

A Modern Approach to the Solution and Analysis of the Simha-Somcynsky Model for the Description of Pressure-Volume-Temperature Properties of Polymer Fluids*

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Abstract We revisit the Simha-Somcynsky model of polymer fluids with the purpose of developing novel theoretical and computational approaches to simplify and speed up its solution as well as the fitting of experimental data, and decrease its level of mathematical complexity. We report a novel method that allows us to solve one of the two equations of the model exactly, thus putting the level of mathematical difficulty on a par with the one of other models for polymer fluids. Moreover, we describe a computational algorithm capable of fitting all five parameters of the model in an unbiased way. The results obtained reproduce literature results and fit experimental pressure-volume-temperature and solubility parameter data for three polymers very accurately. Moreover, the new techniques allow for the investigation of the model at very low temperatures. Unexpectedly, the model predicts behaviors that could be interpreted as a glass transition, as routinely observed in dilatometry and differential scanning calorimetry, and a glass phase. We compared the predicted and experimental T_g 's for *cis* poly(1,4-butadiene) and found an excellent quantitative agreement.

Keywords: Simha-Somcynsky model; PVT properties; Polymer fluids.

INTRODUCTION

For many decades now pressure-volume-temperature, a.k.a. PVT, data have provided a plethora of important information and understanding about the physical behavior of polymeric materials. Indeed, PVT data have been used in many areas of polymer science and engineering like in the optimization of processing parameters in injection molding (instead of determining them by trial and error); in the prediction of polymer-polymer miscibility; in the determination of the reducing parameters of the various equations of state, a.k.a. EOS, used to describe the experimental PVT data; in the prediction of the service performance and service life of polymeric materials and components; in the computation of the surface tension of polymer liquids; in the investigation of the nature of phase transitions in polymeric materials and others^[1, 2]. For example, in the case of injection molding PVT data can be used to understand the compression phase during which the polymer melt is compressed before being released when the nozzle opens. PVT data also allow for the evaluation of the melt quantity or shot weight required to fill the mold as well as the end pressure which is the minimum required pressure to fill the mold^[3].

In more recent times, there has been a renaissance of interest in PVT data, their measurement and analysis thanks to hydraulic fracturing, a.k.a. fracking, and its application in the oil and natural gas industry. This industrial process involves millions of gallons of fluid pumped into the oil and gas well at very high pressures to crack the rock formation and allow for the flow of oil and gas to the wellbore^[4]. Although 99% of the fluid is

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water, it also contains chemical additives, friction reducers, and others^[5, 6]. Some of the compounds used in fracturing fluids are polymeric in nature like polyacrylamide and guar gum^[7]. As recent as 2012 during the BIOPLASTEK forum meeting a new idea was discussed: the development and use of novel biopolymers for fracturing fluids to avoid or reduce well-documented water contamination from drilling^[8, 9]. Understanding the PVT properties of these unexplored polymers will be crucial to understand the behavior of the whole fluid mixture.

This renewed interest in PVT data, measurements and analysis motivated this work. There have been numerous EOS developed for polymeric fluids^[10–18]. However, a previous study by Rodgers^[19, 20] has shown that the Simha-Somcynsky hole theory, SS model^[11, 12], and the modified cell model^[16, 17] give the best fit of the polymer liquid PVT data over a wide range of temperatures and pressures. Therefore, we consider the SS model in this article and leave the modified cell model for a future publication.

The main goal of our work is three fold. First, we employ modern computational tools and methods to carry out a complete study of the SS model. Surprisingly, we found predictions of the model not published before like a transition that has all the characteristics of the glass transition as observed experimentally. Second, we propose a novel mathematical approach that reduces the complexity of the model from two non-linear algebraic equations to only one; thus putting the model on the same level of complexity as the other PVT EOS mentioned before that are described by only one equation. Third, we have developed a novel computational algorithm to solve the model and fit the experimental data that fits all five parameters of the model simultaneously. This is a significant improvement over the traditional route to fit the experimental data where a fit to low pressure data is done first, thus biasing the fitting to low pressures, and a subsequent second fit is done to fit high pressure data under the assumption of the molecular weight being infinite and the ratio of the external degrees of freedom being equal to one third of the number of statistical (Kuhn) segments^[21–24]. These assumptions cannot be justified *a priori*.

This article is organized as follows. In the next section we give a complete description of the theoretical foundations of the SS model without going into the details of the calculations which can be found in the original article^[11]. We provide explicit mathematical expressions for the Helmholtz free energy, EOS, entropy, internal energy and equilibrium condition. Next we give the mathematical details of the procedure to reduce the number of equations that define the model, *i.e.* EOS and equilibrium condition, to only one since the EOS can be solved exactly. Finally, we give the details of the parallel algorithm we have developed to solve the model numerically and mention how it could be optimized even further. The results section describes how the reduced thermodynamic quantities predicted by the model depend on the reduced temperature and pressure, and our analysis of them. These quantities include the EOS, occupied volume fraction, entropy, solubility parameter, thermal expansion coefficient, isothermal compressibility, and heat capacity at constant pressure. We also compare the PVT behaviors and solubility parameters of three polymers, Nylon 6,6, *cis* poly(1,4-butadiene) and poly(ethylene oxide), with experimental data. We end this article with the conclusion section.

THE THEORETICAL MODEL AND ANALYSIS

Review of the Simha-Somcynsky Model

The fundamental concepts upon which the Simha-Somcynsky model, a.k.a. SS model, is constructed can be found in the more general field of hole theories which, in turn, are extensions of the well-studied cell models (CMs)^[25–28]. In CMs the space occupied by the fluid is divided into contiguous cells, each of which occupies a volume Δ , arranged in a regular manner like the cells delimited by the bonds of a cubic lattice. Each molecule is assumed to be confined to its cell and each cell is occupied by only one molecule. The effective potential energy felt by each molecule in its cell is created by the neighboring molecules and is assumed to have a spherical symmetry; otherwise an angular average is computed to obtain a spherically symmetric potential energy. The configurational partition function, Q , can be written in terms of the cell partition function Ψ , also known as free volume, as follows.

$$Q(T, V, N) = \Psi^N e^{-N \frac{\beta u(0)}{2}} \quad (1)$$

where T is the absolute temperature, V is the volume of the total system, N is the number of molecules, $\beta = \frac{1}{k_B T}$, k_B is Boltzmann's constant, z is the number of nearest neighboring cells, $u(0)$ is the minimum potential energy felt by each molecule in its cell and Ψ is given by

$$\Psi(T, \Delta) = 4\pi \int_{\Delta} e^{-\beta(u(r)-u(0))} r^2 dr \quad (2)$$

where $u(r)$ is the potential energy felt by the molecule at position r inside its cell and the integration is done over the volume of the cell Δ . In CMs the molecules are distinguishable because the cells can be numbered thus; the factorial term in the denominator of the partition function does not appear in Eq. (1). Depending on the mathematical expression of the potential energy $u(r)$ the configurational partition function of the cell, *i.e.* free volume, can be computed exactly or approximately using perturbation or numerical methods.

One of the main limitations of CMs is that they assign too much spatial order to the structure of the fluid. Indeed, the fluid has a solid-like structure imposed by the model itself. In other words, there is not enough entropy in these models. This deficiency has been addressed in many ways, for example allowing for the multiple occupation of cells which leads to a supplementary entropic contribution called “communal entropy” or allowing some cells to be empty^[27, 29–34]. The latter concept led to the development of hole theories (HTs)^[27, 29–34]. HTs are described by a configurational partition function very similar to the one defined by Eqs. (1) and (2), but it is modified to take into account the fact that some cells are empty.

