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Molecular Shape Dependent Model of Self-Diffusion in, and the Viscosity of, Large Molecule Liquid Systems: Viscosity, Temperature, and Pressure Relationships for Model Liquid Hydrocarbons

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Abstract: Our earlier molecular shape dependent theoretical model for self-diffusion in, and the viscosity of, liquids of large (nonpolymeric) molecules was modified to incorporate the effect of an applied pressure. In this model, the pressure acts to increase the activation energy for the fundamental molecular hopping event. For large molecule liquids, significant pressure is viewed as causing molecules to crowd against each other as the free volume available for site-to-site hopping decreases and intermolecular interactions become stronger. In this way, the number of translational and rotational degrees of freedom decreases and a decrease in the coefficient of self-diffusion and an increase in viscosity result. Theoretical predictions compared favorably with existing experimental viscosity data for flexible linear and rigid bulky hydrocarbon molecule liquids as a function of both pressure and temperature.

Introduction

The following work is a direct outgrowth of our recent efforts to formulate a hybrid free volume/energetics-based model for the diffusion of large molecules in amorphous polymers above T_g.[1-5] We define a "large" molecule to be one whose size is considerably greater than that of the polymer chain segments through which it is randomly migrating. The most distinguishing aspect of this model is its sensitivity to the conformation, that is, the detailed shape, of the diffusant molecule. The model was shown to apply rather well to the diffusion of phthalate and adipate plasticizers in rubbery PVC on comparison with experimental evidence.

Since the chain segments of the host polymer above T_g are in a dynamic liquidlike state, it was felt that the theory could be easily modified to model self-diffusion in pure liquids (nonpolymeric) in addition to the diffusion of liquids in liquidlike polymers.

On the basis of this idea, a molecular shape dependent model of self-diffusion in, and the viscosity of, large molecule liquid systems was established in previous literature by Wang, Mauritz, Storey, and Carter.[6] In the modified diffusion model, two basic assumptions are made: (1) Each molecule hops while in its minimum free energy conformation. (2) The thermal jump distance of a molecule from one equilibrium position to the next can be from 0 to infinity with a probability as given below.

$$P = \frac{Z\gamma A_i}{\nu_f}\,\frac{1}{1 + e^{-E_A/RT}}\,e^{-\gamma A_i l_i/\nu_f}e^{-E_A/RT} \qquad (1)$$

A_i (i = 1, 2, or 3) is the maximum cross-sectional area of the molecule in a plane that is perpendicular to its ith principal axis of inertia. To avoid confusion in understanding the definition of this geometrical parameter, we point out that A_i is *not* the greatest cross-sectional area presented by the molecule overall, but is the maximum value along the direction i. Of course, these three axes intersect at the center of mass of the molecule. It is natural to describe the translational motion of a particle in terms of the displacement of the center of mass. Consider all such planes that intercept the ith axis within the steric volume of the molecule. A_i, precisely, is an area bounded by the piecewise-continuous closed curve consisting of circular arcs whose radii are the van der Waals radii of the outer atoms of the molecule. This closed curve exists in a plane that is perpendicular to the ith principal axis. If such a perpendicular plane can be envisioned as sliding along the ith axis, then A_i is the largest possible area bounded by the above-described closed curve. In essence, A_i is the minimum area in a plane normal to the hopping direction of the molecule that must be swept clear of nearest neighbor molecules in order for a significant displacement of the center of mass to take place. A "significant displacement" is meant to be one of a magnitude greater than that corresponding to thermal vibrational excursions within a closed cage formed by nearest neighbor molecules, as described in cell theories of the liquid state, but one not greatly smaller than the dimensions of the molecule. It is seen in eq 1, and it is intuitive that the probability of hopping in the direction i increases with decreasing A_i. The jump distance along the ith principal axis is l_i, γ is an unspecified dimensionless factor accounting for both the overlap of free volume and the correction of the cross-sectional area, ν_f is the temperature-dependent average free volume per molecule, Z is the molecular "coordination number" (based on the concept of a "loose" liquid lattice; specifically, Z is the number of adjacent sites which can spontaneously, through thermal fluctuation, form a hole into which the molecule can jump along its principal axes), R is the gas constant, T is the absolute temperature, and E_A is the activation energy, that is, the height of the energy barrier over which a molecule must jump to reach a sufficiently-large adjacent hole.

The A_i values were calculated using the x, y, and z coordinates of the atoms of the molecule in its minimum energy conformation, as described in our early work involving the diffusion of plasticizers in rubbery PVC.[3,4] Minimum-energy conformations were determined using the CHEMLAB-II molecular mechanics software system.

The allowance for jump distances that are but a fraction of the molecular dimensions is motivated by the fact that the molecules of interest are so large that the probability of creating an adjacent free volume pocket large enough to accommodate the entire molecule is very low.

