

# Surface and bulk interchange energy in binary mixtures of chain molecules

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**Abstract.** The interchange (interaction) parameter, controlling the phase behaviour of a binary mixture, is determined for the bulk and the surface of binary mixtures of different types of chain molecules, using surface tensiometry and a mean-field theory. For all mixtures and concentrations studied an identical behaviour is observed at the surface, depending only on the square of the reduced chain length mismatch  $\Delta n/\bar{n}$ , where  $\Delta n$  and  $\bar{n}$  are the difference in and average of the number of carbons of the two components.

**PACS.** 61.30.Hn Surface phenomena: alignment, anchoring, anchoring transitions, surface-induced layering, surface-induced ordering, wetting, prewetting transitions, and wetting transitions – 68.35.Md Surface thermodynamics, surface energies – 68.03.Cd Surface tension and related phenomena

## 1 Introduction

Binary liquid mixtures and their surfaces have been testing grounds of choice for over a century for many fundamental ideas and theories in thermodynamics and statistical mechanics [1]. A few of these are bulk [2] and surface-mediated [3] phase separation, critical adsorption [4], and short- [5] and long-range [6] wetting phenomena [4,7]. Such mixtures are also of great practical importance for lubricants, fuels, paints etc. The phase diagram of binary mixtures of chain molecules is dominated by a delicate balance between entropy, which drives the system towards homogeneity, and the repulsion energy between the unlike constituent molecules, which drives them to segregate and phase separate. The repulsion energy is determined by the so-called interchange, or interaction, parameter  $\omega$ , which is the energy change upon replacing one molecule of the pure phase of one species by a molecule of the other species [1].  $\omega$  is extensively used in diverse areas of phase behaviour and phase stability studies of mixtures, most notably in polymer blends [8], but also in gels, liquid crystals, molten metallic alloys, colloids, emulsions etc. As we show here, the surface freezing (SF) effect [9,10], provides a unique tool for studying  $\omega$  at the surface and the bulk solids of the same mixture. The SF effect is the formation of a solid monolayer (for alkanes, alkenes, semi-fluorinated alkanes) or bilayer (for alcohols, alkyl-oligo-ethyleneglycols,  $\alpha$ ,  $\beta$ -diols) at the free surface of the molten compound at temperatures of up to a few

degrees *above* the bulk melting temperature. In molecules other than chain molecules, this effect is very rare [11], since almost all materials show surface melting, where the solid's surface melts at a temperature *lower* than that of the bulk [12]. The molecules of the SF monolayer are the same as those of the underlying bulk melt and a free exchange between bulk and surface is possible in all phases. By contrast, the confinement of organic molecules to the surface of water (in a Langmuir film [13]), or of a solid (in a self-assembled monolayer [14]), imposes a very high kinetic barrier on phase transitions requiring molecular rearrangement, e.g. macroscopic phase separation, and often effectively prevents their observation. The SF system is, therefore, unique in allowing the study of many thermodynamical and structural properties of a quasi-2D solid practically without kinetic barriers, and the relations between bulk and surface phase behaviour.

Using bulk- and surface-freezing as tools, we have studied the interchange parameter  $\omega$  of chain molecules in both the quasi-2D solid surface layer and the corresponding solid bulk rotator phases in alcohol-alcohol (dry and hydrated) and alkane-alkane (protonated-protonated and deuterated-protonated) binary mixtures, employing surface tensiometry [15].  $\omega$  is obtained from the measured bulk  $[T_b(\phi_l^b)]$  and surface  $[T_s(\phi_l^b)]$  freezing temperatures, where  $\phi_l^b$  is the bulk mole fraction of the longer component in the liquid phase, using the measured (surface) and known (bulk) entropy change upon freezing, and a simple mean-field approach based on ideal solution theory and the theory of strictly-regular mixtures [1]. In spite of the

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different interactions (e.g. van der Waals plus hydrogen bonding for the alcohol mixtures and van der Waals only for the alkanes), and structure of the surface layer (bilayer for alcohols and monolayer for the alkanes) an identical behaviour is found for  $\omega$  at the surface for all mixtures studied, depending linearly on  $(\Delta n/\bar{n})^2$ .

