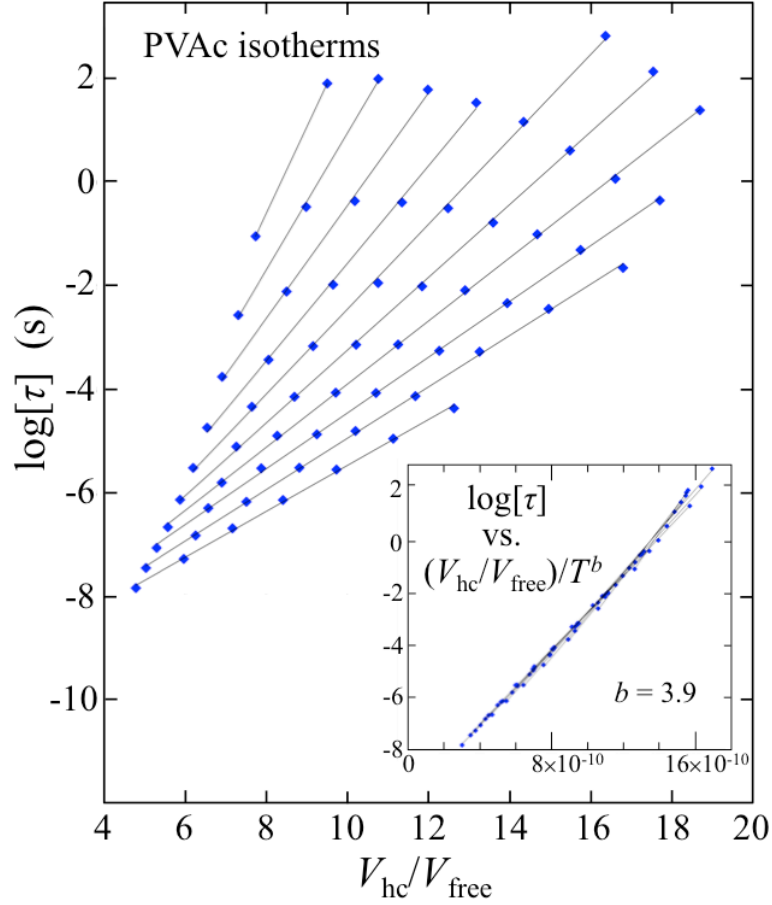


Figure 2. T,P -dependent α segmental relaxation times for PVAc, plotted as isotherms as a function of inverse relative free volume (V_{hc}/V_{free}); data points appear as symbols and lines are the corresponding linear fits. The inset shows that when $\log \tau$ is plotted as a function $(V_{hc}/V_{free})/T^b$, with a choice of parameter $b = 3.9$, the data collapse to a single line (abscissa units K^{-b}). Experimental relaxation times from refs 17 and 18. Isotherms, top to bottom, are $T = 323, 333, 343, 353, 363, 373, 383, 393, 403, 413K$. Pressure values range from 1atm up to as high as 400MPa ($T = 383, 393, 403K$). All correlation coefficients for the isotherms are greater than $R^2 = 0.9985$. See Table 1 for details on the LCL EOS parameterization used to determine the V_{hc}/V_{free} values.

The behavior observed for PVAc is mirrored in the results for six more systems, as illustrated in Figure 3. Plots of $\log \tau$ vs. V_{hc}/V_{free} along isotherms are given for three more polymers (poly vinylmethylether (PVME), poly methylphenylsiloxane (PMPS), poly methyltolylsiloxane (PMTS)), two small molecule glass formers (1,1'-bis(*p*-methoxyphenyl)cyclohexane (BMPS), 1,1'-di(4-methoxy-5-methylphenyl)cyclohexane (BMMPC)), and an ionic liquid (1-butyl-1-methylpyrrolidinium bis[oxalate]borate (BMP-BOB)). As for PVAc, all the τ values correspond to α relaxation times determined via dielectric spectroscopy. We emphasize that in all cases the free volumes are based on PVT data, as

predicted via the LCL EOS; the characterization information is given in Table 1 along with experimental references for PVT ^{28,30-34} and dynamics data ^{17,18,31,33-43}. Figure 3 shows that in each case the use of free volume produces linear isotherms, obeying the general form, $\log(\tau/\tau_{\text{ref}}) = (1/V_{\text{free}}) \times f(T)$. We now consider $f(T)$.