The coefficient of self-diffusion obtained from this model is then given by the following expression:

$$D = \frac{Z}{6\gamma}\left(\frac{RT}{M}\right)^{1/2}\frac{\nu_f}{1+ e^{E_A/RT}}\left(\frac{1}{A_1} + \frac{1}{A_2} + \frac{1}{A_3}\right) \qquad (2)$$

M is the molecular weight. The sum of the reciprocal A_i values in parentheses is a geometrical, conformation-dependent factor

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(1) Mauritz, K. A.; Storey, R. F.; George, S. E. *Macromolecules* **1990**, *23*, 441.

(2) Mauritz, K. A.; Storey, R. F. *Macromolecules* **1990**, *23*, 2033.

(3) Coughlin, C. S.; Mauritz, K. A.; Storey, R. F. *Macromolecules* **1990**, *23*, 3187.

(4) Coughlin, C. S.; Mauritz, K. A.; Storey, R. F. *Macromolecules* **1991**, *24*, 1526.

(5) Coughlin, C. S.; Mauritz, K. A.; Storey, R. F. *Macromolecules* **1991**, *24*, 2113.

(6) Storey, R. F.; Mauritz, K. A.; Carter, M. L.; Wang, D. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32* (1), 130. Wang, D.; Mauritz, K. A.; Storey, R. F. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32* (3), 269. Wang, D. Ph.D. Dissertation, University of Southern Mississippi, 1991, University Microfilms, Ann Arbor.

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that is an index of overall molecular *shape*. This shape factor also arises from the fact that the molecules are large.

Then, the coefficients of viscosity and self-diffusion are inversely linked through Perrin's equation for ellipsoids:[8]

$$\eta = \frac{kT}{6\pi R_0 F D} \tag{3}$$

where R_0 is an equivalent radius that corresponds to a sphere having the same volume as that of the large molecule, F is a shape factor which characterizes the deviation of molecular shape from sphericity, k is the Boltzmann constant, and η is the coefficient of viscosity. F is a function of the semiaxes of ellipsoids that are fitted to the actual, more complex shape of the molecule in its minimum-energy conformation. The shapes can range from oblate through prolate spheroids depending upon whether the molecule is flat, extended, or compacted, overall. The reader is directed to our previous reports[6] for a discussion of the details of this calculation. To the best of our knowledge, eq 3 is the only means of relating η to D. To be sure, one can question whether spheroids can be fitted to molecules of any shape. Our experience is such that this particular geometric representation appears to be reasonable upon inspecting the actual minimum-energy molecular shapes of interest in the CPK (space-filling) graphical representation. In any case, we are unaware of representations of F in terms of other symmetrical, let alone nonsymmetrical geometries.

In fact, this model has been demonstrated to be rather successful in predicting the viscosities of several liquid phthalate and adipate plasticizer systems in our previous paper. The proven ability to differentiate between molecules that are very close in structure, in this way, provided significant reinforcement of the theory's credibility. These positive initial results have encouraged us to test the general theory on other large molecule liquids to establish its generality of application. In this work, we are particularly interested in molecules that are large, but structurally simpler than the two-chained, more complex phthalate and adipate systems. Our search of the literature has uncovered viscosity data for simple linear single chain or cyclic liquid hydrocarbons not having strongly-interacting functional groups, as a function of temperature and pressure.

Molecular Model

Compared with the previously-studied phthalate and adipate liquids, the hydrocarbon molecules in this work are simpler and possess more regular shapes. Experimental η vs temperature and pressure data for a number of bicyclic and n-alkane liquids can be found in a paper by Hogenboom, Webb, and Dixon.[9] The linear hydrocarbons n-C_{12}, n-C_{15}, and n-C_{18} that were studied are essentially in random but noncoiled or nonfolded unsymmetric molecular conformations. On the other hand, the *cis*- and *trans*-decahydronaphthalene molecules in their liquids, also studied by these investigators, are rather rigid[10] and symmetric in shape. We have determined the minimum-energy conformations for these particular molecules using the CHEMLAB II molecular mechanics software system in a fashion as described in our earlier work.[3-7] The space-filling molecular projections onto the planes that are perpendicular to the three principal axes for n-C_{12} and *cis*-decahydronaphthalene in their calculated minimum free energy conformations are shown in Figures 1 and 2, respectively. It is seen in Figure 1 that n-C_{12}, while certainly not in an all-trans state, is rather extended. One might envision that this molecule might have its translational displacements restricted to being mainly along the extended chain in either direction. On the other hand, the cross sections presented along the three principal axes of *cis*-decahydronaphthalene, as seen in Figure 2, do not greatly differ from each other, and it would seem that this molecule can hop with more equal facility in three mutually-orthogonal directions.