## 2 Experimental

The sample was held in a two-stage cell, the temperature of which was controlled to  $\leq 0.005$  °C. The surface tension  $\gamma(T)$  was measured by the Wilhelmy method, using an electronic balance under computer control. The temperature was scanned stepwise at a rate  $\leq 0.1$  °C/minute to ensure ample thermal equilibration. Each data point is an average of 20 measurements at a fixed temperature. The absolute measurement accuracy of  $\gamma(T)$  was  $\pm 0.5$  mN/m. Further details are given in references [10,15,16]. We denote protonated,  $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$ , and deuterated  $\text{CD}_3(\text{CD}_2)_{n-2}\text{CD}_3$  alkanes by  $C_n$  and  $D_n$ , respectively, and alcohols  $\text{CH}_3(\text{CH}_2)_{n-1}\text{OH}$  by  $C_n\text{OH}$ . We have measured the alkane mixtures  $C_{20}+C_{20+\delta}$ , and  $C_{36-\delta}+C_{36}$  for  $2 \leq \delta \leq 10$ , and  $D_{32}+C_n$ , ( $n = 20, 23, 26, 32, 36$ ), and the alcohol mixtures  $C_{18}\text{OH}+C_n\text{OH}$  ( $n = 14, 22, 24, 26, 28$ ) and  $C_{16}\text{OH}+C_{22}\text{OH}$ , in both dry and water-saturated atmosphere. Studies show that under hydrated conditions the SF properties of pure alcohols differ from those of dry alcohols [17], due to the incorporation of water molecules into the liquid and solid phases of both bulk and surface.

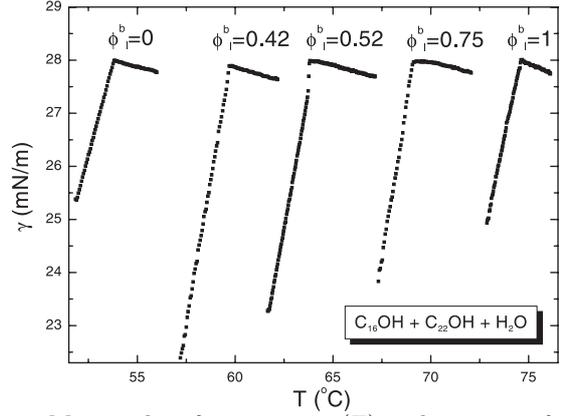
## 3 Theory and results

$\gamma(T)$  is the surface excess free energy over the bulk [18],  $\gamma(T) = \epsilon_s - \epsilon_b - T(S_s - S_b)$ , where  $\epsilon_{s,b}$  and  $S_{s,b}$  are the energies and the entropies for the surface and the bulk, respectively. Thus,  $d\gamma(T)/dT = -(S_s - S_b)$ . For ordinary liquid surfaces, the surface molecules have a slightly higher entropy than those in the bulk,  $S_s > S_b$ , yielding  $d\gamma/dT < 0$ , as indeed observed in the measured  $\gamma(T)$  in Figure 1 above  $T_s$ . Ordering of the liquid surface reduces  $S_s$ , inverting the slope:  $d\gamma/dT > 0$ , as observed clearly in Figure 1. The slope change identifies  $T_s$ , and yields the surface entropy change upon surface freezing,  $\Delta S_s$ , as the slope change at  $T_s$ .  $T_b$ , experimentally determined by the appearance of large instabilities in the  $\gamma(T)$  scan, is the lowest temperature shown for each curve. The resultant  $(\phi_i^b, T)$  solid/liquid phase boundaries are shown in Figure 2 for the bulk ( $T_b(\phi_i^b)$ ) and the surface ( $T_s(\phi_i^b)$ ).

