BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 8, pp. 1673–1681, 1995

0032-3861/95/\$10.00+0.00

The principle of corresponding states for polymer liquid surface tension

Gregory T. Dee* and Bryan B. Sauer
DuPont Company, PO Box 80356, Wilmington, DE 19880-0356, USA
(Received 11 May 1994; revised 15 August 1994)

A corresponding states principle is demonstrated for polymer and oligomer liquids. Scaling the measured surface tension with the thermodynamic properties obtained from pressure, volume, and temperature (PVT) data, one obtains a universal curve. We have developed a discrete interface cell model (DICM), which is a modified form of the Prigogine–Saraga cell model theory of surface tension which had previously been applied to polymer liquids. Using PVT data as input, the model accurately describes the surface tension data. With no adjustable parameters, the DICM theory provides a simple predictive tool for the conversion of the PVT properties of any material into surface tensions, with high accuracy at all temperatures and molecular weights. A strict adherence to the corresponding states principle is observed within each oligomer-to-polymer homologous series. This allows the model to predict the surface tension to within 1% accuracy for such a homologous series. The existence of a strict corresponding states principle implies that for the polymers studied here, the dominant contribution to the surface tension comes from the cohesive and entropic properties of the bulk liquids and is only weakly dependent on the molecular conformations and end groups. A discussion of the experimental difficulties in obtaining accurate PVT data and also extrapolating the thermodynamic properties to atmospheric pressure is given.

(Keywords: surface tension; corresponding states principle; polymer melts)

INTRODUCTION

The principle of corresponding states implies that any model which is based on simple spherical molecules, which interact via an attractive potential characterized by a well depth E and a hard core radius R, can be described by a partition function which can be written in scaled variables (reduced variables) using the energy and length scales E and R. In particular, any physical property which is derived from that partition function can be written as a function of these reduced variables. Therefore, such properties will be described by universal functions regardless of the molecular structure, i.e. polymers or low-molecular-weight substances could be described equally well based on their thermodynamic properties. This is a very strong assertion, but one which is at the heart of many of the empirical methods for the prediction of the thermodynamic properties of liquids[1] and solids[2]. The universal functions are specified by the form of the partition function and will vary from model to model. The existence of such universal functions, however, can be tested by scaling an observable property with the correct dimensional combination of other physical properties of the bulk liquid. The principle is not strictly valid for most real liquids but is approximately true in many systems. This leads to its great predictive value for many physical properties[1,2].

In the case of polymer molecules, the magnitude of the contribution of the conformational entropy to the surface tension is of interest. Polymer molecules in the liquid state adopt random coil configurations. A polymer molecule can no longer retain its random coil configuration near a liquid/vapour interface[3]. This restriction in the number of configurations of the molecule at the surface will lead to a contribution to the surface tension and this contribution cannot be predicted based solely on the bulk thermodynamic properties of the bulk liquid. Other aspects of polymers which one might expect to affect surface properties are the end groups of the polymer[4], side groups, and changes in chemical structure along the molecule, e.g. block copolymer structure. These and other structure features of polymer molecules contribute in varying degrees to the surface properties of polymer liquids.

If a strict corresponding states principle applies to surface tension, then one approach to determining the effects of the polymer character of the molecules on the surface tension is to observe the deviations away from the universal behaviour of the surface properties of polymers which are not described by the bulk properties of polymer liquids. In this fashion one could quantify the magnitude of such effects by changing the structure of the molecules by varying the molecular weight, end groups, side groups, and chemical composition. The work of Roe[5] and Patterson and Rastogi[6] demonstrated the existence of an approximate corresponding states principle which gave a unified picture for both homopolymer and oligomer liquids. These latter authors[6] observed that by scaling the surface tension with the thermodynamic properties of the fluid, they could

---

*To whom correspondence should be addressed collapse the experimental data on to a universal curve with a scatter of ±7%. They used a discrete interface model (known as the Prigogine–Saraga cell model theory of surface tension[7]) in conjunction with the Lennard-Jones and Devonshire[8] cell model of the bulk phase to describe the observed scaling of the surface tension of polymer liquids. They found that the Flory, Orwoll and Vrij (FOV) cell model[9] best described the experimental observations. Poser and Sanchez[10] applied the Cahn–Hilliard (CH)[11] theory with the Sanchez–Lacombe[12] equation of state to the description of polymer liquid surface tensions. They found reasonable agreement between their results and experimental surface tensions for polymer liquids. The theory does not satisfy the corresponding states principle and hence implies that there is no universal function which describes both polymer and oligomer surface tension data. Our recent work has described the use of the Cahn–Hilliard theory in conjunction with equations of state, which do, in fact, satisfy a corresponding states principle, to study polymer and oligomer liquids[13]. For a given polymer series of differing molecular weights we found that the FOV equation of state provided an accurate ($<1\%$) description of both the molecular weight and temperature dependence of the experimental data. This observation illustrates the strong corresponding states principle for homopolymers and oligomers and suggests that the contributions to the surface tension, due to conformational restrictions and other chain architecture contributions at the surface, are comparatively small for the materials that we have studied.

In this work we first describe a discrete interface model which gives some insight into the corresponding states principle for liquids, and also to the dominant contributions governing polymer and oligomer surface tension. The discrete interface model and the CH model are based on similar simplistic assumptions about the microscopic structure and interactions of polymer and oligomer liquids. The practical advantage of the discrete interface model over the CH model is that the computational requirements are trivial for the prediction of surface tension if one has available *PVT* or analogous bulk property data.

An important feature of the present work is the accurate measurement and modelling of the *PVT* data for the various liquids. Under these circumstances the surface tension can be predicted based solely on bulk property variations. In order to achieve an accurate description of the temperature dependence of the bulk thermodynamic properties, one must allow the fitting parameters of the equation of state to vary with temperature[13]. Only in this fashion can a model with a particular equation of state be accurately tested in its ability to model the surface properties.

THEORY

The interfacial tension, γ, for a planar interface is of the following form:

$$\gamma = (F - F_e)/S \tag{1}$$

where F is the Helmholtz free energy of the inhomogeneous system with the interface, F_e is the Helmholtz free energy of the system without the interface (but with the same density as the inhomogeneous system), and S is the surface area. In order to evaluate equation (1) we must compute expressions for F and F_e. An equation of state provides expressions for the enthalpy and entropy of a material at a given density. Using such theories we can compute F_e. To compute the free energy F, we need expressions for the entropic and enthalpic contributions from a system where an interface separates two different phases. Two approaches are possible here.

