PHYSICAL REVIEW E VOLUME 61, NUMBER 1 JANUARY 2000

Effect of long-range forces on surface freezing

Prabir K. Mukherjee and Moshe Deutsch*
Physics Department, Bar-Ilan University, Ramat Gan 52900, Israel

(Received 5 April 1999)

We examine the effect of long-range van der Waals interactions on surface freezing (SF) in linear hydrocarbon chain molecules, and the wetting criteria of the bulk liquid by the crystalline surface phase. We find that although the effect of van der Waals interactions is small for SF of normal alkanes, it is important for SF of dry and hydrated alcohols. We also find that the long-range interactions should not be ignored in the interpretation of wetting phenomena in recent experimental results. The results are in good agreement with recent experiments.

PACS number(s): 68.10.−m, 61.25.Em, 64.70.Dv

I. INTRODUCTION

The recently discovered surface freezing (SF) in normal-alkanes, alcohols (dry and hydrated) and several other chain molecules has attracted much experimental [1–9] and theoretical [10–16] attention. In alkanes [2–4] an ordered crystalline monolayer is found to form at the surface of a single- or bicomponent melt up to 3 °C above the bulk freezing point. In alcohols [5–9] SF results in the formation of a crystalline bilayer at the surface of the melt at temperatures up to 1 °C (dry) or 2 °C (wet) above the bulk freezing point. The molecules in the layer are hexagonally packed and show a number of distinct rotator and crystalline phases. SF should, in principle, depend sensitively on the type and range of interactions between the surface and bulk and, as shown by Tkachenko and Rabin [12] (TR), also on the thermal motion of the molecules in the crystalline surface layer. Surface freezing is also a special case of interfacial wetting. The wetting, however, is incomplete according to the experimental observations: the single monolayer or bilayer persist down to the bulk freezing temperature, and the number of layers does not increase as bulk freezing is approached, as required by a complete wetting scenario [17].

Theoretically, molecular-level calculations [12], lattice-gas models [11], density-functional theory [15], and computer simulations [10,14,16] were used to account for the SF effect. Leermakers and Cohen-Stuart [11] based their lattice-gas model calculations on the surface activity of the less dense CH_3 end groups of the alkane molecules, which induces a surface-normal alignment of the chains. This alignment was confirmed experimentally, even when the surface is liquid, by nonlinear optical measurements [18]. A surface-normal molecular alignment is also found in the density-functional calculations of ten Bosch [15], even though a simple rigid rod model is employed for the molecule. TR [12] proposed a molecular-level theory, employing a fluctuation-based entropic scenario, to account for SF in alkanes. They suggested that the SF layer is stabilized by the free-energy gain due to unusually large up-down thermal motion of the molecules, a few Å in amplitude. Such an amplitude can be accommodated by the surface crystal without violating the Lindemann criterion for the crystalline stability because although large, the amplitude is still only a small fraction of the molecular length for these long molecules. They suggest that the same model is also applicable to other hydrocarbon chain molecules, not just alkanes, though no specific results are presented for, e.g., alcohols. Sirota *et al.* [13], based on the experimental result by Zisman [19], argued that surface freezing can be explained as a pure wetting effect, without the need to resort to a molecular-level theory. Molecular-dynamics simulations by Kawamata and Yamamoto [14] argue that the surface monolayer is due to a preferred bond orientation perpendicular to the surface and the segregation of the chain ends at the surfaces. Smith *et al.* [16], using molecular-dynamics simulations as well, with a potential similar to that of Xia and Landman [10], also find an ordered surface phase in a thin alkane slab near, but above, bulk freezing. The crystalline in-plane order found in the measurements is, however, not reproduced. Rather, a smecticlike order is obtained with an increased in-plane diffusion of the molecules. They also find that the temperature-induced surface-normal motion of the molecules in the layer is larger than that in the bulk rotator phase, supporting the molecular-level theory of TR, where this motion is the stabilizing agent of the surface-frozen layer.

