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The Surface Tension of Polymer Liquids

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Abstract: A brief review of the surface tension of polymer liquids is presented. A strong emphasis is placed on recent measurements of surface tensions of homologous liquid series up to high-molecular-weight polymers, and the thermodynamic liquid properties of these same homologous series obtained from sources such as pressure-volume-temperature (PVT) data. The accuracy and limitations of the thermodynamic information which are used as input to many of the theories applied to the surface properties of polymer molecules are discussed. By scaling the surface tension data using a true measure of the cohesive energy density of the liquid state, we can clearly observe the entropic contribution to the surface tension caused by the conformational restriction of a large molecule at the liquid-vapor interface. The scaling implies the existence of a corresponding states principle for both polymer liquids and for low-molecular-weight liquids. The ramifications of the existence of a corresponding states principle for the surface tension of polymer melts are discussed. One consequence of the corresponding states principle is that it allows us to use surface tension measurements to compute the cohesive energy density of polymer melts using PVT data.

Introduction

The surface tension of polymer molecules has been studied for many years (Ref.1). Polymer melts have high viscosity which leads to long relaxation times for many of the standard methods for the measurement of the surface tension, γ. Many polymers have high melting temperatures or glass transition temperatures. These high temperatures make measurement difficult and the stability of the polymer at these temperatures is often such that degradation of the polymer occurs before a measurement can be made. Finally, polymers are seldom pure. They are usually polydisperse and can have structural defects such as branching. Therefore, much of the experimental literature has been confined to measurements of surface tension for low-molecular-weight liquids.

Numerous theoretical methods have been applied to the study of polymers at interfaces. In many cases the theoretical tools used to model the behavior of small molecule systems have been extended to study polymer systems. The models are of

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two types. The first are those which seek to describe the global properties of the liquid using molecular potentials. This is a very difficult task and currently only semiquantitative success has been achieved for simple short-chain molecules such as the alkanes. Such methods yield details about the microscopic details of the molecular conformations of macromolecules near liquid-vapor or liquid-liquid interfaces. A second more common and older approach is to coarse the grain of the system so that many of the microscopic details are lost and then use macroscopic thermodynamic information to calibrate the model. The model is then used to predict other macroscopic properties such as the surface tension. Such models are numerous and are not limited to the prediction of macroscopic variables. The square gradient theory (Ref. 2), for example, can predict the liquid-vapor interface dimension which is of the order of 10 - 15 Å. The power of such models is that they allow us to explore the meso scale structure of the surface. A combination of these two approaches can yield much information about the behavior of polymer molecules at interfaces and also yield practical tools for the prediction of macroscopic thermodynamic properties as well.

How are polymer molecules different from small molecules at or near an interface? In what follows we will focus on the liquid-vapor interface. Polymers form random coil conformations in the bulk liquid state. The spherical spatial domain occupied by the molecule is characterized by the radius of gyration, R_g, of the molecule. R_g is a function of the molecular weight of the molecule and its chemical composition. This restriction in the number of configurations of the molecule at the surface, will lead to an entropic contribution to the surface tension (Ref. 3). Other aspects of polymers which one might expect to affect surface properties are end groups of the polymer, side groups, and changes in chemical structure along the molecule, i.e. block copolymer structure. These and other structural features of polymer molecules contribute in varying degrees to surface properties of polymer liquids. The challenge is then to quantify these various contributions. A problem which immediately presents itself is the fact that the largest contribution to the surface tension will come from the cohesive energy of the liquid and unless we are able to predict this contribution with sufficient accuracy, we cannot measure the efficacy of any theory which claims to compute the magnitude of other contributions to the surface tension.

Scaling

The surface tension of complex molecules at a liquid vapor interface can be written in the following manner.

$$\gamma\,(T) = \gamma_{\text{isotropic}} + \gamma'_{\text{non-local}} + \gamma'''_{\text{anisotropic}} + \ldots \qquad (1)$$

The first term in the above expression is the contribution to the surface tension from the local interactions where we assume that the system is isotropic and disordered up to the interface. This term is the dominant contribution and the only one in many weakly interacting small-molecule liquids. The second term is the non-local contribution to the surface tension which can result from the presence of large-chain molecules at an interface. The molecules are conformationally constrained and thus even though most of the molecules may occupy the bulk liquid domains away from the interface, these conformational effects contribute an entropic contribution to the surface tension. The magnitude of this effect was predicted by Hong and Noolandi (Ref. 3) to be of the order of 10% of the value of the surface tension. The third contribution comes from situations where molecules order at the interface due to the strong directional interactions between them. This increase in order at the interface also results in an entropic contribution to the surface tension. Water is an example of a molecule which orders at the liquid-vapor interface in order to try to satisfy its hydrogen bonds with neighboring molecules at the interface. In the case of water, this contribution can be very large. Other contributions implied in Eq. 1 may exist whose size will be determined by both molecular interactions and molecular structure.