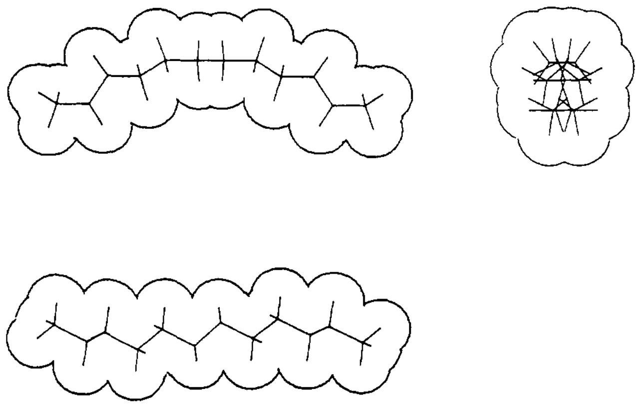

Figure 1. Space-filling projections of the n-C_{12} molecule, in its minimum free energy conformation, along its three principal axes of inertia.

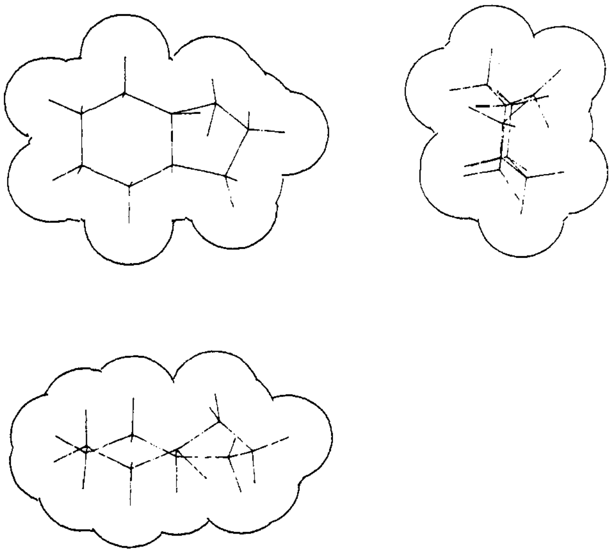

Figure 2. Space-filling projections of the *cis*-decahydronaphthalene molecule, in its minimum free energy conformation, along its three principal axes of inertia.

Due to the rather regular shapes of these hydrocarbon molecules, in contrast with the more complex convoluted shapes of phthalate and adipate molecules, the jump distance of a molecule along its ith principal axis is assumed to continuously vary from $(A_i)^{1/2}$ to infinity with different probabilities. This assignment would have little meaning if the area A_i included, for example, considerable fingerlike projections, that is, if A_i were bounded by a general curve having drastic undulations. In presenting this idea, we are in fact borrowing from the earlier concept developed by Eyring in his analysis of the viscosities of long chain hydrocarbons, namely, that the unit of flow for long unbranched chains is but a fraction of the entire molecule.[11] $(A_i)^{3/2}$ is approximately the volume of the minimum-sized hole that would permit a *significant* jump. This assumption leads to the following expression for the average jump distance of a molecule along its ith principal axis:

$$\bar{l}_i = \int_{A_i^{1/2}}^{\infty} P l_i \, \mathrm{d}l_i \tag{4}$$

where P is given by eq 1. Given this, the hypothetical one-dimensional coefficient of self-diffusion along the ith pricipal axis is

$$D_i = \frac{\bar{l}_i}{2} u \tag{5}$$

where $u = (RT/M)^{1/2}$ is the average velocity of one-dimensional

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(7) Coughlin, C. S. Ph.D. Dissertation, University of Southern Mississippi, 1990.

(8) Perrin, F. *J. Phys. Radium (Ser. 7)* **1934**, *5* (10), 497, 510.

(9) Hogenboom, D. L.; Webb, W.; Dixon, J. A. *J. Chem. Phys.* **1967**, *46* (7), 2586.

(10) Moniz, W. B.; Dixon, J. A. *J. Am. Chem. Soc.* **1961**, *83*, 1671.

(11) Glasstone, S.; Laidler, K. J.; Eyring, H. *The Theory of Rate Processes*; McGraw-Hill: New York, 1941; pp 497–500.

thermal molecular motion, given the existence of a sufficiently-large adjacent transient hole. Following the same reasoning as in our previous report,[6] the overall self-diffusion coefficient is given by

$$D = \frac{1}{3}\sum_{i=1}^{3} D_i = \frac{Z}{6\gamma}\left(\frac{RT}{M}\right)^{1/2} \frac{\nu_f}{1 + e^{E_A/RT}} \sum_{i=1}^{3} B_i \tag{6}$$

where

$$B_i = \frac{1}{A_i}\left(1 + \frac{\gamma A_i^{3/2}}{\nu_f}\right) e^{-\gamma A_i^{3/2}/\nu_f} \qquad i = 1, 2, \text{ or } 3 \tag{7}$$

γ is assigned an average value of 0.75 in this work since these hydrocarbon molecules have relatively regular shapes. In any case, there is no a priori basis for selecting a particular value for this ubiquitous parameter that is often assigned the value of unity in practice. Furthermore, the allowable range of variance ($0.5 \leq \gamma \leq 1.0$) is not great.