Let us start with the expression of the potential energy of the system $\phi(r^N)$

$$\phi(r^N) = \frac{z}{2} (N - \Omega) u(0) + z \sum_{i=1}^N (1 - \omega_i) \{u(r_i) - u(0)\} \quad (3)$$

where r^N represents the spatial coordinates of all N molecules, z is the number of nearest neighboring cells, $z\Omega = z \sum_{i=1}^N \omega_i$ is the total number of the empty cells that are nearest neighbors of an occupied cell, ω_i is the fraction of nearest neighboring cells of the i -th molecule that are vacant and $u(r_i)$ is the potential energy of the i -th molecule at location r_i inside its cell. Therefore, the configurational partition function can be written as follows

$$Q(T, V, N) = \Psi^N e^{-N \frac{\beta u(0)}{2}} \sum (\prod_{i=1}^N j(\omega_i)) e^{\frac{\Omega \beta u(0)}{2}} \quad (4)$$

where the sum is over all possible configurations of the N molecules that differ by more than a permutation of the molecules and $j(\omega_i)$ is the generalized free volume. Its mathematical expression is the following

$$j(\omega_i) = 4\pi \int_{\Delta} e^{-\beta(1-\omega_i)(u(r)-u(0))} r^2 dr \quad (5)$$

If we make a random mixing assumption for the molecules and empty cells such that $\omega_i = \omega$ for all values of i and we call L the total number of cells then we can write

$$\sum (\prod_{i=1}^N j(\omega_i)) = \frac{L!}{N!(L-N)!} (j(\omega))^N \quad (6)$$

where the combinatorial number $\frac{L!}{N!(L-N)!}$ counts all possible configurations of the N molecules that differ by more than a permutation of the molecules.

Rarely the integral in Eq. (5) can be computed analytically. One counter example is the case of $\omega = 1$, which means that all neighboring cells of an occupied one are empty, *i.e.* gas-like free volume^[35]. In this case, $j(1) = \Delta$; this is the volume of a cell. In this limit it can be proven that Eq. (4) gives the configurational partition

function of an ideal gas, $\frac{V^N}{N!}$, as it should. The other limit is the case of $\omega = 0$, which means that all the neighboring cells are occupied, *i.e.* solid-like free volume^[35]. For the specific case of hard spheres Eq. (5) can be computed exactly. The result is $j(1) = \Delta - \nu$ where ν is the volume occupied by one molecule.

Due to the complexity in evaluating the free volume exactly three approximations were developed: the geometric average of $j(\omega)$ evaluated at the limits $\omega = 0$ and $\omega = 1$, *i.e.* $j(0)$ and $j(1)$, the arithmetic average and the cubic power of the arithmetic average of the free lengths. The free length is defined as a cubic root of the generalized free volume. The latter is used in the SS model. In mathematical terms the aforementioned approximations are written as follows

$$j(\omega) = (\Delta - \nu)^{1-\omega} \Delta^\omega \quad (7)$$

$$j(\omega) = (1 - \omega)(\Delta - \nu) + \omega\Delta \quad (8)$$

$$j_{ss}(\omega) = \left((1 - \omega)(\Delta^{\frac{1}{3}} - \nu^{\frac{1}{3}}) + \omega\Delta^{\frac{1}{3}} \right)^3 \quad (9)$$

Finally, using Eqs. (4) and (9) the configurational partition function of the SS model can be written as follows

$$Q(\tilde{T}, \tilde{V}, N; y(\tilde{T}, \tilde{V})) = g(N, y(\tilde{T}, \tilde{V})) \left(j_{ss}(y(\tilde{T}, \tilde{V})) \right)^{cN} e^{-\beta E(\tilde{V}, y(\tilde{T}, \tilde{V}))} \quad (10)$$

$y(\tilde{T}, \tilde{V})$ is the fraction of the total volume occupied by polymer segments (the model assumes that there are N polymers in the system each of which is made of s segments) and is a function of the reduced temperature and volume, *i.e.* $\tilde{T}$ and $\tilde{V}$. The parameter c quantifies the number of external degrees of freedom of the system and, traditionally, it has been assumed to be a constant parameter of the model, though it could also be a function of $\tilde{T}$ and $\tilde{V}$ ^[25]. $g(N, y(\tilde{T}, \tilde{V}))$ is the combinatorial factor similar to $\frac{L!}{N!(L-N)!}$ in Eq. (6). In other words, $g(N, y(\tilde{T}, \tilde{V}))$ counts the total number of configurations for the system with N s -mers and $L - Ns$ empty cells. The SS model borrows the expression for $g(N, y(\tilde{T}, \tilde{V}))$ from the Flory-Huggins model^[36]

$$g(N, y(\tilde{T}, \tilde{V})) \propto y(\tilde{T}, \tilde{V})^{-N} (1 - y(\tilde{T}, \tilde{V}))^{-Ns \frac{1 - y(\tilde{T}, \tilde{V})}{y(\tilde{T}, \tilde{V})}} \quad (11)$$

The free volume term, $j_{ss}(y(\tilde{T}, \tilde{V}))$, is described with the approximation given by Eq. (9). Explicitly, the mathematical expression is

$$j_{ss}(y(\tilde{T}, \tilde{V})) = \left(y(\tilde{T}, \tilde{V}) \left(\sqrt[3]{y(\tilde{T}, \tilde{V}) \tilde{V}} - 2^{-\frac{1}{6}} \right) \right) + \left(1 - y(\tilde{T}, \tilde{V}) \sqrt[3]{y(\tilde{T}, \tilde{V}) \tilde{V}} \right)^3 \quad (12)$$

Finally, the potential energy, $E(\tilde{V}, y(\tilde{T}, \tilde{V}))$, has the mathematical form

$$E(\tilde{V}, y(\tilde{T}, \tilde{V})) = \frac{y(\tilde{T}, \tilde{V}) N q z \epsilon^*}{2} \left\{ \frac{1.011}{(y(\tilde{T}, \tilde{V}) \tilde{V})^4} - \frac{2.409}{(y(\tilde{T}, \tilde{V}) \tilde{V})^2} \right\} \quad (13)$$

where $qz = s(z-2) + 2$ is the number of nearest neighbor sites per chain and ϵ^* is the characteristic interaction energy per segment.