In spite of these, and other, theoretical and experimental efforts there still remain a number of key questions concerning the properties of surface freezing. One such key issue is how these simple theories, all of which address only the simpler case of SF in alkanes, should be modified for other, more complicated, hydrocarbon chain systems like dry and hydrated alcohols. Having established experimentally a partial wetting of the surface by the SF monolayer and bilayer, it is of interest to investigate the forces responsible for this partial wetting. Also, none of the theoretical studies has undertaken to determine specifically the wetting conditions and state. Finally, it is unclear whether SF is a pure fluctuation effect following an entropic scenario or is it both an entropic and a wetting phenomena. This is technically a more difficult question to answer both experimentally and theoretically. The purpose of the present work is to look into these issues. We analyze the effect of long- and short-range forces on surface freezing for alkanes and alcohols (dry and hydrated), by extending and refining the earlier study of TR [12]. We

---

*Author to whom correspondence should be addressed. Electronic address: deutsch@mail.biu.ac.il find that long-range van der Waals (vdW) interactions have a negligible effect on alkanes but play an important role in determining the surface freezing effect in dry and hydrated alcohols. The issues above are discussed in the light of these findings.

II. THEORY

A. General outline

Our aim is to calculate the molecular weight dependence of the temperature range over which a solid monolayer or a bilayer exists at the melt's surface. We start with the model of TR [12], add a long-range vdW interaction term and explore its effect for alkanes. We then explore how well this model accounts for SF in dry and hydrated alcohols, both without and with an additional short-range polar interaction term due to the hydroxyl head groups.

B. Normal-alkane melt

The excess surface free energy per unit area due to the creation of the crystalline surface phase at $T = T_s$ has the form [12]:

$$\overline{\delta\gamma} \equiv \gamma - \gamma_l = (T - T_b)\Delta S_b N/A_0 + \Delta\gamma^{(0)} - \Delta_s . \tag{1}$$

Surface freezing occurs when $\overline{\delta\gamma}$ is negative at $T = T_b$, the bulk freezing temperature. The first term on the right-hand side of Eq. (1) is the free-energy penalty for the creation of a stack of N ordered layers at the surface. In the case of alkanes $N = 1$. ΔS_b is the entropy difference at $T = T_b$ between liquid and solid, and A_0 is the area per molecule. The second term, $\Delta\gamma^{(0)} = \gamma_s + \gamma_{sl} - \gamma_l$, arises from the replacement of the liquid-vapor interface (which exists for $T \geqslant T_s$) by the solid-liquid and solid-vapor interfaces of the crystalline-layer-covered bulk melt. γ_l, γ_s, and γ_{sl} are the equilibrium surface tensions of the liquid-vapor, solid-vapor, and solid-liquid interfaces. The third term in Eq. (1) is an additional correction term of the surface tension due to the deviation of the configurational properties of the surface phase from that of the bulk liquid. This is assigned by TR [12] to up-down molecular fluctuations and is given as

$$-\Delta_s = -[(k_B T_b/2)\ln(T_b/T_0) - 3wn]/A_0 , \tag{2}$$

where $T_0 = 25$ K, w is the internal mismatch parameter, and n is the number of carbons in the chain. The fluctuation contribution $-\Delta_s$ is viewed as a finite-size correction. The condition for the occurrence of surface freezing then becomes [12]:

$$\delta\gamma_1 \equiv [(k_B T_b/2)\ln(T_b/T_0) - 3wn]/A_0 - \Delta\gamma^{(0)}(T_b) > 0. \tag{3}$$