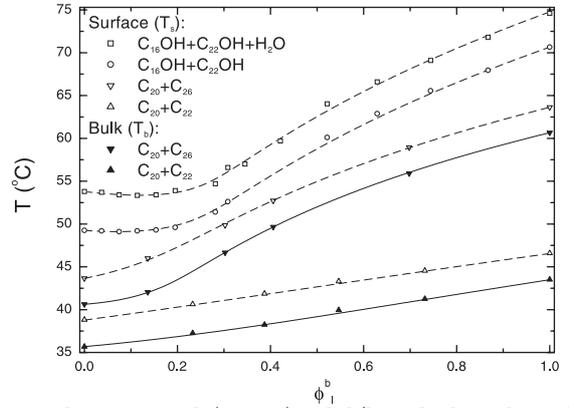
Theoretically, we treat the liquid ( $l$ ) bulk ( $b$ ) and surface ( $s$ ) phases, where the molecules are flexible and space-filling, as ideal mixtures, neglecting the very small mixing enthalpy expected. The free energy  $F_l^j$  per mole of a  $C_n+C_m$  mixture is then [1]

$$F_l^j = \phi_l^j f_l^j(n) + (1 - \phi_l^j) f_l^j(m) + k_B T \left[ \phi_l^j \ln(\phi_l^j) + (1 - \phi_l^j) \ln(1 - \phi_l^j) \right], \quad (1)$$

where  $j = s$  or  $b$ .  $f_l^j(i) = \epsilon_l^j(i) - TS_l^j(i)$ ,  $\epsilon_l^j(i)$ , and  $S_l^j(i)$  are the molar free energy, energy and entropy,



**Fig. 1.** Measured surface tension  $\gamma(T)$  cooling curves for concentrations  $\phi_i^b$  of the longer component in the indicated binary mixture. The bulk ( $T_b$ ) and surface ( $T_s$ ) freezing temperatures are the lowest temperature, and the slope change point, respectively, in each curve.



**Fig. 2.** The measured (points) solid/liquid phase boundaries  $T_b$  and  $T_s$  for several mixtures, with the theoretical fits (lines) discussed in the text.

respectively, of a liquid melt of pure  $C_i$ , with  $i = n, m$ .  $\phi_l^j$  and  $(1 - \phi_l^j)$  are the mole fractions of  $C_n$  and  $C_m$ , respectively. The square-bracket term is due to the mixing entropy [1]. In the crystalline phase ( $c$ ), the chains are extended and aligned in parallel. Interchanging a long and a short molecule now entails a free energy cost of  $\omega^j$  [1]. The free energy is then [1,16]

$$F_c^j = \phi_c^j f_c^j(n) + (1 - \phi_c^j) f_c^j(m) + k_B T \left[ \phi_c^j \ln(\phi_c^j) + (1 - \phi_c^j) \ln(1 - \phi_c^j) \right] + \omega^j \phi_c^j (1 - \phi_c^j), \quad (2)$$

where the notation of equation (1) is employed, with “crystalline” ( $c$ ) replacing “liquid” ( $l$ ). The last term in equation (2) is the repulsion term due to the interchange energy,  $\omega^j$ , in the zeroth-order approximation (nearest neighbour interactions only) of the “strictly-regular” mixture theory [1]. The phase behaviour is determined by the balance between the mixing entropy and the repulsive interchange term. For  $\omega^j \lesssim 2k_B T$  the mixing entropy is dominant and a homogeneous mixing results in the crystalline phase at all  $\phi_c^j$ . For  $\omega^j \gtrsim 2k_B T$ , the repulsive term dominates and induces phase separation in the solid phase for compositions  $\phi_c^j \approx 0.5$  [19]. It is important to note that the only quantity controllable experimentally is

the bulk liquid concentration,  $\phi_l^b$ . The rest are determined by the thermodynamics of the system. The surface  $\phi_l^s$  is modified from the bulk  $\phi_l^b$  by the Gibbs adsorption rule [16,18], whereby the surface is enriched by the lower surface energy component of the mixture. Equating the surface and bulk chemical potentials and taking into account the excess free energy at the surface  $\gamma(T)$  yields:

$$\phi_l^s = \phi_l^b \Gamma_l / (1 - \phi_l^b + \phi_l^b \Gamma_l), \quad (3)$$

where  $\Gamma_l = \exp[(\gamma_m - \gamma_n)A/k_B T]$ .  $\gamma_{n,m}(T)$  are the surface tensions of the pure  $C_{n,m}$ , and  $A \approx 25 \text{ \AA}^2$  is the molecular area [16]. Since  $\gamma_n(T = \text{const} > T_s)$  increases with  $n$  [10,15], equation (3) drives for a slight depletion of the long component at the surface, i.e.  $\phi_l^s \lesssim \phi_l^b$ . However, the difference is small and continuous, so that the general phase behavior of the surface and bulk are similar. Note, in particular, that  $\phi_c^j$  differ, in general, from  $\phi_l^j$ , are not known a priori, and must be determined from the thermodynamics of the system.

The solid and liquid chemical potentials of each component  $m, n$ , calculated from equations (1) and (2), are equal at the bulk ( $T_b$ ) and surface ( $T_s$ ) solid/liquid coexistence temperatures. This yields equations which can be solved for  $T_b$  and  $T_s$  [16,20]. For  $C_n$ :

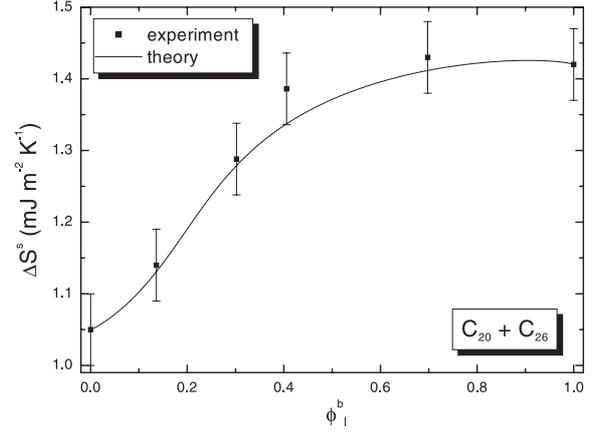
$$T_j(\phi_l^j) = \left[ T_{j,n} \Delta S_n^j - \omega^j (1 - \phi_c^j)^2 \right] / \left[ \Delta S_n^j + k_B \ln \left( \phi_c^j / \phi_l^j \right) \right]. \quad (4)$$

where  $T_{j,n}$  and  $\Delta S_n^j$  are the freezing temperature and the entropy change upon freezing of the pure component  $n$ . The equivalent expression for  $C_m$ , used to solve for  $\phi_c^j$  numerically, is obtained by replacing  $n \rightarrow m$  and  $\phi_l^j \leftrightarrow (1 - \phi_l^j)$ . The pure-material  $T_{j,n}$  and  $\Delta S_n^j$  have been measured [10,17], and  $\phi_l^s$  can be calculated, using equation (3), from the known  $\phi_l^b$ .  $\omega^j$  is determined by fitting equation (4) to the measured  $T_b(\phi_l^b)$  or  $T_s(\phi_l^s)$  at the different  $\phi_l^b$  of each mixture  $C_n + C_m$ . In spite of the single fit parameter,  $\omega$ , for each  $n, m$  combination, excellent fits are found for both bulk and surface of all mixtures studied, strongly supporting the simple theory above. Some fit examples are shown in Figure 2. The only exceptions are dry bulk alcohol/alcohol mixtures, which, unlike all other mixtures studied, exhibit in calorimetric measurements large undercoolings, and which previous experiments showed to require a more sophisticated theoretical approach [16].