In order to study these various contributions to the surface tension we need to be able to partition them in some fashion. One way to achieve this is to choose molecules where only some of the above contributions are operative. In the case of weakly interacting polymers, for example, only the first two terms in Eq. 1 are dominant. If we now scale Eq. 1 using the isotropic contribution, we obtain the following simple expression:

$$\gamma(T)\,/\,\gamma_{\text{isotropic}} = F(T/T^*) + f'(T/T^*) \qquad (2)$$

where the first term on the right-hand side is a universal function for all molecules which form random interfaces and have no non-local contributions to the surface tension and $f'(T/T^*)$ represents the contributions from non-local effects. T^* is an appropriate scale factor for the temperature. Our ability to separate these contributions depends on the degree to which F(T) and f'(T) are truly universal functions. Another way of stating this is that we are assuming that a corresponding states principle exists for the surface tension of molecules which are not extended in space and which do not form strong directional intermolecular bonds.

One approach to studying the non-local contributions contained in the function f'(T) is to study an oligomeric series. The surface tensions of linear-chain molecules of different molecular weights have been measured that span molecular sizes from small compact molecules to long-chain polymer molecules (Ref. 4). Molecules with short chains will not suffer conformational penalties at the interface. As the molecular weight grows, we expect the entropic contribution from these molecules to turn on as a function of increasing molecular weight. Therefore, a possible experiment would be to examine Eq. 2 for such a molecular weight series. Clearly, the above analysis will only be successful if we can compute $\gamma_{\mathrm{isotropic}}$ accurately from the bulk thermodynamic properties of the liquid. It is to this question that we now turn our attention.

Polymer Thermodynamic Properties

Pressure, Volume, and Temperature Data

Many of the models use thermodynamic properties to calibrate their microscopic features. The energy and length scales of the model are fixed by using bulk equilibrium thermodynamic physical properties. This is frequently accomplished in the case of polymer liquids by using equations of state, i.e., a function which relates the density to the pressure and the temperature. The equation of state derived from a model is fit to pressure, volume, and temperature (PVT) data for a given sample and the fitting parameters (P^*,T^*, V^*,..), related to the microscopic model parameters, are obtained which characterize the thermodynamic properties. The microscopic parameters of the model can be obtained by fitting any thermodynamic property derivable from the model to the experimentally determined thermodynamic property. If the model is a good fitting function for that thermodynamic property or properties, then the model should describe those properties with which it has been calibrated but it may not be able to predict other thermodynamic properties. This latter case is more frequently the case. Therefore, depending on the thermodynamic property one wishes to investigate using a model, one should play close attention to the information used to calibrate the model.

PVT data for polymer melts have been lacking in the past. Like surface tension measurements, the measurement of the density of these viscoelastic fluids is not trivial and only recently have dilatometers been developed (Ref. 5) to provide data. An important aspect of any model is therefore the ability to acquire an accurate description of these thermodynamic data. Most three-parameter equations of state cannot provide accurate descriptions of PVT data over large temperature and pressure domains (Ref. 6). One way to circumvent this difficulty is to allow the fitting parameters to be functions of temperature and pressure. In this way one can take full advantage of the thermodynamic information. The only purpose of the temperature-dependent parameters is to capture an accurate description of the thermodynamic properties of the sample. The parameters are not used to fit the surface tension data.

The Cohesive Energy Density (CED)

The cohesive energy density (CED) is defined as the ratio of the internal energy, U, to the volume, V (CED = U/V). It is a measure of the strength of the interactions between the molecules. The solubility parameter is defined to be the square root of the cohesive energy density. It plays a major role in the modeling of the thermodynamic properties of polymer blends and solutions. Hildebrand and Scott (Ref. 7) related the CED to the surface enthalpy and they observed a strong correlation between the surface tension and the CED for a number of small-molecule liquids. In the case of small-molecule liquids, it is possible to calculate the CED using the heat of vaporization. In the case of polymer liquids, which have vanishingly small vapor pressures, it is not possible to compute the CED in this fashion. Numerous other thermodynamic properties depend on the CED and hence a number of correlations exist which relate these properties to the CED.