The first approach is to simply identify the surface region as a homogeneous layer whose density is intermediate between that of the equilibrium phases. Liquid–vapour interfaces are sharp at temperatures below the critical temperature, so it is assumed that the width of this phase is roughly a single layer of molecules. This width and the density in the interfacial region are specified by an ansatz. This fact led theorists to formulate models of this kind to describe the surface properties of small molecular[7] and polymer liquids[6,7]. Many theories[14] exist which differ in their definition and treatment of the interfacial region.

A second approach assumes that the density changes continuously between the high- and low-density phases, i.e. a continuum approach. The van der Waals[15] and Cahn–Hilliard density gradient[11] theories are of this type. Such theories, which assume that the gradients in the density are small, do not seem appropriate for the description of interfaces which are 5–15 Å in extent. However, the Cahn–Hilliard theory, in conjunction with an equation of state, has been used to describe the surface properties of small molecule[13,16] and polymer liquids[13] with equal success. Why do such theories describe the surface tension of liquids well below the critical temperature?

The answer to this question lies in the principle of corresponding states[7]. The corresponding states principle implies the existence of a universal function which describes a reduced surface tension as a function of reduced temperature. It also implies that the surface tension can be determined solely from the thermodynamic properties of the bulk liquid. Any theory which has the same or a similar functional form in terms of these reduced variables will provide an adequate description of the surface tension properties of these liquids. Under these circumstances, the physical significance of the microscopic details of the interface used to construct the model are diminished. In order to reinforce this point, we next derive a version of the discrete interface model which describes the molecular weight and temperature dependence of polymer liquids with the same degree of accuracy as was obtained previously using the Cahn–Hilliard model[13].

DISCRETE INTERFACE MODEL

In the spirit of Prigogine and Saraga[7] and Patterson and Rastogi[6] we consider a discrete interface model theory which uses the Flory, Orwoll, and Vrij (FOV) equation of state[9] to describe the bulk properties of the liquid. The theory can be derived in the context of the cell model formalism developed by Lennard-Jones and Devonshire[8] to describe the properties of small molecular liquids. *Figure 1* shows a two-dimensional cross-section of a lattice of cells occupied by polymer segments or mers. The size of the mers is not the same as the chemical repeat unit of the polymer. All of the cells are occupied

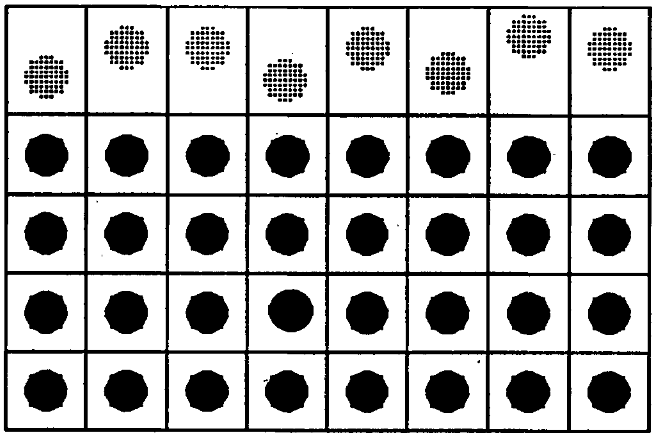

Figure 1 A cross-section showing a cubic lattice model of a condensed state with a free surface at the top

and the lattice has a free surface at the top of the lattice. A total of Nr mers occupy the cells, where each of the N polymer molecules is composed of r mers. Each mer has a hard core volume of v^*. The connectivity of the polymer is taken into account by assuming that each mer has $3c$ degrees of freedom[17] where c is a constant which is less than one. The above construction of partitioning the molecules into r mers with $3c$ degrees of freedom allows us to simply extend to polymers the cell model formalism which was originally developed for small molecular liquids[8]. Each cross-section parallel to the top surface of the lattice contains N_0 mers. The free volume in the cells of the top surface is shown to be greater than that of the bulk, reflecting the fact that the density decreases rapidly on the length scale of the width of a mer. The density of mers in the vapour phase above the liquid is assumed to be negligibly small and is assumed zero (a reasonable assumption for $T \ll T_c$). We will assume that the lattice in the bulk has a cubic geometry.

In order to calculate the surface tension we must compute the partition function for an inhomogeneous system with a free surface. The mers are allowed to wander within their cells but are not allowed to move between cells. The mers in the bulk interact via a spherically symmetrical potential $\phi(r)$. This potential is of the following form:

$$\phi(r) = \varepsilon^* \psi(r/r^*) \qquad (2)$$

where ε^* is the characteristic interaction energy per mer in the close packed configuration and r describes the position of the mer within its cell. The microscopic quantities ε^* and r^* (or v^*, the hard core cell volume) provide the energy and length scales of the model. Using the cell model formalism, we can then write the partition function for the inhomogeneous system in the following form[7]:

$$Z = f(T)\exp(-E_c/kT)v_f^{(Nr-N_0)}v_f'^{N_0} \qquad (3)$$

where v_f and v_f' are the free volumes of a cell in the bulk and one at the surface, respectively. E_c is the cohesive energy of the system when all mers are at the centres of their respective cells, and $f(T)$ is a function of the temperature which is the contribution from the translational kinetic energy, which is assumed to be classical, of the mers within their cells. The free energy of the inhomogeneous system is then obtained as $F = -kT\ln Z$, where k is the Boltzmann constant. Because of the single particle nature of the partition function, F can be divided into a bulk and a surface component so that $F = F_b + F_s$, where:

$$F_b = Nr[\phi(o) - kT\ln(v_f) - \ln(f(T))] \qquad (4)$$

and

$$F_s = N_0[(\phi'(o) - \phi(o)) - kT\ln(v_f'/v_f)] \qquad (5)$$

in which $\phi'(r)$ is the interaction potential between the mers in the surface layer and where the potentials in equations (4) and (5) are evaluated with the mers at the centres of their respective cells. Using equation (1) we find that $\gamma = (F - F_b)/S = F_s/S$. The total surface area S is equal to $N_0 s = (\omega N_0 v^{2/3})$ where ω is a geometrical factor ($\omega = 1$ for a cubic lattice), s is the surface area per mer, and v is the mer cell volume in the bulk. Using this definition of the surface area we obtain the following expression for the surface tension:

$$\gamma = [(\phi'(o) - \phi(o)) - kT\ln(v_f'/v_f)]/s \qquad (6)$$

which is essentially the result obtained by Lennard-Jones and Corner[18], generalized to include polymer molecules. This simple derivation leaves one with a physically intuitive picture of the surface energy and entropy. The first term in the brackets gives the surface energy in terms of the difference in cohesive energies between the bulk and the surface layer. The second term gives the surface entropy in terms of the ratio of the free volumes of a mer at the surface and one in the bulk of the liquid. The quantities $\phi(o)$ and v_f are specified by the cell model of the bulk liquid. An ansatz is required for $\phi'(o)$ and v_f'.