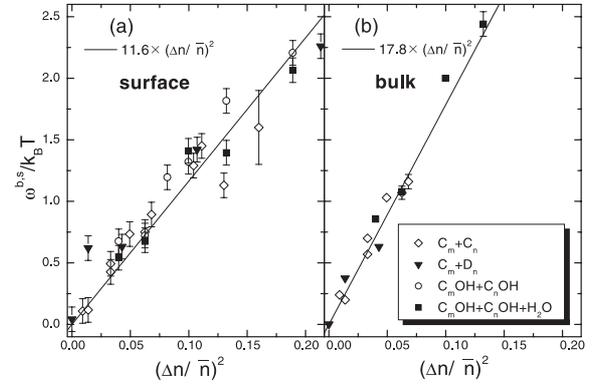
The entropy change upon surface-freezing of the mixture,  $\Delta S^s$ , can be calculated from those of the pure components,  $\Delta S_{n,m}^s$ , as [16]:

$$\Delta S^s = \phi_c^s \Delta S_n^s + (1 - \phi_c^s) \Delta S_m^s + k_B \left[ \phi_c^s \ln \phi_c^s + (1 - \phi_c^s) \ln (1 - \phi_c^s) - \phi_l^s \ln \phi_l^s - (1 - \phi_l^s) \ln (1 - \phi_l^s) \right]. \quad (5)$$

Using now the crystalline surface compositions  $\phi_c^s(\phi_l^b)$  obtained from the  $T_s(\phi_l^b)$  fits, we can calculate  $\Delta S^s$  from equation (5) without any adjustable parameters, and compare it to the values obtained from the slopes of the measured  $\gamma(T)$  for the mixture. The good agreement obtained in all mixtures studied in spite of the high non-linearity, e.g. Figure 3, further supports the validity of the present analysis.



**Fig. 3.** Measured (points) entropy change upon surface freezing. Note the good agreement with the theoretical curve, calculated with no adjustable parameters (line).



**Fig. 4.** The measured (points) and linear fit (lines) of the surface ( $\omega^s$ ) (a) and bulk ( $\omega^b$ ) (b) interchange energies. The linear dependence, common to all types of molecules, is unexpected considering the different interactions in the various mixtures.

## 4 The interchange energy

When all experimentally derived  $\omega^{b,s}$  values are plotted *phenomenologically* against  $(\Delta n/\bar{n})^2$ , a close linear dependence is observed, as shown in Figure 4. This can be rationalized as follows. The interchange energy  $\omega^{b,s}$ , is due to, and should obviously depend on, the chain length mismatch,  $\Delta n$ . However, the sensitivity to a given mismatch  $\Delta n$  should be different for long and short chains, because of the different relative importance of the finite number of chain-end gauche conformations, bending, etc., occurring in the rotator phases. It is therefore reasonable to assume [19] that  $\omega^{b,s}$  should depend on the unitless quantity  $\Delta n/\bar{n}$ , where  $\bar{n} = (n + m)/2$ . Since  $\Delta n/\bar{n} < 1$  for all mixtures studied here, we can expand  $\omega^{b,s}$  in a power series in  $\Delta n/\bar{n}$ . The constant term must vanish, since interchanging equal-length molecules does not cost energy. Odd-power terms must also vanish, since clearly  $\omega^{b,s}(\Delta n/\bar{n}) = \omega^{b,s}(-\Delta n/\bar{n})$ . The first non-zero term in the series is then  $(\Delta n/\bar{n})^2$ , and we can truncate the series after this term, since for large  $\Delta n/\bar{n} \approx 1$ , where higher-order terms may be significant, phase separation of the components occurs anyway, and the theory above is not valid anymore [20]. As shown in Figure 4, the  $\omega^s$  values