Equation (1) does not consider the long-range vdW force between molecules and surfaces, which is the main interaction among the alkane chains [20]. The wetting of the bulk alkane liquid by the solid rotator surface phase is experimentally found to be a partial wetting, as only a single monolayer exists down to T_b. As demonstrated by Fisher [21], any long range interaction always plays an important role in three-dimensional (3D) and 2D wetting problems. Here we consider only the interface-interface vdW interaction. Approximating the SF film to have a continuous and uniform distribution of matter bounded by two interfaces (solid-liquid and solid-vapor) the long-range vdW potential near surface is given by [20]

$$V(d) = \chi_1/(12\pi d^2), \tag{4}$$

where $\chi_1 = \chi_{ls} - \chi_{ll}$ is the difference between the two Hamaker constants [17,20] for the indicated interfaces, and d is the monolayer thickness. In general, partial wetting may occur if the spreading coefficient $S = \gamma_l - (\gamma_{sl} + \gamma_s)$ is negative and $\chi_1 > 0$. For partial wetting, the contact angle θ is finite and is given by Young's equation as

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta, \tag{5}$$

and the spreading coefficient can be written as $S = \gamma_l(1 + \cos\theta) - 2\gamma_s$.

Thus, in the present case $\Delta\gamma^{(0)} = -S$, and for $S < 0$, $\Delta\gamma^{(0)} > 0$. The condition for partial wetting becomes then $\triangle\gamma^{(0)} > 0$ and $\chi_1 > 0$. The wetting effect can be included in the entropic scenario by adding Eq. (4) to the free energy in Eq. (1), so that the excess surface free energy per unit area in the presence of the long-range vdW interaction takes the form

$$\delta\gamma = \overline{\delta\gamma} + \chi_1/(12\pi d^2). \tag{6}$$

The crystalline surface phase exists in the temperature range:

$$\Delta T = A_0\{\delta\gamma_1 - \chi_1/[12\pi(1.27n)^2]\}/\Delta S_b(n), \tag{7}$$

where [2] $d = (1.27 \times n)$ Å is the approximate length of an n-carbon chain, with 1.27 Å being the projection of the C—C bond length on the chain axis. The difference between the surface tension of a free liquid surface and that of a liquid covered by a solid monolayer at $T_b < T < T_s$ is given by

$$\Delta\gamma = \delta\gamma_1 - \chi_1/[12\pi(1.27n)^2]. \tag{8}$$

In Eq. (7) only $\Delta S_b(n)$, $T_b(n)$ and A_0 are experimentally measurable quantities. The Hamaker constant χ_1 can be obtained from the measurement of molecular polarizability, although such data is scarce to nonexistence and inaccurate. The value of $\Delta\gamma^{(0)}$ can be obtained, in principle, from contact angle measurements of a series of liquid alkanes of varying n on a solid alkane substrate [13,19]. The interpretation of contact angle measurements, however, is greatly complicated by surface roughness and inhomogeneities in the solid surface which can introduce hysteresis into the measurement. Moreover, the solid substrate's wetted surface must be a high-symmetry facet of a single crystal of alkane, since only then does the liquid contact an ordered CH_3 layer, as it occurs in the case of a SF layer. In the literature we could find only one such measurement [19], for C_{16} against C_{36}. We have, therefore, fitted Eq. (7) to the measured ΔT data using $\triangle\gamma^{(0)}$, χ_1, and w as fit parameters, with all other parameters taken from experiment [2–4]. The measured data (circles) and fitted curve (solid line) are shown in Fig. 1(a). As can be observed, the agreement of the measured data with Eq. (7) is reasonably good considering the experimental error. For comparison, the TR theory [12], which does not