The summation over the three B_i values in eq 6 is a purely geometrical factor that is a function of *molecular shape* and the available free volume. The quantity $[(A_i)^{3/2}]/\nu_f$ can roughly be viewed as the fractional free volume requirement for a successful molecular jump. Obviously, high values of $\sum B_i$ achieved through lowering the values of A_1, A_2, and A_3, overall, will contribute toward a high coefficient of self-diffusion. Molecules that are rather elongated will possess one very small value of A_i that can make $\sum B_i$ quite high. In this way, this self-diffusion model is sensitive to molecular shape.

For the linear molecules n-C_{12}, n-C_{15}, and n-C_{18}, rotational motion, that is, unrestricted tumbling, cannot take place because of the large difference between longitudinal and lateral molecular dimensions. Translational motion of such a molecule would essentially be restricted to back and forth hopping along the general chain direction, as discussed earlier. Of course, the chain direction itself is constantly undergoing reorientation because of thermal agitation imparted by adjacent molecules. Therefore, Z is reasonably assumed to be equal to 2 for the linear hydrocarbon molecules. For *cis*- and *trans*-decahydronaphthalene molecules, however, since the lateral dimensions are about the same, two-dimensional rotation about the remaining dimensional axis is more likely to occur. Assume now that the time scale of rotational motion is shorter than that associated with site-to-site jumping. Then, the effective cross sections perpendicular to the principal axes of this molecule have equal probability to face four nearest neighbors if a cubic lattice model is considered. Therefore, Z is given a value of 4 for this type of molecule at atmospheric pressure.

To be sure, the assignment of coordination numbers, let alone the representation of dynamic amorphous liquid structures by a lattice construct, can be questioned. Z, within our view of this particular system, is merely a reasonable estimate of the time-averaged state of nearest neighbor packing about a given molecule. One would expect that there would be a distribution of Z over the ensemble of molecules owing to a microscopic distribution of free volume and that Z can therefore assume nonintegral values. It is important to point out that Z in this work is not of the usual "static" variety, but is dynamic in the sense of only counting the directions in which the molecule is capable of hopping. As the pressure on the liquid increases and the molecules become more crowded, it is reasonable to expect that Z, so defined, decreases in monotonic fashion. While the Z vs P relationships for the liquids analyzed in this work are not known on either a direct experimental or theoretical predictive basis, we suggest simple relationships based on an inspection of the experimental pressure–volume curves.

In Figure 3 we have graphed applied pressure vs molar volume for n-C_{12} liquid at 37.8 °C using data taken from the tabulation of Hogenboom, Webb, and Dixon.[9] It is seen that the data are very well represented by an equation of the form $P = a - bv + cv^2$, where the values of a, b, and c are listed in the figure. It is seen that, with increasing pressure, the quantity $(\partial v/\partial P)_T$ decreases until it becomes rather constant. This behavior is typical for the hydrocarbons and indicates that the resistance of the liquid to volume deformation increases with increasing P. We suggest that the linear behavior in the high-pressure regime describes a liquid "rigidity" that reflects molecular crowding accompanied by (1) a decrease in the number of translational and rotational degrees of freedom and (2) an increase in overall intermolecular interaction strength. An intermolecular, orientation-averaged potential energy curve arising from attractive (strictly van der Waals, in this case) and repulsive forces would crudely appear as seen in Figure 4. Owing to thermal kinetic energy, the molecules would lie, on the average, on the curve to the right of the mininum. An increase in pressure would move the ensemble-averaged separation distance closer to the minimum point, that is, the molecules will "stick" to each other to a greater degree. We assume here that the P–V work performed on the liquid is absorbed more or less uniformly by all such intermolecular nearest neighbor secondary "bonds". Only nearest neighbors need be considered for these systems because of the short-range nature of the predominant dispersion interactions. In short, the P–V work performed on the liquid raises the energy of activation for molecular self-diffusion.

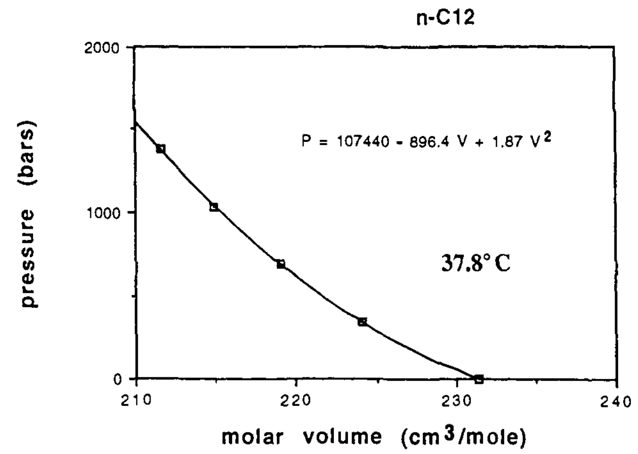

Figure 3. Applied pressure vs molar volume for liquid n-C_{12} at 37.8 °C.[9] For this, as well as for other hydrocarbons, the curve becomes more linear at higher pressures.