The reduced variables $\tilde{T}$, $\tilde{V}$ and $\tilde{P}$ are related to the absolute temperature T , volume V , and pressure P by the following equations

$$\begin{aligned}
\tilde{V} &= \frac{V}{V^*} = \frac{V}{Nsv^*} \\
\tilde{T} &= \frac{T}{T^*} = \frac{ck_B T}{qz \epsilon^*} \\
\tilde{P} &= \frac{P}{P^*} = \frac{sv^* P}{qz \epsilon^*}
\end{aligned} \tag{14}$$

Equations (10), (11), (12), (13), and (14) define the configurational partition function of the SS model for polymer fluids. The Helmholtz free energy is computed from Eq. (10) following the standard formula from statistical mechanics

$$F(\tilde{T}, \tilde{V}, N; y(\tilde{T}, \tilde{V})) = -k_B T \ln [Q(\tilde{T}, \tilde{V}, N; y(\tilde{T}, \tilde{V}))] \tag{15}$$

and, since the fluid is in equilibrium, its free energy must be a minimum with respect to any free parameter or function. Therefore, we can write the equilibrium condition as follows

$$\left. \frac{\delta F(\tilde{T}, \tilde{V}, N; y(\tilde{T}, \tilde{V}))}{\delta y(\tilde{T}, \tilde{V})} \right|_{\tilde{T}, \tilde{V}} = 0 \tag{16}$$

where δ indicates functional derivative in this case only (later the symbol δ will be used to refer to the solubility parameter). Replacing Eq. (15) into Eq. (16) gives the following mathematical expression for the equilibrium condition

$$\frac{s}{3c} \left\{ \frac{s-1}{s} + \frac{\ln(1-y)}{y} \right\} = \frac{2^{-\frac{1}{6}} y(y\tilde{V})^{-\frac{1}{3}} - \frac{1}{3}}{1 - 2^{-\frac{1}{6}} y(y\tilde{V})^{-\frac{1}{3}}} + \frac{2.409 - 3.033(y\tilde{V})^{-2}}{6y\tilde{T}\tilde{V}^2} \tag{17}$$

where it is understood that y means $y(\tilde{T}, \tilde{V})$. The second equation that defines the model is the equation of state,

$P = -\left. \frac{\partial F}{\partial V} \right|_T$. Explicitly, this equation reads as follows

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{2}{y\tilde{T}\tilde{V}^2} (1.011(y\tilde{V})^{-2} - 1.2045) + \frac{1}{1 - 2^{-\frac{1}{6}} y(y\tilde{V})^{-\frac{1}{3}}} \tag{18}$$

Therefore, Eqs. (17) and (18) define the SS model completely and should be solved simultaneously to determine the occupied fraction $y(\tilde{T}, \tilde{V})$ and reduced pressure $\tilde{P}(\tilde{T}, \tilde{V})$ as a function of the (reduced) temperature and volume. Note that all the thermodynamic variables are reduced, *i.e.* they depend on the parameters V^* , T^* and P^* . These parameters together with s and c have the information about the specific chemistry under study. In other words, different polymers will have different values for these parameters as shown later in this article. It is noteworthy to observe that, even though the independent variables are $\tilde{T}$ and $\tilde{V}$ when the Helmholtz free energy is used, experimentally it is not the volume but the pressure that is controlled. Consequently, in practice Eqs. (17) and (18) are used to determine $y(\tilde{T}, \tilde{P})$ and $\tilde{V}(\tilde{T}, \tilde{P})$.

The SS model is based on Statistical Mechanics thus, we should be able to extract other thermodynamic quantities from it. Indeed, the entropy, S , can be computed using the equation

$$S = -\left. \frac{\partial F}{\partial T} \right|_V \tag{19}$$

The final expression for the reduced entropy is

$$\tilde{S} = \frac{S - S_0}{Nk_B c} = 3 \ln \left(\left(\sqrt[3]{y \tilde{V}} - 2^{-\frac{1}{6}} y \right) (1-y)^{-\frac{s(1-y)}{3c-y}} \right) \quad (20)$$

where S_0 is some reference entropy. Similarly, the internal energy U can be calculated from the expression

$$U = k_B T^2 \left. \frac{\partial \ln(Q)}{\partial T} \right|_V \quad (21)$$

The final expression for the reduced internal energy is

$$\tilde{U} = \frac{U}{Nqz \epsilon^*} = \frac{y}{2(y \tilde{V})^2} \left(\frac{1.011}{(y \tilde{V})^2} - 2.409 \right) \quad (22)$$

It is common practice to use the reduced Hildebrand solubility parameter $\tilde{\delta} = \sqrt{\frac{|\tilde{U}|}{\tilde{V}}}$ instead of the reduced internal energy, $\tilde{U}$, due to the availability of experimental data.

Other higher order derivatives like the reduced thermal expansion coefficient ($\tilde{\alpha}$), reduced isothermal compressibility ($\tilde{\kappa}_T$) and reduced heat capacities ($\tilde{C}_V$ and $\tilde{C}_P$) can also be calculated numerically from Eqs. (18) and (20).

In conclusion, Eqs. (17) and (18) should be solved simultaneously to solve the SS model. This is a major computational challenge because of the presence of the natural logarithm and the multiple powers of $y(\tilde{T}, \tilde{P})$ and $\tilde{V}(\tilde{T}, \tilde{P})$ present in the equations. However, the mathematical analysis presented in the next subsection shows a completely novel approach to reduce this system of two non-linear algebraic equations to only one which facilitates the numerical solution of the model significantly.

A Modern Approach to the Solution of the SS Model

The traditional algorithm used to determine the values of the parameters V^* , T^* and P^* for a specific polymer has been to assume that $s \rightarrow \infty$, $\frac{s}{3c} = 1$, and solve the model. The latter has been done with a two-step approach. The first step is to use an accurate numerical fit to the solution of the SS model. This fit was obtained under the aforementioned conditions and is valid only when $\tilde{P} = 0$. The numerical fit is the following^[37]

$$\ln(\tilde{V}) = -0.10335 + 23.8345 \tilde{T}^{\frac{3}{2}} \quad (23)$$

Thus, the procedure consists of fitting a straight line $\ln(V)$ versus $T^{\frac{3}{2}}$ to the experimental data and using the coefficients from the regression and Eq. (23) to determine V^* and T^* as follows

$$\begin{aligned} V^* &= e^{\text{intercept} + 0.10335} \\ T^* &= \left(\frac{23.8345}{\text{slope}} \right)^{\frac{2}{3}} \end{aligned} \quad (24)$$

The second step consists of determining P^* from high pressure data by solving the SS model numerically.

The problem with this two-step procedure is twofold. First, the assumption $\frac{s}{3c} = 1$ cannot be justified *a priori*. Only a good fit of the experimental data can justify it *a posteriori*. However, s and c are also parameters of the model and should be extracted from the experimental data. Second, the two-step solution of the SS model clearly biases the fitting to low pressure data over high pressure data. An unbiased fitting procedure should fit all

five parameters simultaneously without any assumption about their numerical values. This is precisely what we accomplish in this article. We have developed a numerical procedure to estimate the five parameters of the model in an unbiased way that gives a significantly better fit of the experimental data over the whole temperature and pressure range, and assigns more appropriate values to the parameters V^* , T^* and P^* .

Let us define two new variables as follows

$$\begin{aligned}\gamma &= \sqrt[3]{yV} \\ \zeta &= \frac{y}{2^{\frac{1}{6}} \sqrt[3]{y\tilde{V}}}\end{aligned}\quad (25)$$

Replacing these definitions into the equation of state, Eq. (18), and after some algebra we get the equation

$$\left(\zeta^3 - \zeta^2\right)^{\frac{1}{3}} \left(2.409\gamma^6 - 2.022\right) + 2^{\frac{1}{6}} \zeta \gamma^{11} \left(\tilde{T} + \tilde{P}\gamma^2 2^{-\frac{1}{6}}\right) - \tilde{P}\gamma^{13} = 0 \quad (26)$$

which is a cubic equation in ζ that can be solved exactly. This effectively reduces the solution of the SS model from two non-linear algebraic equations to only one which is a significant simplification when solving the model. We do not describe the analysis of the three roots of Eq. (26) in this article because it can be easily done using modern software packages like Mathematica from Wolfram Research or Maple from Maplesoft, or the old fashioned way with paper and pencil. However, we mention some results observed during our studies of these roots. The three solutions of Eq. (26) can be all real, or one real and two complex (conjugates). Complex roots are unphysical since ζ is real by definition. Moreover, $\zeta > 0$ therefore any root that is negative is unphysical. In the case of a single real root there is no ambiguity; there is only one possible mathematical expression for ζ . However, if all three roots are real then all of them must be analyzed. The challenge is to identify which of the three roots is the correct one. We answer this question below.