The free volume in the bulk is approximated by the following expression which is the Tonk's gas approximation[19,20] to the free volume in the cell, i.e. $v_f = (v^{1/3} - v^{*1/3})^{3c}$. The factor $3c$ takes account of the fact that the mers have less than 3 degrees of freedom, reflecting the fact that they are chemically bonded to their nearest neighbours. For the free volume of the mers in the surface layer we have chosen the following definition:

$$v_f' = (bv^{1/3})^c(v^{1/3} - v^{*1/3})^{2c} \qquad (7a)$$

i.e. the free volume of a surface mer has $2c$ degrees of freedom, which is similar to the bulk but has a different dimension perpendicular to the interface. Equation (7a) deviates from that used by Prigogine and Saraga[7] but remains within the spirit of the model. The form of v_f' used by Patterson and Rastogi[6] is shown by equation (7b) as follows:

$$v_f' = (v^{1/3} - bv^{*1/3})^c(v^{1/3} - v^{*1/3})^{2c} \qquad (7b)$$

In defining the surface energy we will use the approximation used by Prigogine and Saraga[7] which is stated as follows. If we assume that the difference in the interaction potentials reflects a decrease in the number of nearest neighbours at the interface, then a possible ansatz for this difference is the following:

$$\phi'(o) - \phi(o) = -m\phi(o) \qquad (8)$$

where m denotes the fraction of nearest neighbours lost at the surface. Inserting these definitions, i.e. equations (7a) and (8), into equation (6) we obtain the following:

$$\gamma=\{(-m\phi(\mathrm{o}))-ckT\ln[(bv^{1/3})/(v^{1/3}-v^{*1/3})]\}/v^{2/3} \tag{9}$$

To relate the microscopic parameters of the model to the properties of real systems we will obtain the equation of state for the bulk and by fitting this equation to the thermodynamic data we obtain the characteristic parameters. The equation of state for a homogeneous bulk phase consisting of Nr mers, i.e. no interface present, can be obtained from the expression for F_{b} in equation (4), as follows:

$$P=-\mathrm{d}F_{\mathrm{b}}/\mathrm{d}V|_T=-(1/Nr)\,\mathrm{d}F_{\mathrm{b}}/\mathrm{d}v|_T$$

$$P=-\varepsilon^*v^*/v^2+ckTv^{-2/3}/(v^{1/3}-v^{*1/3}) \tag{10}$$

where a $1/r^3$ potential was used for the interparticle potential. We can write equation (10) in terms of the reduced pressure, temperature and volume variables $\tilde{P}$, $\tilde{T}$ and $\tilde{V}$. The reduction variables P^*, T^* and V^* are defined as follows:

$$\tilde{T}=Tck/\varepsilon^*=T/T^* \tag{11}$$

$$\tilde{P}=Pv^*/ckT^*=P/P^* \tag{12}$$

$$\tilde{V}=v/v^*=v_{\mathrm{sp}}/v_{\mathrm{sp}}^* \tag{13}$$

where v_{sp}^* is the hard core specific volume such that $N_{\mathrm{A}}rv^*=Mv_{\mathrm{sp}}^*$, with N_{A} the Avogadro constant and M the molecular weight of the molecule. The parameters r, v^*, ε^* and c are the microscopic parameters of the model. Using the above definitions and assuming a cubic cell geometry we obtain the FOV equation of state, which has the following form:

$$\tilde{P}\tilde{V}/\tilde{T}=\tilde{V}^{1/3}/(\tilde{V}^{1/3}-1)-1/(\tilde{T}\tilde{V}) \tag{14}$$

Scaling equation (9) using ε^* and v^* and the definitions of the reduced variables as above, we obtain the following expression for the reduced surface tension:

$$\tilde{\gamma}=\gamma/\gamma^*=\{(-m/\tilde{V})-\tilde{T}\ln[(b\tilde{V}^{1/3})/(\tilde{V}^{1/3}-1)]\}/\tilde{V}^{2/3} \tag{15}$$

where $\gamma^*=\varepsilon^*/v^{*2/3}=P^{*2/3}T^{*1/3}(kc)^{1/3}$. If we use the form of v_{f}' used by Patterson and Rastogi, i.e. equation (7b), we obtain the following equation used by these authors in ref. 6, and shown in equation (16) as follows:

$$\tilde{\gamma}=\gamma/\gamma^*=\{(-m/\tilde{V})-\tilde{T}\ln[(\tilde{V}^{1/3}-b)/(\tilde{V}^{1/3}-1)]\}/\tilde{V}^{2/3} \tag{16}$$

Equation (15) provides a simple expression for the surface tension of liquids which depends on the reduced variables $\tilde{T}$ and $\tilde{V}$. The reduction parameters, P^*, T^* and V^*, can be obtained by fitting an equation of state to the bulk properties. It provides a surface tension and a surface width, but it does not provide details about the shape of the surface profile. To obtain this information one must resort to continuum models[11–13,15]. We should not expect the model to describe the surface properties as T approaches T_{c} because of the sharp interface width assumption.

As defined above, γ^* is a function of c. We must fix the value of c in order to determine the surface tension from equations (15) or (16). Clearly, the value chosen is not critical since the parameters m and b can be adjusted to obtain a good fit to the data. This was also the case with the CH model[13] where the square gradient coefficient could be adjusted in order to compensate for changes caused by a choice of the parameter c. This is not always possible, however, and we will illustrate this problem below. In ref. 13 we chose a value of c so that the hard core volume, v^*, was of the order of the dimension of the chemical repeat unit of polyethylene. Using equations (11)–(13) we find that $v^*=ckT^*/P^*$. Using a value of $c=0.11$ gives values for v^* which have the correct dimension. In the work of Patterson and Rastogi[6] a value of $c=1$ was used, which corresponds to a hard core volume which is approximately ten times bigger than the repeat unit dimension. The consequences of this choice are discussed below.