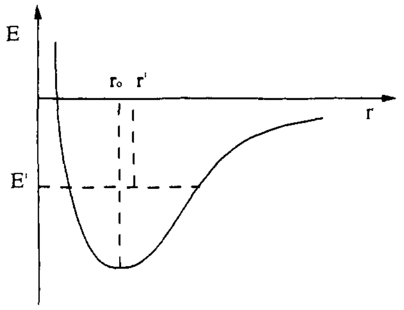

Figure 4. Hypothetical, orientation-averaged intermolecular potential energy curve. Due to thermal molecular kinetic energy of translation, the ensemble-averaged intermolecular separation distance, r', is greater than r_0. r' increases with increasing T at constant P and decreases with increasing P at constant T.

We note somewhat of a historical precedent for this concept in the very early work of Ewell, Eyring, Frisch, and Kincaid.[12,13] If E_{act} is the activation energy for viscosity (a quantity similar to, but not neccessarily the same as, our definition of E_A) as determined by experiment at atmospheric pressure, then an applied pressure $P > 1$ atm increases E_{act} by an amount Pv/n', where v is the original molar volume and n' is defined so that v/n' is the activated molar volume required for flow. It was seen by these investigators in the case of n-pentane at 30 °C, for example, that n' increased from 6.0 to 10.8 as the pressure increased from 10^3 to 10^4 kg/cm^2. The method of extracting n' from experimental η vs P data in conjunction with the use of simple activated rate theory is explained in the two above-cited references. The

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(12) Ewell, R. H.; Eyring, H. *J. Chem. Phys.* **1937**, *5*, 726.
(13) Frisch, D.; Eyring, H.; Kincaid, H. F. *J. Appl. Phys.* **1940**, *11*, 75.

straightforward interpretation of the results of this rather simple approach can be summarized by the following equivalent statements regarding the application of pressure: (1) The ensemble-averaged, temperature-activated volume into which molecules can hop decreases. (2) The number of possible jump directions available for the molecule decreases (related to our above-mentioned concept of a decrease in rotational and translational degrees of freedom with increasing pressure). (3) The number of molecular "holes" distributed throughout the liquid decreases.

Returning to our theoretical model, as the applied pressure increases beyond 1 atm, rotational motion is considered as becoming increasingly restricted for the decahydronaphthalene molecule and the value of Z is assumed to drop from 4.00 at 1 atm to 2.00 at "sufficiently large" pressures. Of course, on inspecting Figure 2, it is obvious that the decahydronaphthalene molecule possesses higher symmetry, i.e., is more "round", than the *n*-alkane molecules of interest, but even at atmospheric pressure might execute somewhat restricted tumbling in the liquid state. More so under high stress, owing to the inevitable crowding of these molecules, the deviation of their shape from sphericity must strongly influence liquid physical properties. For this reason, we subtract 2 from the 6 possible hopping possibilities on a cubic lattice to reflect this concept *at atmospheric pressure*. In other words, molecular displacement, in either direction, along the principal axis having the greatest A_i is assumed largely prohibited. Hence, the subtraction of 2 from 6 at atmospheric pressure. We are expressing the view that molecular motions become increasingly inhibited in the sense that hopping along axis k will essentially cease before hopping along axis m, with increasing pressure, if $A_k > A_m$. In considering the net hopping displacement as the vector sum of three orthogonal component displacements along the principal inertial axes and allowing the molecule to hop along each of the three axes in either of the two directions, it is our view that a steady and sufficient increase in pressure will first cause 2, and then 4, degrees of hopping freedom to be subtracted from the original (hypothetical) value of 6. The graph of the experimental P vs v data for decahydronaphthalene[9] is similar to those of the *n*-alkanes, again following the relationship $P = a - bv + cv^2$, and our conclusions regarding molecular packing and molecular hopping trends are essentially the same as those just discussed. This graph, in fact, was used as a rough guide to assign values of Z at different pressures, that is to say, the decreasing trend of Z with increasing pressure was linked to v vs P trends by noting the linear and curved graphical domains. Accordingly, the values of Z for decahydronaphthalene are assumed to be 4.0, 3.5, 3.0, and 2.8 at the external pressures of 1 atm and 400, 800, and 1200 bar, respectively. We stress that these four numbers are "estimates" based upon the above discussion of molecular crowding as a function of applied pressure. Note that we have caused Z to decrease by equal amounts for the first two equal pressure increases. However, at the highest pressure, the liquid is less compressible so that the final and equal pressure increase is not considered to diminish Z by the same increment as for the two previous pressure increases, but by a lesser amount. Strictly speaking, Z should be a function of temperature as well as pressure, but this complication will be reserved for consideration as a model refinement in a future study.