Replacing the definitions in Eq. (25) into the equilibrium condition, Eq. (17), we get

$$\left(6\tilde{T}\gamma^{11} \frac{s}{3c} \left(1 - \frac{1}{s} + \frac{\ln\left(1 - 2^{\frac{1}{6}} \zeta \gamma\right)}{2^{\frac{1}{6}} \zeta \gamma}\right) - 2^{\frac{1}{6}} \zeta (2.409\gamma^6 - 3.033) \right) (1 - \zeta) - 2\tilde{T}\gamma^{11} (3\zeta - 1) = 0 \quad (27)$$

If there is only one real root that is solution of Eq. (26), then Eq. (27) is solved to get the corresponding value of γ . Once γ and ζ are known, then Eq. (25) can be used to obtain γ and $\tilde{V}$. However, if there are three real roots, then all of them must be studied. Eq. (27) will have three solutions for γ . The root that is in agreement with previous studies of the SS model at atmospheric pressure^[37] is the one that is the largest of the three. The value of this root is slightly lower than 1 and usually close to 0.98. Thus, this value of γ together with the root ζ that led to it were used to compute y and $\tilde{V}$ using Eq. (25) for each value of $\tilde{T}$ and $\tilde{P}$ of interest. The next subsection describes the methodology used to solve Eqs. (26) and (27).

Computational Details

The first algorithm we developed was the one to solve the SS model numerically. Eq. (26) can be solved exactly, which is what we did, but Eq. (27) must be solved numerically using the exact solutions from Eq. (26). The main challenge is the presence of a logarithm in Eq. (27). The argument of the logarithm must always be positive. Otherwise, the solution will be complex which is unphysical. Keeping the argument of the logarithm positive between zero and one is a numerical challenge which limited the number of methods that could be used to solve Eq. (27). Indeed, the methods based on gradients failed because they attempted to evaluate the logarithm with a negative argument. Thus, we ended up choosing the bisection method^[38] which is known to be slower than

others, but guarantees finding the solution. Improvements in the speed of the calculation could be easily achieved with faster numerical methods that do not evaluate derivatives^[39].

Hereafter, we describe a simple OpenMP version of the algorithm we used to solve the model. A CUDA-based algorithm was also successful but was not employed due to hardware limitations, *i.e.* we had only one CUDA-enabled NVidia card available, which reduced the algorithm's performance when compared with the eight kernels launched in the OpenMP version.

The code consists of two nested loops; the outer loop was used for the $\tilde{P}$ variable which covered a large range of possible values from zero to two. This loop was parallelized and the interval was split into eight intervals which were assigned to the eight kernels. The inner loop was for the variable $\tilde{T}$ which was decreased from 0.07 to 0. This was done on purpose since we know that at low enough temperatures the occupied fraction has to be equal to one. By decreasing $\tilde{T}$ we could identify a value for the reduced temperature below which setting $y = 1$ would be very accurate and we only had to solve Eq. (18) for $\tilde{V}$.

Once the values of $\tilde{T}$ and $\tilde{P}$ were specified, the value of γ was initially varied from 1 to 0.9 in very small steps; we chose a step of 0.0001. This value of γ was used in Eq. (26) to obtain one or three values of ζ . In the latter case all three roots were considered. These values were used in Eq. (27) until an interval containing a root for γ was identified. Afterwards, the value of the root was refined using the bisection method fifteen times. Once γ and ζ were known, then Eq. (25) was used to obtain y and $\tilde{V}$. These values were stored in matrices and the procedure was started again with new values of $\tilde{P}$ and $\tilde{T}$.

The aforementioned algorithm solves the SS model very efficiently and it was used to obtain values for the parameters s , c , V^* , T^* and P^* for many polymers of interest. For this purpose we defined the following function

$$G(s, c, V^*, T^*, P^*) = \sqrt{\frac{1}{J-5} \sum_{l=1}^J \left(V_j - V^* \times \tilde{V} \left(\frac{T_j}{T^*}, \frac{P_j}{P^*}, s, c \right) \right)^2} \quad (28)$$

which is nothing else than the root mean square error of the fit (RMSE), J is the total number of experimental data points, $J-5$ is the total number of degrees of freedom of the fit, V_j , T_j and P_j are the experimental values for the j -th experimental data point, and $\tilde{V}$ is the solution of the SS model for the values

$$\begin{aligned} \tilde{T} &= \frac{T_j}{T^*} \\ \tilde{P} &= \frac{P_j}{P^*} \end{aligned} \quad (29)$$

Thus, the algorithm consisted of finding the values of s , c , V^* , T^* , and P^* that minimize Eq. (28) for each polymer of interest.

RESULTS AND COMPARISON WITH EXPERIMENTAL DATA

We illustrate the general predictions of the model in Fig. 1 through Fig. 7. For the purpose of illustration we made the traditional assumptions that $s \rightarrow \infty$ and $s = 3c$. However, similar results were observed for other values of s and c . Let us start by studying the $\tilde{P}\tilde{V}\tilde{T}$ behavior predicted by the model for homopolymer fluids. Figure 1 clearly shows that an increase in $\tilde{T}$ at constant $\tilde{P}$ leads to an increase in $\tilde{V}$, as it is known to be the case. In addition, an increase in $\tilde{P}$ at constant $\tilde{T}$ leads to a decrease in $\tilde{V}$, as expected. Therefore, from a physics perspective the model predicts a reasonable behavior for the temperature and pressure dependencies of the volume of polymer fluids. Moreover, Figure 1 shows that as $\tilde{P}$ is increased the temperature dependence of $\tilde{V}$ decreases. In other words, the reduced thermal expansion coefficient $\tilde{\alpha}_T$, decreases.

Figure 1 also shows an unexpected result. A close observation of the plot clearly shows a significant change

in the derivative $\left. \frac{\partial \tilde{F}}{\partial \tilde{V}} \right|_{\tilde{P}}$ for values of $\tilde{T} \sim 0.02$. This behavior is observed routinely in dilatometric studies of polymer fluids and is a consequence of the glass transition. Thus, even though the SS model is a thermodynamic model, therefore only applicable to equilibrium states, it is predicting an equilibrium glass-like phase at low enough temperatures. This result is in the same spirit of many theoretical treatments of the glass transition based on equilibrium concepts^[40–43]. The figure shows two dashed lines: a short-dashed and a long-dashed line. Both of them indicate where the glass transition should occur based on the SS model for different values of $\tilde{P}$. The short-dashed line was obtained from Fig. 1 by fitting straight lines to $\tilde{V}$ in the low and high $\tilde{T}$ windows for values of $\tilde{P}$ between 0.01 and 0.5, and determining the value of $\tilde{T}$ where the lines intersected. This is how it is routinely done in experimental dilatometric studies. From each value of $\tilde{T}$ we determined the corresponding value of $\tilde{V}$. The result is the short-dashed line in Fig. 1. The long-dashed line also represents the glass transition but as determined by the behavior of the reduced heat capacity at constant pressure, $\tilde{C}_p$. The value of $\tilde{T}$ that corresponds to the reduced glass transition temperature was obtained as the one where $\left. \frac{\partial \tilde{C}_p}{\partial \tilde{T}} \right|_{\tilde{P}}$ was a maximum at the value of $\tilde{P}$ of interest. We discuss the behavior of $\tilde{C}_p$ later in this article. Figure 1 shows that the glass transition predicted by the change in the heat capacity occurs for values of $\tilde{T}$ lower than the ones predicted by the $\tilde{P}\tilde{V}\tilde{T}$ plot.