extracted from the measured  $T_s(\phi_i^b)$  indeed conform exceedingly well to the expected  $(\Delta n/\bar{n})^2$  dependence for all mixtures studied, i.e. for  $(\Delta n/\bar{n})^2 \leq 0.23$ .  $\omega^b$  shows this dependence up to  $(\Delta n/\bar{n})^2 \approx 0.13$ . As expected, this value of  $(\Delta n/\bar{n})^2$  corresponds to  $\omega^b \approx 2.5k_B T$ , close to the limit of phase separation, which is also the limit of validity of our theory. For the surface, all mixtures studied correspond to  $\omega^s \lesssim 2.5k_B T$ , as observed in Figure 4a. Hence, the limit for the surface can not be confirmed from our present measurements. Note, that the functional form of  $\omega^b$  and  $\omega^s$  is the same (albeit with different prefactors) despite the large difference in the interactions in the quasi-2D surface film and the 3D bulk. The higher prefactor (17.8 vs. 11.6) clearly indicates a higher inter-chain repulsion in the bulk. This possibly reflects significantly larger strains resulting from the need to accommodate different chain lengths in a multilayered 3D solid, than those in packing them in a single surface mono or bilayer. This may be also the reason for the reduced linearity range observed in Figure 4 for the bulk ( $(\Delta n/\bar{n})^2 \leq 0.13$ ) relative to the surface (all mixtures studied, i.e.  $(\Delta n/\bar{n})^2 \leq 0.23$  at least). The D–H isotope effect on  $\omega^{b,s}$  seems to be very small, since a significant effect would result in a non-zero interchange energy even at  $\Delta n \rightarrow 0$ , in contrast with the zero-crossing line, and relevant points (inverted triangles), observed for both bulk and surface for these mixtures in Figure 4.

Perhaps the most striking feature of the measured  $\omega^{b,s}$  shown in Figure 4, in addition to its strictly following a linear  $(\Delta n/\bar{n})^2$  dependence, is the fact that all points fall on the *same* line, regardless of the components of the mixtures. This “quasi-universal” behaviour is unexpected in view of the additional interactions existing in some of the mixtures: hydrogen bonding in alcohols and isotope mismatch repulsion in the deuterated-protonated alkane mixtures. While the isotope effect is expected, and indeed found to be small as discussed above, the hydrogen bonding is strong enough to induce the formation of a SF bilayer, rather than the monolayer observed in alkanes. The increased temperature and chain-length ranges of existence of SF in hydrated alcohols relative to those of dry alcohols indicate an increased stability, and stronger hydrogen bonding [17]. Nevertheless, the identical behavior found in Figure 4 indicates that the length-mismatch repulsion energy of the chains dominates over any of the other interactions.

Experimental-uncertainty-sized changes in the values of the input parameters to the theory above (the pure-material  $T_{j,n}$  and  $\Delta S_n^j$ , the measured  $T_b, T_s$ , etc.) change only slightly the  $\omega^{b,s}$  values derived from the fits. This is also true for a different model using the Flory approach [1], where *in the liquid phase* a monomer is taken as a methylene group. However, the main conclusions, a quadratic dependence of  $\omega^{b,s}$  on  $\Delta n/\bar{n}$  and a “quasi-universality” remain unchanged, albeit with a somewhat larger scatter in the  $\omega^s$  values in Figure 4, and slightly different line slopes. These results demonstrate that our main conclusions are rather robust with respect to changes in the model and the input parameter values.

## 5 Conclusion

The  $\Delta n$  dependence of the repulsion energy is currently ill-understood theoretically. A naive assignment of  $\omega^{b,s}$  to a loss of van der Waals contacts between short-long neighbours, as compared to long-long neighbours, leads to a linear  $|\Delta n|$  dependence, and a numerical overestimation of the experimental values obtained here for  $\omega^{s,b}$  by one order of magnitude [20]. The repulsion energy in bulk alkane mixtures was assigned [19] to local lattice deformations induced by a crystal structure comprising different-length molecules. This, however, leads to a theoretical  $\omega^{b,s} \sim |\Delta n/\bar{n}|$ , which is linear rather than the quadratic dependence observed experimentally. Moreover, this theory may not be directly applicable to our case since it treats a bulk orthorhombic solid with interlayer couplings, while in our case all solids are rotators [10,17], and no interlayer coupling exists for the single solid layer at the surface. We conclude, therefore, that while the mean-field “quasi-universal”  $\omega^{b,s} \sim (\Delta n/\bar{n})^2$  dependence found experimentally is well justified by the symmetry of the repulsion term in the free energy, a more sophisticated theoretical approach is required taking into account the presence of voids, gauche kinks [21], short-range clustering of equal-length molecules etc.

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