ν_f is a function of both temperature and pressure and is derived from the difference between the total and the steric ("hard") volume per molecule. The total volume per molecule is simply obtained from the experimental density data of Hogenboom, Webb, and Dixon[9] and of Cutler, McMickle, Webb, and Schiessler.[14] The steric volume is determined using a model the authors presented in previous literature.[6] In this model, it is assumed that the steric volume does not depend on pressure, but on temperature. Each of the chemically-bonded atom pairs in the large molecule is considered to vibrate as a simple harmonic oscillator. The time-averaged shapes of all bonded vibrating atoms are considered to be ellipsoidal, and the lengths of the semiaxes are determined by the van der Waals radii, bonding force constants, and the resultant amplitudes of vibration. Of course, as the temperature increases, these vibrations gradually sweep out a greater effective hard volume for the molecule. Hypothetically, this volume is largely independent of molecular conformation as the vibrations are localized within single chemical bonds. Of course, these individual bond vibrations are coupled in theory, but it is reasonable to expect that the molecular conformation will affect the vibrational modes, and therefore the hard volume, in a minor way, at best.

Table I. Calculated Free Volume per Molecule of n-C_{12} Liquid as a Function of Temperature and Applied Pressure

	ν_f (Å^3/molecule)			
T (°C)	1 atm	400 bar	800 bar	1200 bar
37.8	126.2	112.8	102.6	95.4
60.0	133.7	119.5	108.4	99.9
79.4	140.5	124.3	112.1	102.9
98.9	147.8	130.0	116.5	106.6
115.0	154.5	135.3	121.0	110.6
135.0	163.5	141.1	124.9	113.5

A major outcome of this model is that the steric volume of a molecule is proportional to the square root of the temperature around and below room temperature. For example, the calculated values of ν_f for n-C_{12} at different temperatures and pressures are given in Table I. These ν_f values were utilized in the subsequent calculation of D and η.

Adjustment of Viscosity Activation Energy for $P-V$ Work. If the temperature range of interest is not extremely broad, the activation energy for viscosity can be considered as a function of pressure only. At atmospheric pressure, the activation energies of our systems were experimentally determined in the same manner as for the phthalate and adipate plasticizer liquids, as described earlier.[6] As the applied pressure increases, the average intermolecular spacing becomes smaller, and intermolecular interactions consequently become stronger. The enhanced attractive forces serve to raise the energy required to activate the hopping of molecules to adjacent pockets of free volume. The increase of the intermolecular interaction energy, ΔW, of the liquid due to an increase in applied pressure is given in the usual way:

$$\Delta W = -\int_{v_1}^{v_2} P\,dv \tag{8}$$

where v_1 and v_2 are the initial and final volumes of the system, respectively, and P is a monotonically decreasing function of volume (e.g., $a - bv + cv^2$, for the systems of interest in this work). If experimental P vs v data are available, the above integral can be determined numerically. When the change in P is not very large, eq 8 can be expressed approximately by the following simple expression:

$$\Delta W = P\Delta V \tag{9}$$

where $\Delta V = v_1 - v_2$, and P is the average pressure applied during the volume change, or say, the pressure that maintains the volume at v_2.

In order to determine the upward shift in the viscosity activation energy barrier corresponding to a given ΔW applied to the liquid, it is necessary keep an accounting of the number of nearest neighbor intermolecular interactions, L. Realize that this quantity is not neccessarily the same as Z. If N is the total number of molecules in a system, then the total number of nearest neighbor intermolecular interactions, M, is given by

$$M = \frac{L}{2}N \tag{10}$$

The increase in interaction energy per nearest neighbor bond is given by the following equation:

$$\Delta\epsilon = \frac{\Delta W}{M} = \frac{2\Delta W}{LN} \tag{11}$$

The increase in the flow activation energy, ΔE, is approximately

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(14) Cutler, W. G.; McMickle, R. H.; Webb, W.; Schiessler, R. W. *J. Chem. Phys.* **1958**, *29* (4), 727.