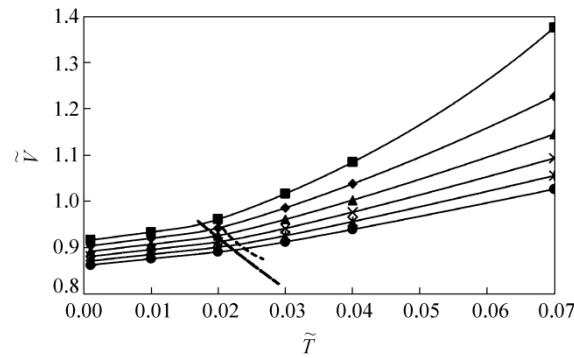


Fig. 1 Plot of $\tilde{V}$ as a function of $\tilde{T}$ for six values of $\tilde{P}$ assuming $s \rightarrow \infty$, $\frac{s}{3c} = 1$: $\tilde{P} = 0.01$ (■), $\tilde{P} = 0.1$ (◆), $\tilde{P} = 0.2$ (▲), $\tilde{P} = 0.3$ (×), $\tilde{P} = 0.4$ (*) and $\tilde{P} = 0.5$ (●). The short-dashed line indicates the glass transition as determined from this plot. The long-dashed line indicates the glass transition as determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot (Fig. 7).

Figure 2 shows a plot of the occupied volume fraction y as a function of $\tilde{T}$ for six values of $\tilde{P}$. It is interesting to observe the linear behavior of y as a function of $\tilde{T}$ for high enough values of $\tilde{T}$. This linear relationship between the occupied volume fraction and temperature has been confirmed experimentally using positron annihilation spectroscopy^[44]. As expected, an increase in pressure increases the occupied volume fraction at high temperatures. However, at low enough temperatures the occupied volume fraction reaches its maximum possible value of one.

Figure 2 also shows the two lines that determine the glass transition as predicted by the $\tilde{P}\tilde{V}\tilde{T}$ plot in Fig. 1 and the $\tilde{C}_p\tilde{T}\tilde{P}$ plot in Fig. 7. In both cases the glass transition is predicted to occur for large values of the occupied volume fraction. In particular, when the glass transition is determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot in Fig. 7, the value of the occupied volume fraction at the glass transition point is equal to 0.997 and increases to 0.999 as the reduced pressure is increased. Thus, the SS model is predicting a transition to a glass phase when the

occupied volume fraction reaches one. This occurs at reduced temperatures above zero and is in agreement with the original works of Batchinski, Doolittle, Cohen, and subsequent studies^[45–50].

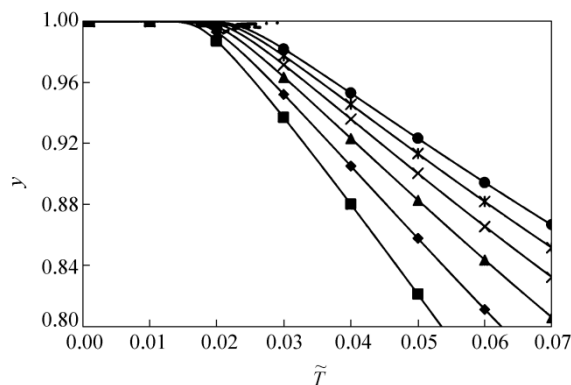


Fig. 2 Plot of y as a function of $\tilde{T}$ for six values of $\tilde{P}$ assuming $s \rightarrow \infty$, $\frac{s}{3c} = 1$: $\tilde{P} = 0.01$ (■), $\tilde{P} = 0.1$ (◆),

$\tilde{P} = 0.2$ (▲), $\tilde{P} = 0.3$ (×), $\tilde{P} = 0.4$ (*) and $\tilde{P} = 0.5$ (●)

The short-dashed line indicates the glass transition as determined from the $\tilde{P}\tilde{V}\tilde{T}$ plot (Fig. 1). The long-dashed line indicates the glass transition as determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot (Fig. 7).

Figure 3 shows the reduced solubility parameter as a function of $\tilde{T}$ for six values of $\tilde{P}$. For the purpose of completeness, the computation was extended to very low values of the reduced temperature, *i.e.* into the equilibrium glassy phase discussed before. The plot clearly shows that an increase of the reduced temperature decreases the solubility parameter for all values of the reduced pressure. This behavior is correct since an increase of the temperature should weaken the intermolecular forces between polymers thus reducing the amount of energy needed to break those forces. By the same argument, an increase in pressure should increase the amount of energy needed to break the intermolecular forces. Consequently, the solubility parameter should increase as shown in the plot. Figure 3 also shows a significant change in the temperature dependence of the reduced solubility parameter at the glass transition curves. In particular, the curve determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot in Fig. 7 agrees very well with the temperature where the slope change is observed.

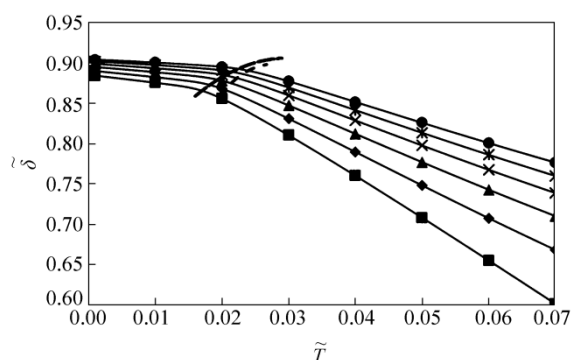


Fig. 3 Plot of $\tilde{\delta}$ as a function of $\tilde{T}$ for six values of $\tilde{P}$ assuming $s \rightarrow \infty$, $\frac{s}{3c} = 1$: $\tilde{P} = 0.01$ (■), $\tilde{P} = 0.1$ (◆),

$\tilde{P} = 0.2$ (▲), $\tilde{P} = 0.3$ (×), $\tilde{P} = 0.4$ (*) and $\tilde{P} = 0.5$ (●)

The short-dashed line indicates the glass transition as determined from the $\tilde{P}\tilde{V}\tilde{T}$ plot (Fig. 1). The long-dashed line indicates the glass transition as determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot (Fig. 7).

Figure 4 shows the reduced entropy change as a function of $\tilde{T}$ for six values of $\tilde{P}$. As expected, an increase in the reduced temperature at constant reduced pressure leads to an increase in the reduced entropy change, while an increase in the reduced pressure at constant reduced temperature leads to a decrease in the reduced entropy. The lines that indicate a transition to a glassy phase are also showed in the plot. Again, the curve obtained from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot in Fig. 7 agrees very well with the temperature where the temperature dependence of the entropy changes significantly. Observe that, by construction, the model predicts an occupied fraction of one at low enough temperatures, as shown in Fig. 2. This implies that every cell is occupied by one molecule. Intuitively, one would say that this is a crystalline phase. However, the crystallization transition is a first order phase transition in the thermodynamic sense. But, the volume and entropy predicted by the SS model do not show any discontinuity. Therefore, there is no phase transition. The concept of “caging” characteristic of glassy materials describes the low temperature situation more appropriately. The polymer segments rattle inside their individual cages created by the surrounding segments without adopting a fixed spatial position like in the case of crystals. This reinforces the idea that the SS model predicts a glass-like phase at low temperatures. Further investigation of this topic is needed.