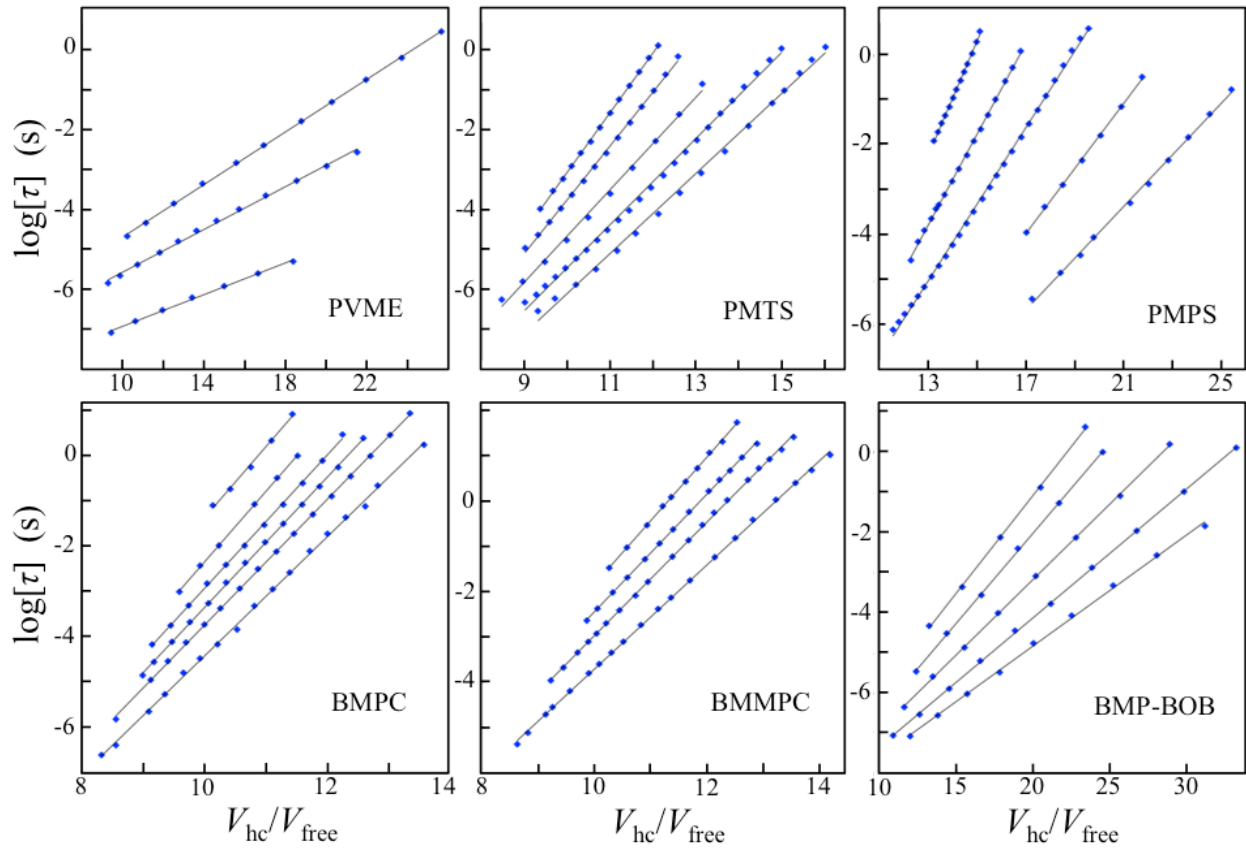


Figure 3. T,P -dependent α relaxation times, plotted as isotherms as a function of inverse relative free volume ($V_{\text{hc}}/V_{\text{free}}$); data points appear as symbols and lines are the corresponding linear fits. Systems include polymers, PVME, PMTS, and PMPS, small molecules, BMPC and BMMPC, and the ionic liquid, BMP-BOB. All but one of the isotherms have correlation coefficients of at least $R^2 = 0.997$ (most are closer to 0.999). See Table 1 for sources to experimental details/data on systems, and the LCL EOS parameterization used to determine the $V_{\text{hc}}/V_{\text{free}}$ values.