Table II. Activation Energy Increase, ΔE, vs Applied Pressure, P, for n-C_{12} Liquid

P (bar)	1 atm	400	800	1200
ΔE (kJ/mol)	–	0.642	0.934	1.793

Table III. Viscosity Activation Energies, E_A, of Liquid Hydrocarbons

compd	E_A (kJ/mol)
n-C_{12}	10.49
n-C_{15}	11.29
n-C_{18}	13.54
trans-decahydronaphthalene	11.61
cis-decahydronaphthalene	11.42

equal to the sum of the contributions from all intermolecular interactions within the liquid, or

$$\Delta E = L\Delta\epsilon = \frac{2\Delta W}{N} \tag{12}$$

ΔE in eq 12 is expressed on a *per molecule* basis. Since activation energies are usually expressed on a per mole basis, we write

$$\Delta E = \frac{2\Delta W_A}{N_A}N_A = 2\Delta W_A \tag{13}$$

where N_A is Avogadro's number and ΔW_A is calculated via eq 8 using experimental pressure–volume data employing *molar* volumes. As an example, the increases of activation energy for n-C_{12} liquid at different above-atmospheric pressures, calculated through the use of eqs 8, 9, and 13, are listed in Table II. Then, the total pressure-modified activation energy is $E_A + \Delta E$, where E_A, as before, is the activation energy at atmospheric pressure.

E_A was determined from the slope of the linear plot of ln (η/B_0) vs $1/T$, where B_0 is given by

$$B_0 = \frac{\sqrt{T}}{\nu_f\left(1 + \dfrac{\gamma A_i^{3/2}}{\nu_f}\right)} \tag{14}$$

In combining eqs 3, 6, and 7, it is seen that the preexponential factor in the resultant expression for η is a function of both T and ν_f, which in turn is a function of T. When the experimental data is plotted in this fashion, the true rather than apparent activation energy is obtained as

$$E_A = R(\text{slope}) \tag{15}$$

This graphical treatment, of course, is based on the assumption that the temperature dependence of the preexponential factor in the theoretical viscosity equation is correct. It was our observation that this is the case. The derived values of E_A for the hydrocarbons in this study are listed in Table III.

It is seen, on comparing Tables II and III, that the activation energy for n-C_{12} increases by about 17% upon increasing the pressure from 1 atm to 1200 bar. This is a significant increase.

Results and Discussion

In calculating the theoretical viscosities of the n-alkane and decahydronaphthalene liquids using the mathematical model outlined above, the only required experimental input parameters were specific volume vs T data and viscosity activation energies derived as explained above. In these calculations the temperature range was 15.56–135.0 °C, and the pressure ranged from 1 atm up to 1200 bar, corresponding to the ranges within the available experimental data. Despite the rather broad range of temperatures, the deviation of predicted from experimental viscosity is less than 3.4% for n-C_{12} and *cis*-decahydronaphthalene, less than 3.9% for n-C_{15}, less than 3.1% for n-C_{18}, and less than 6.5% for *trans*-decahydronaphthalene liquids at 1 atm. The accuracy of viscosity prediction is roughly the same for all of the tested molecules, *regardless of their size or shape*, although the agreement of the *trans*-decahydronaphthalene values is a little poorer. The values of the predicted alongside the corresponding experimental viscosities taken from ref 9 are listed in Table IV. An inspection of this table reveals that the theoretical viscosities track the experimental values very closely throughout and that there are no systematic deviations of the theoretical from experimental values either with temperature at constant pressure or with pressure at constant temperature. The activation energies used in calculating the viscosities at P = 400 bar were obtained using the combination of eqs 9 and 13. The constant pressure assumption apparently gives a rather good approximation for ΔE at relatively low pressures. The combination of eqs 8 and 13 was used to determine ΔE at 800- and 1200-bar pressure. The considerable variability in P from atmospheric up to this high pressure