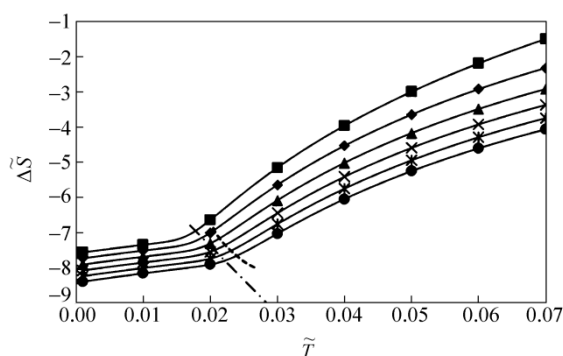


Fig. 4 Plot of $\Delta\tilde{S}$ as a function of $\tilde{T}$ for six values of $\tilde{P}$ assuming $s \rightarrow \infty$, $\frac{s}{3c} = 1$: $\tilde{P} = 0.01$ (■), $\tilde{P} = 0.1$ (◆), $\tilde{P} = 0.2$ (▲), $\tilde{P} = 0.3$ (×), $\tilde{P} = 0.4$ (*) and $\tilde{P} = 0.5$ (●). The short-dashed line indicates the glass transition as determined from the $\tilde{P}\tilde{V}\tilde{T}$ plot (Fig. 1). The long-dashed line indicates the glass transition as determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot (Fig. 7).

Figures 5 and 6 show the behaviors of the reduced thermal expansion coefficient and isothermal compressibility as functions of $\tilde{T}$ for six values of $\tilde{P}$, respectively. Both thermodynamic properties show a significant change close to the glass transition line predicted by the $\tilde{C}_p\tilde{T}\tilde{P}$ plot in Fig. 7. As expected, the higher the reduced pressure, the weaker the temperature dependence of both properties.

Figure 7 shows the reduced heat capacity at constant pressure as a function of $\tilde{T}$ for six values of $\tilde{P}$. It is worth noting that the SS model accounts only for the configurational partition function. Thus, any intramolecular motions are not captured by the model. These intramolecular motions like C—H vibrational motions or methyl group rotations do contribute significantly to the heat capacity. However, this contribution is not captured by the SS model. Therefore, the heat capacity shown on Fig. 7 is a consequence of the external, intermolecular, degrees of freedom only. The figure shows the typical behavior observed for polymeric materials when they undergo the glass transition. Starting from very low reduced temperatures, as the reduced temperature is increased, the heat capacity increases slowly and independently of the value of the reduced pressure. At the glass transition temperature, the reduced heat capacity increases significantly to its value in the melt state where it remains approximately constant. Experimentally it is observed that the heat capacity keeps increasing with increasing temperature. This is a consequence of the intramolecular motions like C—H stretching and others that keep

absorbing thermal energy as the temperature increases. However, these motions are not included in the SS model.

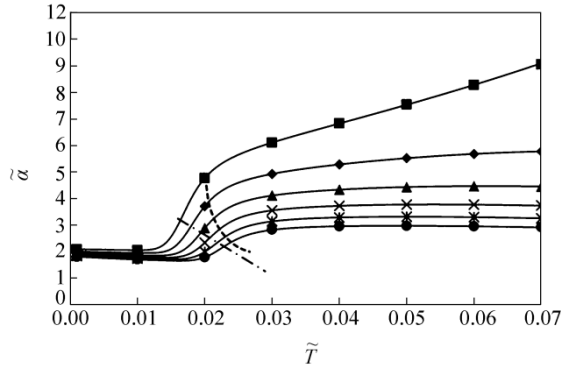


Fig. 5 Plot of $\tilde{\alpha}$ as a function of $\tilde{T}$ for six values of $\tilde{P}$ assuming $s \rightarrow \infty$, $\frac{s}{3c} = 1$: $\tilde{P} = 0.01$ (■), $\tilde{P} = 0.1$ (◆), $\tilde{P} = 0.2$ (▲), $\tilde{P} = 0.3$ (×), $\tilde{P} = 0.4$ (*) and $\tilde{P} = 0.5$ (●). The short-dashed line indicates the glass transition as determined from the $\tilde{P}\tilde{V}\tilde{T}$ plot (Fig. 1). The long-dashed line indicates the glass transition as determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot (Fig. 7).

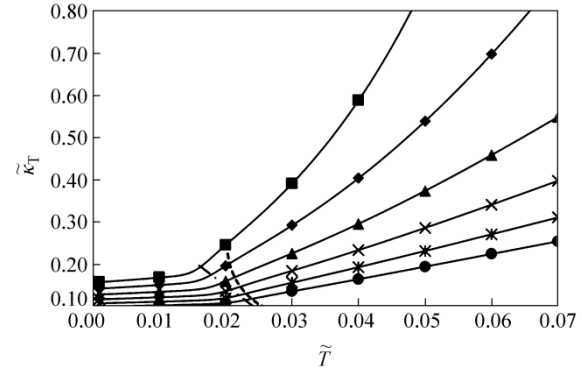


Fig. 6 Plot of $\tilde{\kappa}_T$ as a function of $\tilde{T}$ for six values of $\tilde{P}$ assuming $s \rightarrow \infty$, $\frac{s}{3c} = 1$: $\tilde{P} = 0.01$ (■), $\tilde{P} = 0.1$ (◆), $\tilde{P} = 0.2$ (▲), $\tilde{P} = 0.3$ (×), $\tilde{P} = 0.4$ (*) and $\tilde{P} = 0.5$ (●). The short-dashed line indicates the glass transition as determined from the $\tilde{P}\tilde{V}\tilde{T}$ plot (Figure 1). The long-dashed line indicates the glass transition as determined from the $\tilde{C}_p\tilde{T}\tilde{P}$ plot (Fig. 7).

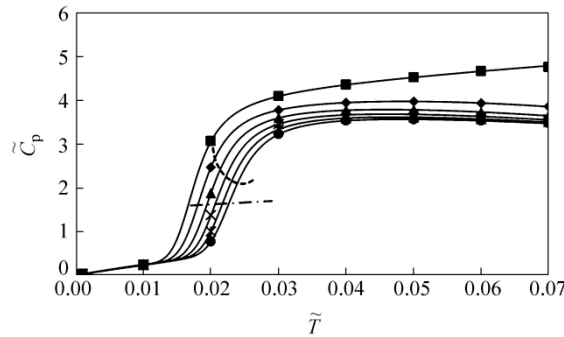


Fig. 7 Plot of $\tilde{C}_p$ as a function of $\tilde{T}$ for six values of $\tilde{P}$ assuming $s \rightarrow \infty$, $\frac{s}{3c} = 1$: $\tilde{P} = 0.01$ (■), $\tilde{P} = 0.1$ (◆), $\tilde{P} = 0.2$ (▲), $\tilde{P} = 0.3$ (×), $\tilde{P} = 0.4$ (*) and $\tilde{P} = 0.5$ (●). The short-dashed line indicates the glass transition as determined from the $\tilde{P}\tilde{V}\tilde{T}$ plot (Fig. 1). The long-dashed line indicates the glass transition as determined from this plot.