Finally, equation (7a) suggests a definition of the interfacial layer thickness. The width of the surface volume element in the direction perpendicular to the interface, λ, is equal to $bv^{1/3}=b(v^*\tilde{V})^{1/3}$. As we will see below, the value of b which produces a good fit to the data is of the order of 2. Since v^*, the mer hard core volume, has a value close to the volume of the repeat unit, i.e. $v^{*1/3}$ is a few Å, and $\tilde{V}$ is of the order of 1, the interface dimension is of the order of 10–15 Å.

EXPERIMENTAL

The molecular weights and polydispersities of the polymers used are given in refs 21–23; some of the polymers were obtained from Scientific Polymer Products, Inc. and Polysciences, Inc. The molecular weights were determined by gel permeation chromatography (polystyrene standards), zero shear viscosity, and light scattering for some of the polymers. Details of the polymer characterization have been given elsewhere for polystyrene (PS)[21], poly(dimethylsiloxane) (PDMS)[22], polyethylene (PE)[22], poly(ethylene oxide) (PEO)[22], poly(propylene oxide) (PPO)[22], poly(methyl methacrylate) (PMMA)[23], and poly(tetramethylene oxide) (PTMeO)[23].

The pressure, volume, and temperature (PVT) data were obtained using a dilatometer manufactured by Gnomix (Denver, CO). The data were measured in what the manufacturer refers to as the isothermal mode. The details of the apparatus and the different modes of operation are described elsewhere[24]. Most of the PVT data are described in refs 21 and 22; the data were measured at elevated pressures starting at 10 MPa. In the present application we use the data at high pressures to extrapolate to atmospheric pressure. Any extrapolation procedure, however, will lead to errors in the predictions at low pressures, and this point is discussed further in the Results section. Another source of error is the fact that the temperature of the sample is not always in equilibrium with the measuring thermocouple during the measurement of the volume, and this point is also addressed in the Results section.

The molten polymer surface tensions were measured by using a modified Wilhelmy vertical probe method, the details of which are described elsewhere[25].

RESULTS

An important aspect of this present work is an accurate description of the thermodynamic data. PVT data for each sample were obtained and surface tension measurements were made on the same sample. Equations

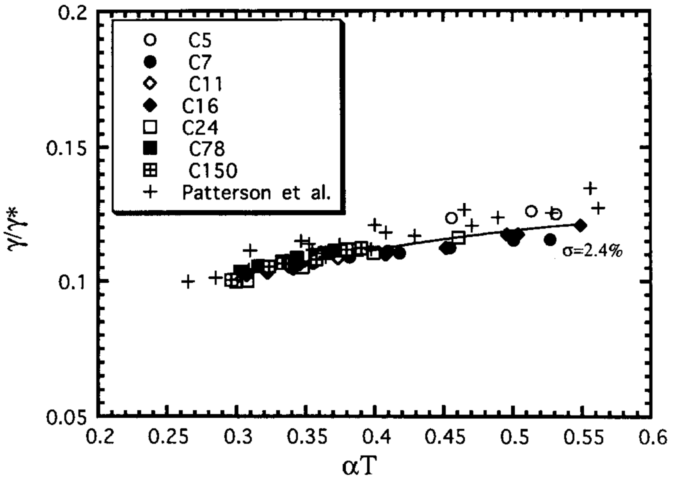

Figure 2 A plot of the scaled surface tension, γ/γ^*, as a function of αT for a series of alkanes where $\gamma^* = (k/\alpha)^{1/3}\beta^{-2/3}$

of state were fitted to the data in order to describe the thermodynamic properties of each sample. Most three-parameter equations of state cannot provide accurate descriptions of PVT data over large temperature and pressure domains. One way to circumvent this difficulty is to allow the fitting parameters to be functions of temperature and pressure. In the present application, where we are only interested in low pressures, it is sufficient to let the parameters be functions of the temperature only. The only purpose of the temperature-dependent parameters P^*, T^*, and V^* is to capture an accurate description of the thermodynamic properties of each sample. These parameters are not used to fit the surface tension data.

The work of Roe[5] and Patterson and Rastogi[6] demonstrated the existence of an approximate corresponding states principle for the surface tension of liquids. In order to test for the existence of such a principle, one must scale the surface tension appropriately. This was done by using a combination of thermodynamic functions which have the same physical dimensions as the surface tension. Plotting a scaled surface tension *versus* a reduced temperature for a number of alkanes and polymers, they observed a scatter of ±7% about a universal curve. If we are to use the existence of this principle as a means to search for surface effects which cause departures from a universal surface tension, then we must first revisit their work with our own data in an effort to see if we can reproduce and improve on their results, which were mainly based on selected literature data. The surface tension is scaled using the isothermal compressibility, β, and the thermal expansivity, α. Following refs 5 and 6 we define a reduced surface tension $\tilde{\gamma} = \gamma/\gamma^*$ where $\gamma^* = (k/\alpha)^{1/3}\beta^{-2/3}$, and k is the Boltzmann constant. Scaling the temperature using the expansivity we can plot γ/γ^* *versus* αT. Clearly such scaling is independent of any model assumptions.

Figure 2 shows the results of this effort for a number of alkanes. For each measurement of the surface tension we measured α and β using the PVT data from refs 21 and 22 for each sample at various temperatures. The data from ref. 6 are shown by the cross symbols. On the positive side the standard deviation (σ) in the new data is of the order of 2%, which is an improvement on the value of 7% in the data of Patterson and Rastogi[6]. It is clear from *Figure 2* that the two data sets do not perfectly overlap. One cause of this shift in our data are the errors introduced in our determination of α and β caused by extrapolating the PVT data to atmospheric pressure. The values of α and β were obtained by fitting the FOV equation of state to low-pressure ($10 < P < 40$ MPa) PVT data and then using the equation to calculate α and β at atmospheric pressure. Using a different equation of state will give different estimates for α and β. We used the FOV equation because it provided accurate estimates of α and β when compared with the directly measured atmospheric-pressure literature values of α and β for low-molecular-weight alkanes. Extrapolation procedures usually underestimate the compressibility with errors in the range of 2–10%[26]. This would account for the downward shift in our data. However, some equations of state will overestimate α and β.