The Internal Pressure

It was Hildebrand and Carter (Ref. 8) who pointed out the correlation between the CED and the internal pressure. Although not usually stated, many equations of state are formulated based on the idea that the internal pressure is equal to the CED. The quantity of physical interest to us is the cohesive energy density (CED) of the polymer melt under study. This quantity cannot be directly computed from PVT data. A quantity which can be computed directly from PVT data is the internal pressure (P_i) which is defined as follows:

$$P_i = (\partial U/\partial V)_T = T(\alpha/\beta) - P \tag{3}$$

where U is the internal energy, V is the volume, T is the absolute temperature, α is the volume expansivity, β is the isothermal bulk compressibility, and P is the pressure. Hildebrand and Carter (Ref. 8) noted that at room temperature, the ratio of the internal pressure to the CED was close to unity for numerous hydrocarbon liquids with varying degrees of complex chemical structure. For alkanes for example, this ratio, which Hildebrand denoted as n, (where, $n = P_i/CED$), varied between 1.05 and 1.12 in the range C5-C14. This implied that if one used P_i as an estimate of the CED for alkanes, one would overestimate the CED by 5 - 10 %. Clearly, if one knows the value of n, then one can calculate accurately the CED from the internal pressure. Therefore, P_i provides us with information on the cohesive forces of the melt with accuracy in the range of 5-15% for alkanes.

Figure 1 shows a plot of the ratio $n(T,M_n)$ ($n = P_i/CED$) for alkanes where P_i was determined using PVT data and the CED was determined from heat of vaporization data. The plot shows clearly that for molecules with more than 12 carbon atoms, n is independent of molecular weight. Therefore for high molecular weights, we can use this function, n(T), to determine the CED using the internal pressure of the liquid for that material.

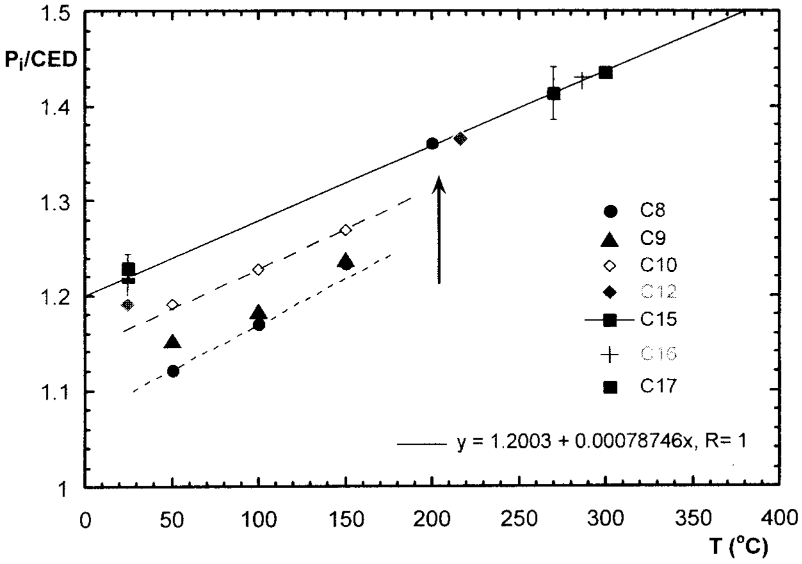

Fig. 1 Alkane thermodynamic data. A plot of $n(T,M_n)$ versus temperature for the alkanes

The Corresponding States Principle

Patterson and Rastogi (Ref. 9) tested the corresponding states principle for the surface tension of polymer melts. They scaled the surface tension using the bulk compressibility, β and volume expansivity, α. They defined a reduced surface tension $\gamma = \gamma/\gamma^*$, where $\gamma^* = \beta^{2/3} \alpha^{1/3} k^{1/3}$ and k is the Boltzmann constant. They found that plotting this reduced surface tension versus a reduced temperature, αT, the data for a number of polymers and small-molecule liquids fell on a universal curve with a scatter of 7-10%. The verification of the existence of a corresponding states principle depends on the availability of accurate bulk thermodynamic data for polymer and oligomer melts. Therefore, some of the scatter may be due to inaccuracies in the limited thermodynamic data.