Figures 8, 9 and 10 show the plots of the specific volume of nylon 6,6, *cis* poly(1,4-butadiene) and poly(ethylene oxide) in the melt state only as a function of temperature for a wide range of values of the pressure. The experimental data were taken from Ref. [51]. The symbols represent experimental data while the dashed lines are the predictions of the SS model after fitting the five parameters by minimizing $G(s, c, V^*, T^*, P^*)$, Eq. (28). Table 1 shows the values of the various parameters of the model for each of the three polymers together with the root mean square error (RMSE) of the predicted specific volume. The figures clearly show the high degree of accuracy of the SS model in reproducing and predicting the PVT behavior of polymer fluids, even for such a large range of pressures. Indeed, Table 1 shows that the average error in the fitting of the specific

volume is significantly lower than 1%. This high level of accuracy has also been observed with many other polymers for which we have experimental data and have studied.

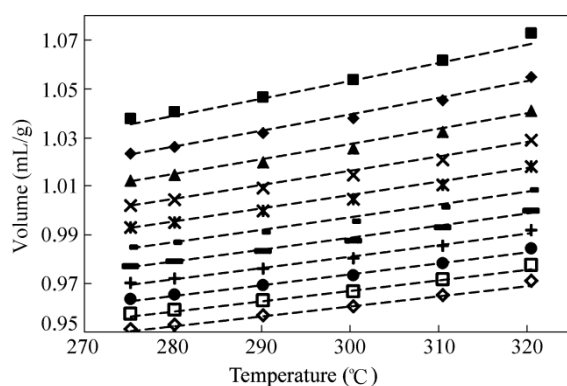


Fig. 8 Plot of the specific volume of Nylon 6,6 (in mL/g) as a function of temperature for various pressures (in MPa)

The symbols are experimental data points. The dashed lines are the predictions of the SS model after fitting the parameters of the model. $P = 0.1$ (■), $P = 20$ (◆), $P = 40$ (▲), $P = 60$ (×), $P = 80$ (*), $P = 100$ (-), $P = 120$ (—), $P = 140$ (+), $P = 160$ (●), $P = 180$ (□) and $P = 200$ (◇).

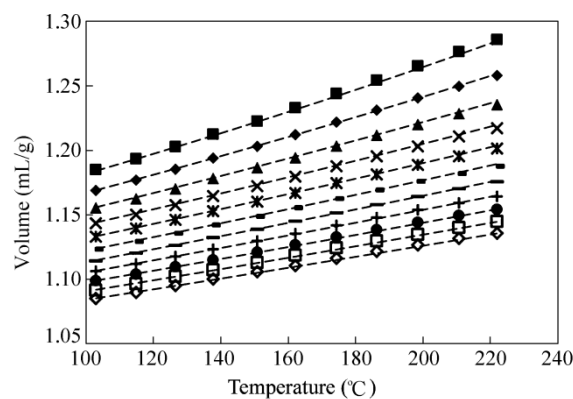


Fig. 9 Plot of the specific volume of *cis* poly(1,4-butadiene) (in mL/g) as a function of temperature for various pressures (in MPa)

The symbols are experimental data points. The dashed lines are the predictions of the SS model after fitting the parameters of the model. $P = 0.1$ (■), $P = 20$ (◆), $P = 40$ (▲), $P = 60$ (×), $P = 80$ (*), $P = 100$ (-), $P = 120$ (—), $P = 140$ (+), $P = 160$ (●), $P = 180$ (□) and $P = 200$ (◇).

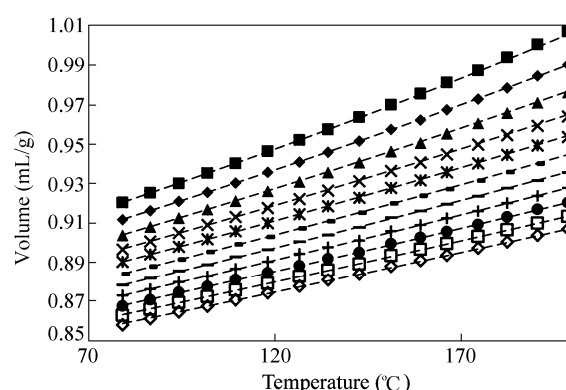


Fig. 10 Plot of the specific volume of poly(ethylene oxide) (in mL/g) as a function of temperature for various pressures (in MPa)

The symbols are experimental data points. The dashed lines are the predictions of the SS model after fitting the parameters of the model. $P = 0.1$ (■), $P = 20$ (◆), $P = 40$ (▲), $P = 60$ (×), $P = 80$ (*), $P = 100$ (-), $P = 120$ (—), $P = 140$ (+), $P = 160$ (●), $P = 180$ (□) and $P = 200$ (◇).

Table 1. SS parameters and RMSE for the three polymers used in this study: nylon 6,6, *cis* poly(1,4-butadiene), and poly(ethylene oxide)

Polymer	P^* (MPa)	T^* (K)	V^* (mL/g)	$\frac{s}{3c}$	s	RMSE (mL/g)
Nylon 6,6	1400.9	15859	0.9113	2.3004	11479	0.0012
Poly(1,4-butadiene)	789.8	10208	1.1149	0.9010	9823	0.0009
Poly(ethylene oxide)	1091.0	10004	0.8682	1.0687	9668	0.0003

Figure 11 shows a plot of the experimental solubility parameter, δ_{EXP} , for the three aforementioned polymers as a function of the solubility parameter predicted from the SS model, δ_{SS} , with no adjustable parameters. The data used to construct Fig. 11 are shown in Table 2^[52]. Some comments are in order to understand the plot and its limitations. First, although the (Hildebrand) solubility parameter is uniquely defined there are various experimental approaches to determine it like using the van Laar-Hildebrand equation, the Huggins or Bristow-Watson equation, using a Gee plot and other methods. As it would be expected the values obtained for the solubility parameter vary from one method to another. In many cases, the experimentally measured values differ substantially from one another. Thus, when constructing Fig. 11 we used literature data to determine the range of values of the solubility parameter. Any value between the maximum and minimum values found in the literature is considered an acceptable value for the solubility parameter. Still, the maximum and minimum values are not unequivocally defined since other experimental methods might yield values of the solubility parameter larger than the maximum value used here or smaller than the minimum value used in this study. Second, these numbers are reported at room temperature and atmospheric pressure even though some of the pure homopolymers might be in the semicrystalline or glassy phases under these conditions. Clearly, the values of the solubility parameter are not uniquely or even well-defined experimentally, but they have been used to study or predict the miscibility of polymer alloys and solutions for many decades. Therefore, we will use the numbers as reported in the literature. The value of the solubility parameter predicted by the SS model, δ_{SS} , was computed at room temperature (300 K) and atmospheric pressure (0.1 MPa) from its definition using the parameters in Table 1. Figure 11 shows δ_{SS} on the abscissa, which is a very well defined number, and δ_{EXP} on the ordinate where the range of possible values is indicated by the vertical line segments. In the ideal case where both solubility parameters were identical, $\delta_{\text{EXP}} = \delta_{\text{SS}}$, the relationship would be described by the dashed line shown in the plot. However, since $\delta_{\text{EXP}} \neq \delta_{\text{SS}}$ the best we can hope for is that the dashed line passes through the line segments. The plot shows that the dashed line crosses two of the three line segments and barely misses the third one, *cis* poly(1,4-butadiene). Thus, this result shows that the SS model is very capable of predicting reasonably accurate values for the solubility parameter of polymers. Utracki has reported similar results in the past^[53, 54]. Moreover, the model can predict how the solubility parameter depends on pressure and temperature. A more detailed study of this property covering a large number of chemistries and large temperature and pressure windows will be done in a future article.