Another source of error in the PVT data is the fact that we do not always determine the temperature of the sample accurately. In the so-called 'isothermal mode' of operation the sample is pressurized from 10 MPa to 200 MPa over the course of 6 min. The volume and temperature are recorded as the pressure passes each decade. Due to the adiabatic heating of the sample, and the mercury and oil used to maintain the hydrostatic pressure, the temperature of the sample is not perfectly defined. In order to quantify this error we remeasured the PVT data for a number of alkane samples. For these samples the measurements were taken after the sample temperature had equilibrated for 2 min at each pressure and hence the temperature of the sample was more accurately determined. A comparison of the PVT data measured using the different procedures showed small differences in the density at low pressures. *Figure 3* shows the results of this effort where we again compare the data of Patterson and Rastogi[6] with our data. The data scaled using the new PVT data are shifted up slightly and show better overlap with the previous data at higher values of the reduced temperature, while still retaining their lower scatter. It should be noted that this effect will depend on the properties of the liquid. In a study on water[27] it was demonstrated that the mode of measurement of the PVT data gave similar values to within the accuracy of the

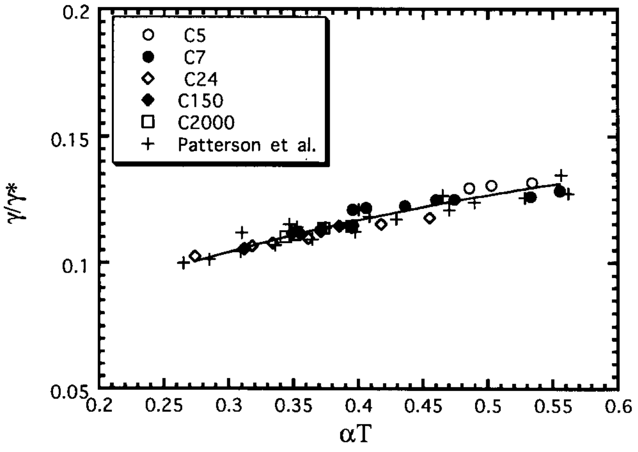

Figure 3 A plot of the scaled surface tension, γ/γ^*, as a function of αT for a series of alkanes where $\gamma^* = (k/\alpha)^{1/3}\beta^{-2/3}$, using remeasured PVT data (see text for details)

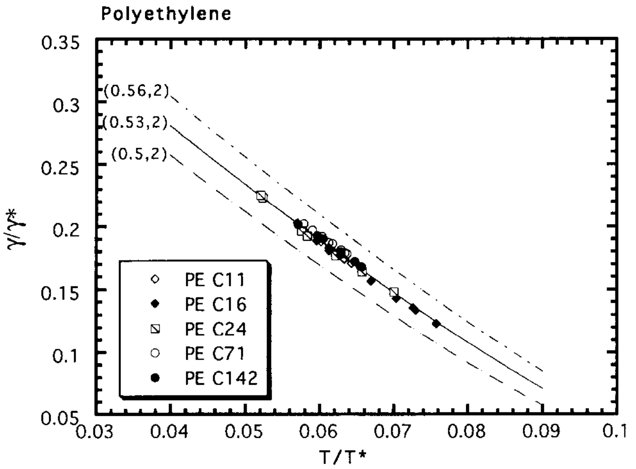

Figure 4 A plot of the scaled surface tension, γ/γ^*, as a function of reduced temperature, T/T^*, for a series of alkanes where $\gamma^* = P^{*1/3}T^{*2/3}(ck)^{1/3}$; the lines denote the DICM theory for values of $m=0.5$, 0.53, and 0.56, with $b=2$

measurements because of its lower compressibility and higher thermal conductivity. Since the effect is small, and since much of the data available to us were measured in the 'isothermal mode' we will ignore this effect and use the data measured in this fashion[21,22] for the rest of the results described here.

The lower level of scatter in our data results from the fact that the *PVT* data were obtained for these samples by using the same apparatus and experimental procedure, in addition to measuring the surface tension on the same samples. Patterson and Rastogi had to obtain their data from literature values and the different data for the different samples were from different sources[6]. For the purposes of this paper it is the existence of a universal curve for the surface tension and not its absolute value that is of interest to us. We are interested in the deviations from a universal scaling within a group of molecules with a similar chemical structure but differing in molecular weight.

One is not restricted to scaling the data with α and β. Any physical variables, or combination of variables, which have the correct physical dimensions can be used. We scaled the surface tension measurements using fitting parameters, i.e. the reduction parameters obtained from fitting the FOV equation of state to small pressure and temperature domains. A small temperature and pressure domain is chosen in order to ensure that the reduction parameters (P^*, V^* and T^*) accurately reflect the thermodynamic properties of the system in that domain[13]. The reduction parameters obtained in this fashion are thus temperature dependent. Using P^* and T^* we can define a reduced surface tension as follows[13]:

$$\gamma^* = \varepsilon^*/v^{*2/3} = P^{*1/3}T^{*2/3}(ck)^{1/3} \qquad (17)$$

If we scale the temperature with T^* and replot the data we obtain the plot shown in *Figure 4* for the alkane data. Plotting the data in this fashion further reduces the scatter in the data to a σ of 1.2%. Since γ^* is a function of c, the scaled surface tension in this representation will depend on the choice of c.

The solid lines in *Figure 4* are the results of the DICM theory for $\tilde{\gamma}$ as computed by equation (15) where values of $m=0.5$, 0.53, and 0.56, and $b=2.0$ have been used. The theory describes the data to the same degree of accuracy (<1%) as obtained previously[13] with the CH theory. The CH and DICM theories give similar predictions and can be made to coincide by a suitable choice of the parameters m and b for the case of the DICM model. *Figure 5* shows the results of the model described by equation (16) as used by Patterson and Rastogi, where the values of $m=0.43$ and $b=0.5$ were used to provide an optimal fit. Unscaled variables are used to illustrate the magnitude of the changes in the surface tension for this series of alkanes. In both cases a value of $c=0.11$ was used. From the work of Patterson and Rastogi[6] we know that this theory should provide a better description than that shown in *Figure 5*. The discrepancy lies in the value of c that is used. Patterson and Rastogi[6] used a value of $c=1$. Under these conditions the DICM model described in this previous work[6] (equation (16)) should be able to provide a description of the data comparable to that shown in *Figure 4*. However, the functional form of that model is such that any variation of the m and b parameters, in order to produce an accurate description of the data for values of $c=0.11$, is not possible. The functional form which we derived and used here (equation (15)) is more flexible in that one can choose values of m and b to optimize the fit to the data for a wide range of values of c, including values which set the mer size equal to the chemical repeat unit, i.e. $c=0.11$. Both equation (15) and equation (16)[6] are equally able to describe the experimental data under various conditions depending on the choice of c, so at this time we conclude that they are effectively equivalent when considering the semi-empirical nature of the theoretical development.