Table IV. Predicted/Experimental Viscosities of Liquid Hydrocarbons

compd	T (°C)	viscosity (cP) 1 atm	400 bar	800 bar	1200 bar
n-C_{12}	37.78	1.14/1.102	1.77/1.70	2.35/2.50	3.74/3.52
	60.00	0.819/0.803	1.23/1.23	1.65/1.75	2.60/2.39
	79.44	0.631/0.63	0.965/0.98	1.28/1.36	1.99/1.82
	98.89	0.497/0.516	0.755/0.80	1.00/1.11	1.54/1.46
	115.0	0.411/0.41	0.623/0.69	0.825/0.97	1.26/1.26
	135.0	0.330/0.34	0.505/0.58	0.677/0.82	1.02/1.07
n-C_{15}	37.78	1.96/1.953			
	60.00	1.38/1.335	2.18/2.10	3.02/3.11	5.19/4.37
	79.44	1.04/1.01	1.66/1.56	2.30/2.27	3.87/3.14
	98.89	0.806/0.796	1.28/1.24	1.78/1.75	2.95/2.37
	115.0	0.656/0.67	1.04/1.06	1.45/1.48	2.38/1.98
	135.0	0.519/0.54	0.829/0.87	1.16/1.22	1.88/1.60
n-C_{18}	60.00	2.06/2.06	3.26/3.40	4.47/5.07	7.32/7.28
	79.44	1.52/1.48	2.37/2.40	3.26/3.54	5.29/4.93
	98.89	1.15/1.15	1.79/1.81	2.45/2.64	3.92/3.65
	115.0	0.929/0.94	1.45/1.49	1.98/2.12	3.12/2.92
	135.0	0.727/0.75	1.13/1.19	1.55/1.67	2.40/2.26
cis-decahydronaphthalene	15.56	3.68/3.71	5.95/6.59	9.21/10.7	14.6/17.3
	37.78	2.37/2.31	3.82/3.76	5.91/5.81	9.19/8.81
	60.00	1.60/1.57	2.61/2.57	4.05/3.95	6.29/5.89
	79.44	1.18/1.17	1.92/1.93	3.00/2.84	4.60/4.05
	98.89	0.885/0.916	1.47/1.50	2.30/2.19	3.50/3.06
trans-decahydronaphthalene	15.56	2.45/2.30	3.86/3.76	5.79/5.84	8.93/8.81
	37.78	1.62/1.55	2.54/2.45	3.81/3.70	5.83/5.38
	60.00	1.12/1.114	1.78/1.76	2.67/2.58	4.05/3.63
	79.44	0.839/0.86	1.34/1.35	2.01/1.94	3.04/2.70
	98.89	0.644/0.696	1.04/1.08	1.57/1.53	2.34/2.12

necessitates the use of the work integral.

From the observation, in Table IV, that our predicted viscosities closely follow the experimental values with both temperature and pressure variance, it is concluded that this model, while in an initial stage of development, is rather successful. It is generally true that in past as well as contemporary efforts to predict coefficients of diffusion and viscosity, "success" is usually viewed as the ability to predict general trends while being in the correct order of magnitude. There are numerous entries in Table IV that lead to the conclusion that the model presented here is uncommonly accurate.

We are concerned, of course, that a number of model refinements be implemented in the future. A significant improvement would reside in the calculation of E_A from fundamental molecular energetics, rather than depending on the availability of, or need to generate, experimental values. The reliance on experimental viscosity activation energies is a great encumbrance in the use of this model in a purely predictive mode. In an earlier effort to model the above-T_g diffusion of large molecules through rubbery polymers we introduced the concept of *reverse solvation* and a method of determining polymer–penetrant energetics for the purpose of calculating diffusion activation energies.[4] Perhaps this approach, which incorporates a temperature dependence and is sensitive to the size, shape, and chemical identity of the diffusant molecule, might also be applicable within the similar context of self-diffusion in large molecule liquids. In this way, intermolecular interactions would be accounted for in a rather explicit way.

As in our work with large molecule diffusion in rubbery polymers, there remains the rather basic question of whether the diffusant molecule in reality undergoes site-to-site hopping *in its minimum-energy conformation.* One might imagine that, given sufficiently-low bond-rotational potential energy barriers at liquid-state temperatures, the hopping molecule will be rapidly exchanging between two or more low free energy conformations in a state of dynamic equilibrium. One might then pose the question as to whether one of these higher-energy, although probable, conformations might present a shape that results in a higher diffusion coefficient. As diffusion is mainly a random process that seeks to maximize entropy, investigators may do well in the future to inspect molecular conformations that maximize D in addition to those which minimize the conformational energy. Fortunately, the molecular shape sensitivity explicitly factored into our model makes this analysis possible. Ultimately, the computation of a value of D that constitutes a Boltzmann average over an ensemble of most-probable conformations at a given liquid temperature might be the most complete and realistic approach in this simulation.

The requirement for liquid specific volume vs temperature data does not pose a very serious problem, although a lack of availability of experimental isothermal P vs specific volume data would be a considerable inconvenience if it were required that this information be generated independently.

It was also evident in an earlier discussion that a more rational procedure for determining the parameter Z, as well as its dependence on pressure and temperature, is needed as its present assignment is rather intuitive.

Finally, and especially with regard to elongated molecules in liquids under high pressure, the effect of high shear, i.e., hydrodynamic orientation, would need to be factored into the model for some important applications.

The primary and modest goal of this paper was to present a reasonable prototype model for the viscosities of large molecule liquids that is explicitly sensitive to molecular structure as well as to important thermodynamic state variables such as temperature and pressure. While we earlier reported on the mathematical modeling of diffusion in, and viscosity of, large molecule systems, the work reported here is our first attempt to factor the effect of pressure into the model.

Given the encouraging results of this exploratory study as well as the rather good results earlier exhibited in predicting the viscosities of single and mixed plasticizers, we feel that these simulations can be of practical use in a number of industrial arenas involving material design and process optimization. We envision, for example, useful applications in the important industrial areas of coatings and lubricant additive technologies, and in the dryblending of polymer resin particles with plasticizers.