Table1. Characterization Parameters for Dynamics Analysis (eq 6) and LCL *PVT* Analysis^a

	T_g (K)	b	T^* (K)	$\log \tau_{\text{ref}}$ (s)	r/M_w (mol/kg)	v (mL/mol)	$-\varepsilon$ (J/mol)	$\langle T_{\text{fit}} \rangle$ (K)	data refs $T_g / \tau / PVT$
PVAc	305	3.96	420	-10.1	137.9	5.499	1805	369	42/18/28
PVME	242	5.89	272	-8.28	130.6	6.635	1782	341	43/35/30
PMPS	246	2.70	356	-16.4	114.7	7.095	1901	338	31/36/31
PMTS	261	2.22	465	-16.5	107.8	6.658	1717	338	31/37/31
BMPC	241	1.77	536	-17.7	224.2	3.648	1677	328	39/38/32
BMMPC	261	1.61	568	-15.4	196.1	4.252	1858	328	39/39/32
OTP	244	2.71	380	-14.7	141.0	5.817	1720	325	33/40/33
BMP-BOB	231	3.70	266	-10.6	165.5	4.293	1807	326	34/41/34

^a b , T^* , and τ_{ref} are parameters for the dynamics expression in eq 4. See refs 26 and 27 for details on the LCL model. The LCL molecular parameters are: r , the number of segments (occupied lattice sites) per molecule, v , the volume per lattice site, and ε , the segment-segment nonbonded interaction energy. The hard-core volume, V_{hc} , per molecule, is obtained from the product, rv . M_w is molecular weight. In the LCL fitting, $\langle T_{\text{fit}} \rangle$ is the average temperature of the *PVT* data. For the dynamics data points, the pressure ranges for most systems typically covered $P = 1$ atm (0.1MPa) to around 200MPa; PVAc covered 0.1 to 400MPa, and BMP-BOB 50 to 500MPa. Temperature values varied with system and are available in the experimental references. Typically we use graph digitizer software to collect relaxation data from plots in the experimental references. Note for PVAc the plots in ref 17 were used, with original data from ref 18.

As we analyze the results in Figures 2 and 3 and elaborate on $f(T)$, we note that our approach is analogous to a category of dynamics relationships called "Thermodynamic Scaling"^{1,4,44-54} and in an upcoming paper we will present a fuller discussion. In those methods a scaling exponent is often applied to the volume. Consistent with our conclusion that (inverse) free volume is a "natural variable" for the dynamics we do *not* apply our material specific scaling exponent (b) to it, but instead, we apply it to the temperature. In Figure 4 we show that the data can be collapsed for each of the systems, including the six systems in Figure 3, and, an eighth system, ortho-terphenyl (OTP), the data⁴⁰ for which are T,P -dependent but were not published in the form of isotherms.