Figure 4 indicates that the alkane surface tension data obey a strong corresponding states principle. No obvious deviations from a universal curve can be seen as a function of an increasing molecular weight. The observance of the principle implies that bulk properties dominate the surface properties of this series of liquids and that contributions due to the polymer character of high-molecular-weight liquids are negligibly small. This

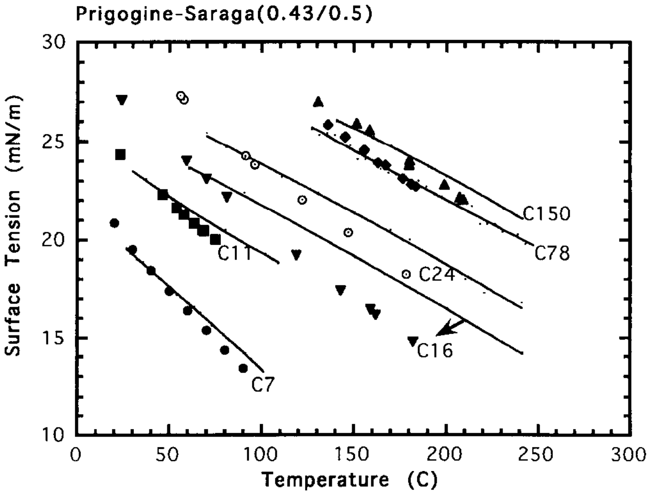

Figure 5 A plot of the surface tension *versus* temperature for a series of alkanes; the lines denote the Patterson–Rastogi theory (equation (16)) for $m=0.43$, $b=0.5$ and $c=0.11$

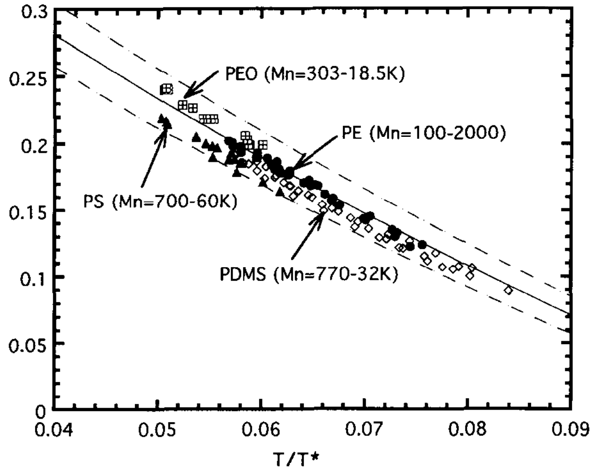

Figure 6 A plot of the scaled surface tension, γ/γ^*, as a function of T/T^* for a series of PEO, PE, PDMS, and PS samples of differing molecular weights where $\gamma^* = P^{*1/3}T^{*2/3}(ck)^{1/3}$

indicates that it is the local structure of the liquid, which is dictated by short-range interactions, which dominates the surface properties of the liquid. Is this true for other polymers? *Figure 6* shows the results for four different polymer series. Also shown in *Figure 6* are the predictions of our DICM theory (equation (15)) for values of $m = 0.5$, 0.53, and 0.56, with $b = 2$. In all of the polymers studied a strong scaling is observed within each series. The local properties of these molecules are not well described by a spherically symmetric potential and so we should not expect a strict scaling to be obeyed between polymers with different chemical structures.

The data in *Figure 6* also imply that the contributions from the surface depletion or excesses of end groups are also not observed. This is quite surprising for the series of PEOs where one might expect a surface depletion of OH groups to affect the surface tension, as has been shown by the recent work of Koberstein and coworkers[28] for poly(dimethylsiloxane) (PDMS). They studied PDMS with modified end groups, which are very high in surface energy relative to the main chain. While our data do not exclude such an effect, they do demonstrate that the effect of such an excess is not manifest in the surface tension data for typical materials without surface-energy-disparate end groups. In the case of PEO, we do not expect the liquid to be homogeneous right up to the interface, but expect that some surface rearrangement occurs to reduce the number of OH groups at the surface. This implies a reduction in the configurations available to the molecules at or near the surface, and a consequent entropic contribution to the surface tension. We saw in the case of the PE series that such restrictions in the configurations of the molecules near the surface have little effect on the surface tension. In addition, any surface excess of the low-surface-energy methyl terminating groups in PE could not be observed, and so these must have a very small contribution to the measured surface tension[13].

To explore this point further let us consider the surface tensions of water and ethylene glycol. These pure liquids form hydrogen bonded networks, which at temperatures well below their critical temperatures leads to a high degree of local order. The surfaces of these liquids also exhibit a high degree of order. The molecules arrange themselves to try to satisfy the directional nature of the hydrogen bonds. We do not expect such liquids to satisfy a surface corresponding states principle, as the surface properties are not simply related to the properties of the bulk liquid. *Figure 7* shows the scaled surface tensions of water and ethylene glycol. As expected, these materials do not fall on the universal curve common to the other liquids. If we focus on ethylene glycol we observe that as the temperature increases, the scaled surface tension approaches the universal curve. A possible interpretation of this is that at higher temperatures the local order (hydrogen bonding) in the bulk and at the surface is reduced, and the system becomes more disordered. To test this idea we measured the bulk and surface properties of n-heptane diol. In this compound we allow the molecule many more configurations and in particular, the molecules at the surface have many configurations, which they can choose so that the OH groups are not exposed at the surface. The data obtained for n-heptane diol are denoted by the cross symbols in *Figure 7*. We observe that in this system the scaled surface tension again returns to a universal curve. It is not surprising, therefore, that the PEO and PPO series exhibit a strong corresponding states behaviour over the molecular weight range being studied.