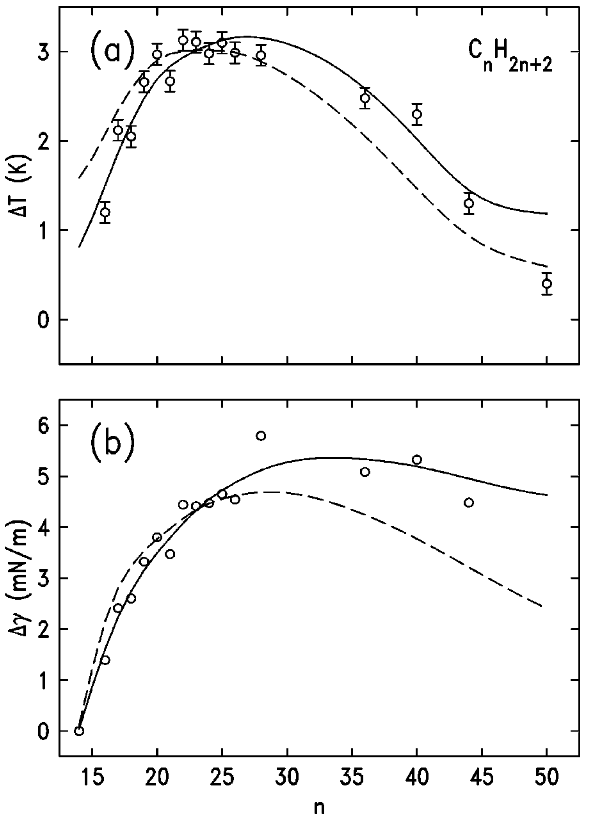

FIG. 1. (a) The chain length n dependence of the temperature range existence ΔT for the surface crystalline phase of alkanes. The open circles are measured points from Ref. [3]. The solid and dashed lines are fits to Eq. (7) with and without the van der Waals term, respectively. The fit values are given in Table I. (b) The chain length dependence of the correction of liquid surface tension due to surface freezing for alkanes. The open circles are the measured values and the lines are plots of Eq. (8), corresponding to the two cases in (a), using the fit parameters obtained there and without any adjustable parameters.

include the vdW term, is shown in a dashed line. Its agreement with the measured points, though somewhat less good than the present fit, is still reasonable. The fit parameters are listed in the first line in Table I. The fitted $\chi_1 = 3.27 \times 10^{-20}$ J is in close agreement with the literature values [20] $3–5\times 10^{-20}$ J for similar molecules. The fit values of our other parameters are close to those obtained from the TR theory [12], listed in line 2 of Table I. Note, however, that in the TR theory w was the only fitting parameter. The value of $\Delta\gamma^{(0)}$ was calculated there from Young's equation assuming, mistakenly, a zero contact angle. The contact angle is, in fact, finite [13]. Taking, therefore, both w and $\Delta\gamma^{(0)}$ as fitting variables in TR's theory [12] (i.e. Eq. (7) without the vdW term) yields a line which overlaps our solid line everywhere in Fig. 1(a), and the parameter values listed in the third line in Table I. Again, the numbers are close to those of the original TR theory and to those of ours. In Fig. 1(b) we show the measured $\Delta\gamma$ values (circles) and the lines [according to Eq. (8)] corresponding to the fits in Fig. 1(a), using the parameters in Table I, and without any adjustable parameters. The agreement with experiment is, again, satisfactory, especially for the theory presented here.

TABLE I. Values of the various fitted parameters of alkanes, dry, and hydrated alcohols.

	$\Delta\gamma^{(0)}$ (mN/m)	w (J)	$\chi_{1,2,3}$ (J)
Alkanes:			
With vdW int.	19.73	1.25×10^{-23}	3.27×10^{-20}
No vdW int. (A)	18	1.78×10^{-23}	
No vdW int. (B)	20	1.19×10^{-23}	
Alcohols (dry):			
With vdW int.	18.20	2.64×10^{-23}	2.42×10^{-18}
No vdW int.	25.98	1.09×10^{-23}	
Alcohols (hydrated):			
With vdW int.	21.01	1.64×10^{-25}	1.47×10^{-19}
No vdW int.	20.98	1.99×10^{-23}	

The conclusion from the results presented so far, and in particular from the overlap between the lines fitted using TR's theory and ours, is that the effect of the long-range vdW interaction does not seem to be important in normal-alkanes. Note, however, that for conclusions regarding wetting the vdW interaction term is essential. The positive values of both $\triangle\gamma^{(0)}>0$ and $\chi_1>0$, obtained in the fit, are required in order to satisfy the conditions for the experimentally observed partial wetting of the bulk liquid by the crystalline monolayer.