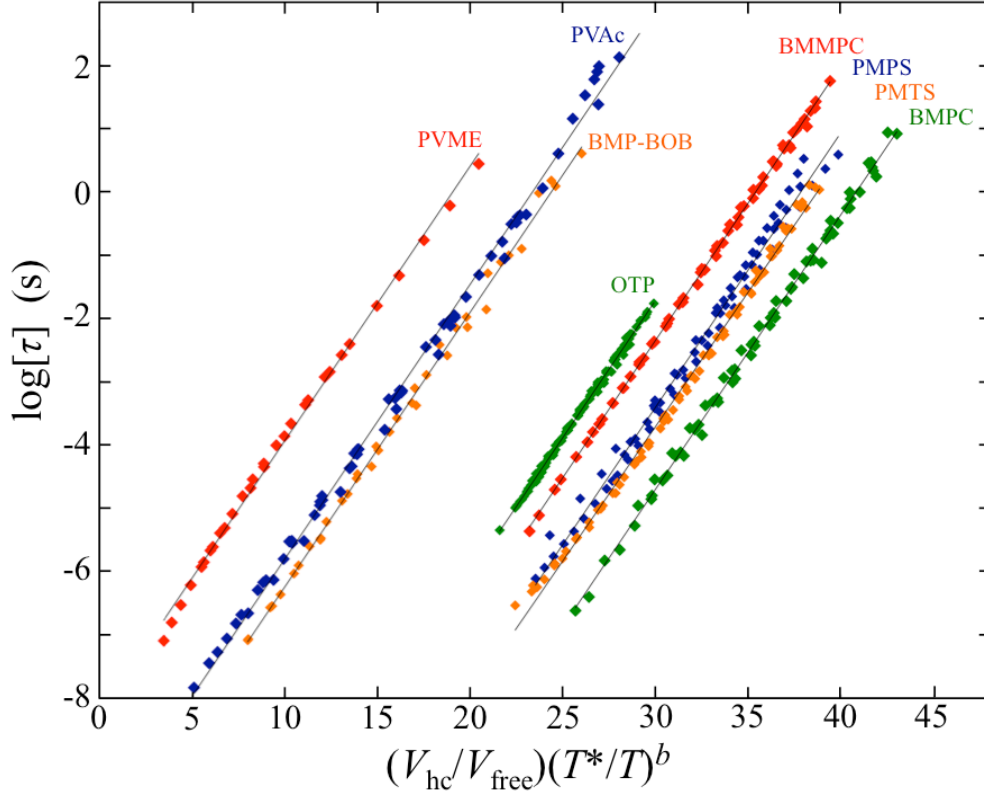


Figure 4. T,P -dependent α relaxation times described for eight systems (as marked). Data points appear as symbols and lines are the corresponding linear fits to eq 4. The data shown in collapsed form here, correspond to the same data appearing in the form of isotherms in Figures 2 and 3 (for all systems other than OTP). Experimental relaxation times are from refs 17,18,35-41. See Table 1 for experimental references, parameters for eq 4, and the LCL EOS used to determine the V_{hc}/V_{free} values.

An advantage of our free volume-based thermodynamic scaling is that $\ln \tau$ becomes a *linear* function of the combined variable, $1/(V_{free}T^b)$, once the single parameter b is determined. In practice, we use $V_{hc}/(V_{free}T^b)$ since the reduced variable of "relative free volume", V_{hc}/V_{free} , is convenient. As with the Figure 2 inset showing results for PVAc, the correct choice of b in plotting $\log \tau$ vs. $V_{hc}/(V_{free}T^b)$ leads to a collapsed straight line for each of the seven substances and, once each data set is collapsed, the slope of the line (T^{*b}) yields a second material-specific parameter, T^* , which serves as a characteristic temperature, and the intercept, $\ln \tau_{ref}$, a third. Note that V_{hc} is fixed from the PVT analysis and thus is not determined from the system's dynamics data. Because the collapse is of known form (linear, not just a curve), this leads to a readily-formulated analytic expression for the relaxation times, given by

$$\ln \tau = \ln \tau_{ref} + (V_{hc}/V_{free})(T^*/T)^b \quad [4]$$

We emphasize that this simple 3-parameter expression describes broad PVT space; the 3-parameter VFT equation can only describe one single isobar or isochore. The values for the three system dependent parameters: τ_{ref} , T^* , b are compiled in Table 1. As an aside: natural logarithms of τ ($\ln \tau$) are used in eq 4 and thus define the numerical value of T^* , but on the y -axes of the plots we typically plot $\log \tau$ (the base 10 logarithm) to match with experimental presentations.

Our application of the analysis described by eq 4, is as follows: we start with a set of $\tau(T, P)$ results for a system of interest, for which we also have PVT data. Using our LCL EOS analysis we determine the hard-core volume, V_{hc} (which is a constant) and predict V_{free} values for the set of (T, P) conditions associated with the $\tau(T, P)$ data. Then, there are several options: one is simply to produce $\ln \tau$ vs. $V_{\text{hc}}/(V_{\text{free}}T^b)$ plots for varied b values (e.g. trial and error); the "optimized b " value is the one that yields the best collapse of the data. Once b is obtained, T^* and τ_{ref} are easily determined by a linear fit of $\log \tau$ vs. $V_{\text{hc}}/(V_{\text{free}}T^b)$. Alternatively a direct three parameter fit of the $\tau(T, V_{\text{hc}}/V_{\text{free}})$ points to eq 4 can be performed, obtaining all three parameters at once. While the latter method was the one we used to obtain the $b, T^*, \tau_{\text{ref}}$ parameter set corresponding to Figure 4 and Table 1, we have found there to be effectively no difference in the two "fitting routes", provided a good spread of experimental data.