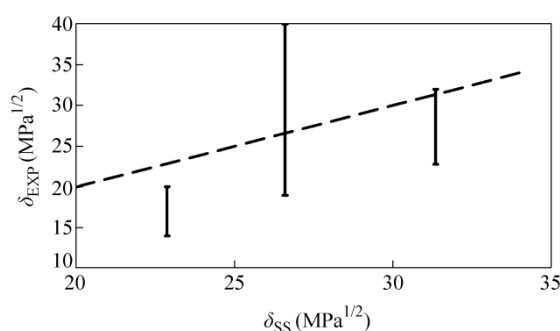


Fig. 11 Plot of the experimental solubility parameter as a function of the one obtained from the SS model for nylon 6,6, *cis* poly(1,4-butadiene) and poly(ethylene oxide)

All numbers are extrapolated or computed at room temperature and atmospheric pressure. The vertical lines indicate the ranges of possible values of the experimental solubility parameters as reported in the literature. The dashed line represents the equation $\delta_{\text{EXP}} = \delta_{\text{SS}}$. The unit of solubility parameter used is $\text{MPa}^{1/2}$.

Finally, let us look at the glass transition temperature predicted by the model. The purpose of this last result is not to predict an accurate number for T_g since two of the three polymers studied are semicrystalline: Nylon 6,6 and poly(ethylene oxide). Table 2 shows the melting temperatures of the three polymers. The SS model does not account for crystallinity. The goal here is to check that the quantitative predictions for T_g are reasonable and

behave as expected. In other words, since the SS model is an equilibrium model, the T_g predicted should be lower than the experimentally measured one. In addition, since two polymers are semicrystalline, then the dynamics of the amorphous phase is slowed down due to the confinement which leads to a higher value for T_g . Thus, we have two strong reasons to expect the experimental T_g to be higher than the predicted one for semicrystalline polymers. The question is by how much.

Table 2. Predicted and experimental values for the solubility parameter (in $\text{MPa}^{1/2}$), glass transition and melting temperatures (in K) (Some data are shown for completeness purposes only. The computational error for T_g^{SS} is 10 K)

Polymer	δ_{SS} ($\text{MPa}^{1/2}$)	$\delta_{\text{EXP}}^{\text{MIN}}$ ($\text{MPa}^{1/2}$)	$\delta_{\text{EXP}}^{\text{MAX}}$ ($\text{MPa}^{1/2}$)	T_g^{SS} (K)	T_g^{EXP} (K)	T_M^{EXP} (K)
Nylon 6,6	31.24	22.8	32.00	190	330	534
Poly(1,4-butadiene)	22.88	14.00	20.00	180	171	280
Poly(ethylene oxide)	26.60	19.00	40.00	160	206	338

Let us start with nylon 6,6. The predicted value for T_g is 140 K below the experimental one and the experimental T_M is 534 K. The high melting temperature indicates that the crystals are thermodynamically very stable due to hydrogen bond formation. Moreover, it is known that the degree of crystallinity is very high with a typical value around 40%. Thus, it is clear that the polymers in the amorphous regions are highly constrained and their dynamics slowed down significantly by the crystalline regions. Consequently, a difference of 140 K between the predicted and experimental values of T_g is not surprising. In this case the important point is that $T_g^{\text{EXP}} > T_g^{\text{SS}}$ as expected. For poly(ethylene oxide) the predicted value for T_g is 46 K below the experimental one and the experimental T_M is 338 K. The melting temperature is much lower than the one of nylon 6,6 which indicates that the crystals are not as thermodynamically stable as the ones in nylon 6,6. However, the degree of crystallinity for poly(ethylene oxide) has been reported to be very high which explains the 46 K difference. Finally, *cis* poly(1,4-butadiene) has been reported to have very low or zero crystalline content. Therefore, the prediction of the SS model for the T_g of this polymer should be appropriate. Indeed, Table 2 shows that the prediction is in very good quantitative agreement with the experimental value. This strongly suggests that the SS model might be a suitable tool to make accurate predictions for the T_g of polymers. This subject will be pursued in more detailed in a future article.

SUMMARY AND CONCLUSIONS

Over the last few decades the SS model has proven to be very accurate in fitting the experimental PVT behavior of many polymer fluids. PVT properties have received a renewed interest in recent times because they are needed as input information for the processing of polymers and for new engineering applications in the field of hydraulic fracturing. In this article we have shown the conceptual and physical foundations of the SS model starting from very fundamental formulas from Statistical Mechanics. Afterward, we discussed the traditional fitting method used to obtain the values of the various parameters. We discussed the bias of the method towards low pressure data, the unjustified assumptions $s \rightarrow \infty$, $\frac{s}{3c} = 1$, and proposed a completely novel approach to the problem that reduces the two non-linear algebraic equations that define the SS model to one. This reduction is exact and no information or accuracy is lost. Moreover, we indicated how the algorithm to solve the equation worked and how we implemented it using OpenMP concepts. This reduction in the complexity of the equations allowed us to optimize the fitting of the experimental data using all five parameters of the model. For the purpose of illustration we showed the experimental data for three well-known commodity polymers and the predictions of the SS model after the determination of the five parameters. The root mean square error was always smaller than 1% and differences between experimental data and the model are difficult to see in the plots. This clearly shows the high level of accuracy of the model.

We also discussed the thermodynamic properties predicted by the model using reduced variables and concluded that all the properties behave in a reasonable way from a Physics perspective. Moreover, results presented agree on a qualitative basis with results already published in the literature or results routinely observed in experimental studies. In addition, the model predicts low temperature behaviors that agree with glass formation. For example, the $\tilde{P}\tilde{V}\tilde{T}$ plot clearly shows a significant change in the volume-temperature slope, *i.e.* thermal expansion coefficient, which is routinely interpreted as the transition from a liquid to a glass. Similarly, the $\tilde{C}_p\tilde{T}\tilde{P}$ plot shows a rapid increase in the reduced heat capacity at a reduced temperature close to the one where the change in the thermal expansion coefficient is observed. The behavior of the reduced heat capacity at this temperature is similar to the one observed experimentally for polymers undergoing the glass transition. Thus, even though the SS model is based on statistical mechanics, therefore it is only applicable to systems in equilibrium, it is predicting physical behaviors that are routinely identified with the glass transition. This result is clearly unexpected and novel. What is even more surprising are the quantitative predictions for T_g . In the case of *cis* poly(1,4-butadiene) which has a very low or even null degree of crystallinity, consequently the SS model should apply to it, the prediction for T_g and the experimental number are within the numerical error of the computational method.

Finally, we also used the SS model to predict the solubility parameter for the three polymers studied in this article. Even though the solubility parameter is not unequivocally defined from an experimental perspective, we showed that the predictions from the SS model are in reasonable quantitative agreement with the numbers reported in the literature, in agreement with previous studies by Utraki.

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