By scaling in this manner, Patterson and Rastogi are using the internal pressure as an approximation to the CED of the liquid. This same information can be cast in many equivalent forms. For example, we could fit an equation of state to the PVT data for the liquid and use the reduction parameters of the model (P^*,V^*, and T^*) as scaling variables where $\gamma^* = \alpha\ P^{*2/3}\ T^{*2/3}$ and T scaled with T^*. The universal functions obtained will have different forms but the information content will be the same in each case (Ref 10). This work of ours showed that scaling the surface tension data for polymers and oligomers did not show any evidence of an entropic contribution to the surface tension. It also showed that using the internal pressure as a measure of the CED of the liquid state, we could predict the surface tension of numerous polymers with varying chemical structure to within 7 to 10 %. For molecules with the same chemical structure but with different molecular weights, we observed a strong corresponding states principle and could predict the surface tension to within 1-2 % using the internal pressure. This leads us to the conclusion that if we could scale the data with the CED for the liquid state, we could possibly collapse all the data for polymer liquids onto a single universal curve.

Given that we know the relation between the CED and the internal pressure for polyethylenes above C12, we can fit the equation of state directly to the CED and the density of the liquid. In doing so we are demanding that the equation of state give the correct CED and density at any given temperature and it is these properties of the bulk liquid that are most closely related to the surface tension. Figure 2 shows the surface tension of a number of alkanes scaled in this fashion. At low molecular weights, the data seem to fall on a lower curve and as the chain length increases, the data shift to a second higher curve with lower slope. This is the expected behavior predicted from our earlier simple picture of a polymer molecule at the liquid-vapor interface. Therefore, we expect very long chain molecules to lie on the upper curve and small molecules whose spatial dimensions are comparable to or smaller than the the interface width to scale on the lower curve. The magnitude of the effect is of the order of 10% of the surface tension as predicted in Ref. 3. These results demonstrate clearly that the simple idea of decoupling the contributions to the surface tension is possible in the case of polymer molecules. This fact opens up some new tools for the analysis of the thermodynamic properties of polymer melts which are enumerated in the conclusions.

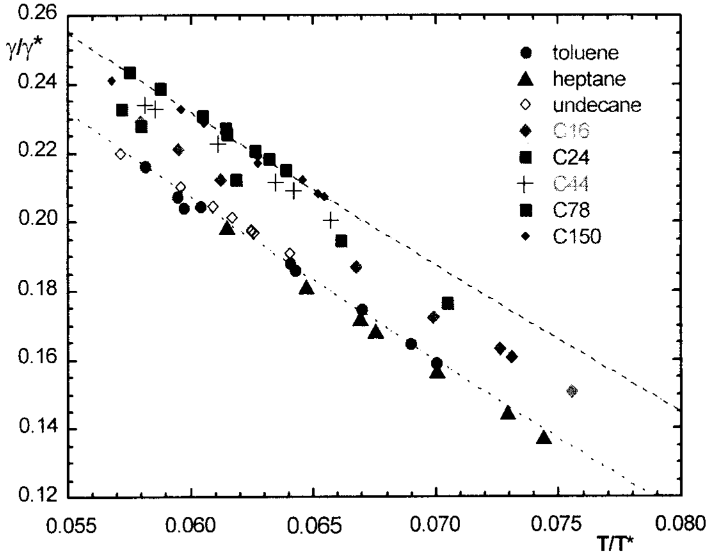

Figure 2. A plot of the scaled surface tension versus scaled temperature

Conclusions

The universal scaled surface tension provides a method for the calculation of the CED for a given polymer knowing its surface tension and the internal pressure of the melt determined from PVT data. By using the internal pressure to scale the surface tension data, we will obtain a scaled curve which will not correspond to the universal function we obtained for PE. If we assume that the curve we obtained for PE will be the same for all weakly interacting polymers, then the mapping of the curve scaled with the internal pressure onto the curve scaled with the CED specifies the relationship between the CED and the internal pressure. Using this approach, we will obtain different functions, n(T), for polymers with different chemical structure. This is a very powerful result since there is no direct method of measuring the CED for many polymer melts. We are currently using this method to obtain accurate thermodynamic properties of polymer melts.

We have demonstrated that one can decouple the entropic contribution to the surface tension of a polymer molecule from that which results from the local interactions between disordered molecules. Using accurate thermodynamic bulk properties and the corresponding states theory for surface tension, we can decouple the surface tension into those terms which satisfy the principle and those which do not. For chain molecules, two universal curves exist. One for low molecular weights and one for high. The difference between the curves is a manifestation of the non-local entropic contribution to the surface tension from polymer molecules at a liquid-vapor interface.

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