The results we have presented in this work demonstrate a clear link between our predictions for free volume and dynamic relaxation. Our definition ($V_{\text{free}} = V - V_{\text{hc}}$) means that V_{free} changes *only* when the overall volume changes, since V_{hc} is a constant for a given system. There are other metrics for free volume, one of which is embodied in the Debye-Waller factor ($\langle u^2 \rangle$), a measure of the "rattle space" swept out by a segment on a picosecond time scale. It has been shown to be closely connected to segmental relaxation⁵⁵⁻⁵⁸ and links to master curves have also led to 3-parameter thermodynamic scaling formulations.^{52,53} We note that the Debye-Waller factor can change with temperature when the volume is fixed, thus it is distinct from the simpler free volume definition employed here.

Our free volume-based scaling (eq 4) shows considerable predictive potential. For example, it is common to have only ambient pressure relaxation data available, and would be

desirable to be able to make predictions for relaxation or viscosities at pressures or temperatures relevant to realistic processing conditions. Here are two examples of our approach applied in a predictive way.

A single ambient pressure data set can be fit to the three parameter eq 4 in much the same way as the three parameter VFT equation. We have tested this for the case of PVAc and found the resulting parameters to be reasonable: $\log \tau_{\text{ref}} = -9.48556$, $T^* = 395.913\text{K}$, $b = 4.5187$. The ambient P -only fit parameter set leads to a partial data collapse that would be good enough to predict the change in $\log \tau$ for say a 200 MPa increase in pressure with about 20% error.

There is an even more promising route, requiring only PVT and ambient pressure dynamics data, that begins by first resolving the b parameter. Consider (eq 4) under isochronic conditions: If we know T_g values for two pressures ('1' and '2') and take the common experimental condition that $\tau = 100\text{s}$ (i.e. it's the same value) at T_g at both pressures, then we can write

$$(T_2/T_1)^b = (V_{\text{free}}/V_{\text{hc}})_1 / (V_{\text{free}}/V_{\text{hc}})_2 \quad [5]$$

Again, eq 5 only applies to an isochronic point ($\tau_1 = \tau_2$), but it is not necessarily restricted to T_g .

In order to apply eq 5 we turn to PVAc. Using $dT_g/dP = 0.22 \text{ K/MPa}$ from PVT data,¹ we take $T_1 = T_{g,1} = 305\text{K}$ at $P_1 = 0.1 \text{ MPa}$, then consider for example, $P_2 = 100 \text{ MPa}$ such that $T_2 = T_{g,2} = 327\text{K}$. The LCL EOS can then be used to predict $V_{\text{free}}/V_{\text{hc}} = 0.1162$ (at $T_{g,1}$, 0.1 MPa) and $V_{\text{free}}/V_{\text{hc}} = 0.0897$ (at $T_{g,2}$, 100 MPa). Thus, with $V_{\text{free}}/V_{\text{hc}}$ values at these two T, P points, use of eq 5 yields $b = 3.71$. This b value can be tested by plotting $\ln \tau$ vs. $V_{\text{hc}}/(V_{\text{free}}T^b)$ for the full P -dependent data set, and doing so shows that it leads to very effective data collapse. Again, this required only bulk thermodynamic data (PVT data to obtain $V_{\text{hc}}/V_{\text{free}}$ values) and glass transition temperatures for two pressures (dT_g/dP , also accessible from PVT measurements) to fix b .

Using the PVAc atmospheric data (same data as in Figure 1) with $b = 3.71$ fixed, we apply a linear fit to the already collapsed data, and this yields the two remaining parameters $T^* = 420.133\text{K}$ and $\log \tau_{\text{ref}} = -10.0675$ (almost identical to T^* and $\log \tau_{\text{ref}}$ in Table 1). We can now

predict higher pressure results. For example, with $T = 373\text{K}$ this route predicts that in going from ambient pressure to 200 MPa, $\log[\tau]$ increases from -6.134 to -2.080 . Experimentally $\log[\tau]$ goes from -6.134 to -2.017 . Our predicted change is very close, differing from experiment by only 1.5%.

In future work, we will delve deeper into this free volume-based dynamics relationship and present a theoretical derivation, along with supporting simulation results. We will also explore ways to expand predictive power and convenience of application. We expect our analysis will lead to fundamental insight into the dynamic behavior of a broad swathe of experimental systems.

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