What is the cause of the shifts between the different polymers in *Figure 6*? The DICM model (equation (15)) can accommodate such shifts for each polymer by allowing for different values of the parameter m (the fraction of nearest neighbours lost at the interface). If we interpret the shifts in this fashion then we would conclude that as we progress from PEO, through PE, PDMS, to PS the number of neighbours of a mer in the surface layer is increasing. While this is a possibly interesting extension of the model, we instead will focus on the fact that the correction to the model affects the local characteristics of the mers in the surface layer. An analogous observation was made in the case of the CH model applied to a similar series of polymers[23]. To bring the CH prediction into agreement with each of the different polymer series, one can choose a different value of the reduced square gradient coefficient, $\tilde{\kappa}$, for each polymer. The coefficient $\tilde{\kappa}$ can be related to the local

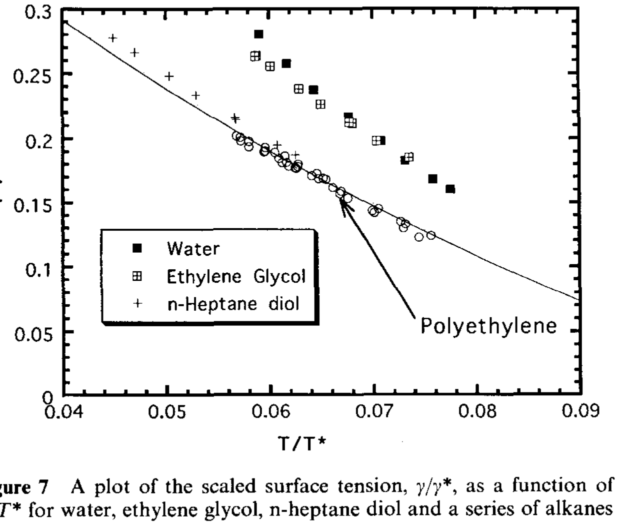

Figure 7 A plot of the scaled surface tension, γ/γ^*, as a function of T/T^* for water, ethylene glycol, n-heptane diol and a series of alkanes (○) where $\gamma^* = P^{*1/3}T^{*2/3}(ck)^{1/3}$

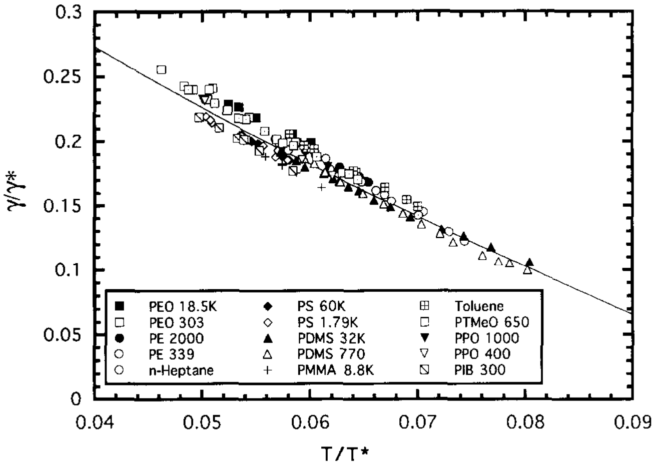

Figure 8 A plot of the scaled surface tension, γ/γ^*, as a function of T/T^* for a number of polymer and oligomer liquids where $\gamma^* = P^{*1/3}T^{*2/3}(ck)^{1/3}$

structure in the liquid[23,29,30] and hence plays a similar role to the parameter m. Thus, there are some small local structural differences between materials with different repeat units which cause deviations away from a perfect corresponding states principle. These are not seen for an oligomer-to-polymer homologous series of the same repeat unit, as was shown in *Figures 4* and *6*. In the case of the CH model, we feel that the ability to relate this local structure to values of $\tilde{\kappa}$ in a quantitative way is still far in the future.

Figure 8 shows a plot of the scaled surface tension for a large range of low- and high-molecular-weight liquids which we have studied. Such a plot enables us to devise an optimum value of the parameter m which describes all liquids ($\pm 6\%$). A value of $m = 0.52$ gives the best fit to these data. It must be remembered that this value depends on the way the values of the reduction parameters are obtained. As we have demonstrated above, different procedures for obtaining these parameters can cause shifts in the position of the universal curve by as much as 10–15%. If we take the data in *Figure 8* and partition them into two groups, defined by polymers with side groups (PPO, PDMS, PS, PMMA) and polymers without side groups (PE, PEO, PTMeO), then we obtain a plot as shown in *Figure 9*. This apparent clustering of the data into two groupings can be explained by again appealing to the nature of the local structure as mimicked by the parameter m in the DICM model or the square gradient coefficient in the case of the CH model.

From a practical standpoint, the DICM model (equation (15)) offers a simple and intuitive means for describing the surface properties of all liquids below their critical point, as was shown by Patterson and Rastogi[6]. Its simple algebraic form offers a simple predictive tool which will yield accurate predictions ($\pm 6\%$) based on the local thermodynamic properties of that liquid. We have shown that higher accuracy predictions can be made for high-molecular-weight polymer liquids by measuring the surface tension of an oligomer with the same chemical repeat unit. Using PVT data for that oligomer one can optimize the value of m in equation (15) necessary to describe any molecular weight sample of that species knowing only the PVT properties. In this fashion, predictions for the surface tension for high-molecular-weight liquids can be made with an accuracy of less than 1% with no adjustable parameters. The Cahn–Hilliard model and the DICM model can also be extended to describe the properties of mixtures.

CONCLUSIONS

The existence of a universal function for the surface tension of chain-like molecules is of practical importance. It offers a simple means of predicting the surface properties of almost any liquid using the thermodynamic properties of that liquid and no other adjustable parameters. We have demonstrated that two quite dissimilar models can describe the surface tensions of liquids well below their critical temperatures. The physical content of these models is primitive; all that is required by such a model is the ability to describe the scaled data. We feel that many such models can be made to satisfy this requirement and hence no deep significance can be apportioned to the fine details of these models, a fact that was pointed out by Patterson and Rastogi[6]. However, there are some basic requirements that the model must have: (a) the equation of state used to describe the liquid properties must satisfy the corresponding states principle, and (b) the functional form of the surface tension as derived from a theory must be such that it can reproduce the universal function by adjusting the free parameters of the model.

Most equations of state provide poor global descriptions of the thermodynamic PVT properties of polymer liquids. Therefore, one must allow the PVT fitting parameters to be functions of the temperature[13] in order to recover the accurate thermodynamic information. Upon obtaining an accurate description of the thermodynamic properties of bulk liquids, one can show that the changes in the bulk properties with molecular weight and temperature are the dominant factors governing γ. More importantly, from the perspective of a predictive tool, the two parameters in the DICM model (equation (15)) can be fixed for one polymer, and then used to predict the surface properties of other polymers as a function of molecular weight, chemical composition, and temperature. Thus,

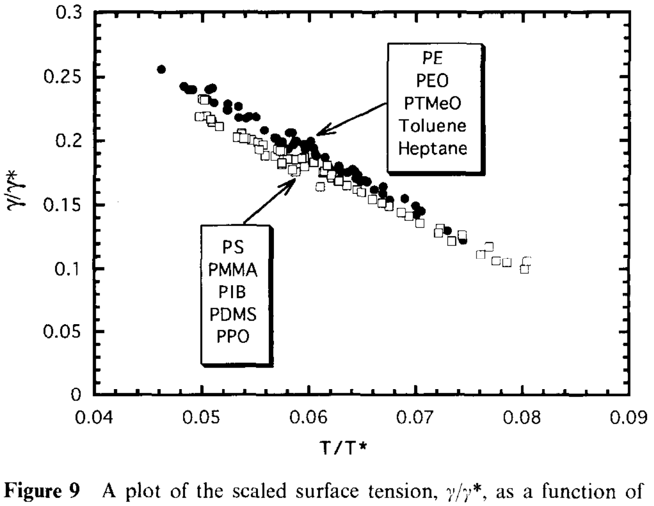

Figure 9 A plot of the scaled surface tension, γ/γ^*, as a function of T/T^* for the same polymer and oligomer liquids as shown in *Figure 8* where $\gamma^* = P^{*1/3}T^{*2/3}(ck)^{1/3}$: □, polymers with side groups; ●, polymers without side groups

the corresponding states principle can be of great practical use.

The principle is approximately observed for all polymers and oligomers illustrating the dominance of short-range forces in governing γ. The existence of a strict principle for a series of molecules with the same chemical repeat unit, but with differing molecular weights, has the following implications:

(a) The surface tension of polymer liquids does not exhibit any noticeable effects due to the restriction of the polymer conformations at the liquid–vapour interface.

(b) Within experimental error, end group excesses or depletions exhibit negligible effects on the surface tension for the polymers presented in this study.

(c) Any universally applicable quantitative theory of the vapour–liquid interface must satisfy the corresponding states principle.

ACKNOWLEDGEMENTS

The authors would like to thank Benjamin Haley for his able assistance in measuring the *PVT* properties of the materials used in this study and Nick DiPaolo for his work in gathering the experimental surface tension data.

REFERENCES

1. Reid, R. C., Prausnitz, J. M. and Poling B. E. 'The Properties of Gases and Liquids', McGraw-Hill, New York, 1987
2. Bondi, A. 'Physical Properties of Molecular Crystals, Liquids, and Glasses', Wiley, New York, 1968
3. Silberberg, A. *J. Colloid Interface Sci.* 1988, **125**, 14
4. De Gennes, P.-G. *C.R. Séances Acad. Sci.* 1988, **307**, 1841
5. Roe, R.-J. *Proc. Natl. Acad. Sci. USA* 1966, **56**, 819
6. Patterson, D. and Rastogi, A. K. *J. Phys. Chem.* 1970, **74**, 1067
7. Prigogine, I. and Saraga, L. *J. Chim. Phys.* 1952, **49**, 399
8. Lennard-Jones, J. E. and Devonshire, A. F. *Proc. R. Soc. London A* 1937, **163**, 53
9. Flory, P. J., Orwoll, R. A. and Vrij, A. *J. Am. Chem. Soc.* 1964, **86**, 3507
10. Poser, C. I. and Sanchez, I. C. *J. Colloid Interface Sci.* 1979, **69**, 539
11. Cahn, J. W. and Hilliard, J. E. *J. Chem. Phys.* 1958, **28**, 258
12. Sanchez, I. C. and Lacombe, R. H. *J. Phys. Chem.* 1976, **80**, 2352
13. Dee, G. T. and Sauer, B. B. *J. Colloid Interface Sci.* 1992, **152**, 85
14. Couchman, P. R. and Van Ness, K. E. *Polym. Eng. Sci.* 1987, **27**, 324
15. van der Waals, J. D. 'Verhandel. Konink. Akad. Weten.', (Section 1), Vol. 1, (No. 8), ?, Amsterdam, 1893, 56 pp. An English translation can be found in *J. Stat. Phys.* 1979, **20**, 197
16. Carey, P. S., Scriven, L. E. and Davis, H. T. *AIChE J.* 1978, **24**, 1076
17. Prigogine, I., Bellemans, A. and Mahot, V. 'The Molecular Theory of Solutions', North-Holland, Amsterdam, 1957
18. Lennard-Jones, J. E. and Corner, J. *Trans. Faraday Soc.* 1940, **36**, 1156
19. Tonks, L. *Phys. Rev.* 1936, **50**, 955
20. Eyring, H. and Hirschfelder, J. O. *J. Phys. Chem.* 1937, **41**, 249
21. Ougizawa, T., Dee, G. T. and Walsh, D. J. *Polymer* 1989, **30**, 1675
22. Dee, G. T., Ougizawa, T. and Walsh, D. J. *Polymer* 1992, **33**, 3462
23. Sauer, B. B. and Dee, G. T. *J. Colloid Interface Sci.* 1993, **144**, 25
24. Zoller, P., Bolli, P., Pahud, V. and Ackermann, H. *Rev. Sci. Instrum.* 1976, **47**, 948
25. Sauer, B. B. and DiPaolo, N. V. *J. Colloid Interface Sci.* 1991, **144**, 527
26. Hayward, A. T. J. *J. Phys. D* 1971, **4**, 938
27. He, J. and Zoller, P. *Rev. Sci. Instrum.* 1991, **62**, 1304
28. Jalbert, C., Koberstein, J. T., Yilgor, I., Gallagher, P. and Krukonis, V. *Macromolecules* 1993, **26**, 3069
29. Rowlinson, J. S. and Widom, B. 'Molecular Theory of Capillarity', Clarendon, Oxford, 1982
30. Bongiorno, V., Scriven, L. E. and Davis, H. T. *J. Colloid Interface Sci.* 1976, **57**, 462