C. Dry alcohol melt

We now apply the same model, Eq. (6), to the SF of dry normal-alcohols. The only difference from normal-alkane is that here a crystalline bilayer is formed on the surface above the bulk freezing temperature. The bilayer thickness is roughly twice the corresponding fully extended molecular length. Hence, the excess surface free energy per unit area due to the creation of the crystalline bilayer can be written as

$$\delta\gamma = \overline{\delta\gamma +} \chi_2/12\pi D^2, \tag{9}$$

where D is the total bilayer thickness and [5,8] $D=(2\times 1.27\times n+1.46)$ Å. Accordingly, the crystalline surface bilayer's temperature existence range is

$$\Delta T = A_0\{\delta\gamma_1 - \chi_2/[12\pi(2.54n+1.46)^2]\}/\Delta S_b(n). \tag{10}$$

The difference between the surface tension of the liquid and that of the liquid covered by a solid bilayer in the vicinity of the bulk phase transition, is

$$\Delta\gamma = \delta\gamma_1 - \chi_2/[12\pi(2.54n+1.46)^2]. \tag{11}$$

Figure 2(a) shows the measured ΔT for dry alcohols [5,8] (circles) and fits of Eq. (10), including (solid line) and excluding (dashed line) the vdW term. The corresponding parameter values are listed in Table I. Now the fit which includes the vdW term agrees considerably better with the measurements than that without the vdW term. The fitted χ_2 is considerably higher than the corresponding χ_1 for alkanes. This reflects a stronger vdW interaction, as compared to al-

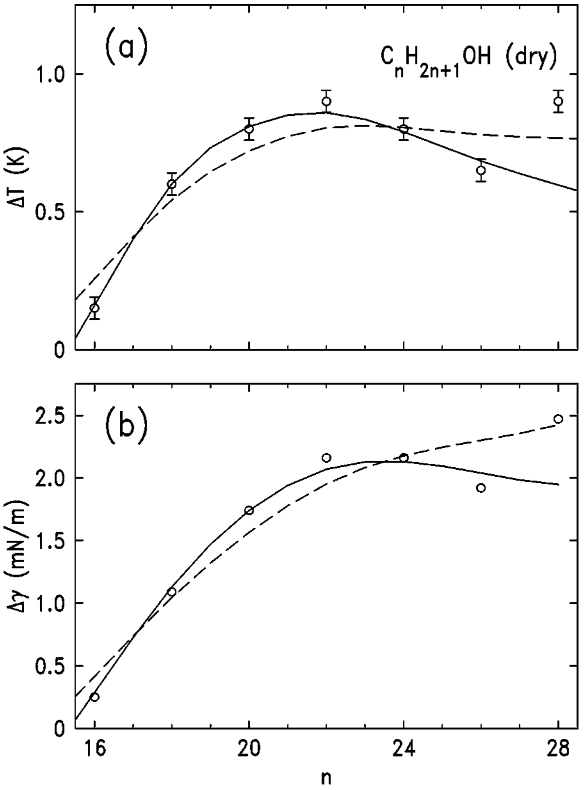

FIG. 2. (a), (b) Same as Fig. 1, but for dry alcohols. The relevant equations are Eqs. (10) and (11).

kanes, for a layer where the strong hydrogen bonding induced an increased order, as reflected in having a bi- rather than a monolayer, and, perhaps, also fewer defects. Thus, the higher value of χ_2 seems reasonable on physical grounds. The fit without the vdW term yields, in addition to having a worse agreement with the data, also has a much higher value of $\Delta\gamma^{(0)}$ which, based on the only extent contact angle measurement [19], is on the verge of being unphysical [13,3]. Using the same parameters obtained in the fits, and without any adjustable parameters, we plot in Fig. 2 (b) the $\Delta\gamma$ curves calculated from Eq. (11), along with the measured values (circles). The agreement of the curve including the vdW term with the measured values is considerably better than that without the vdW term, as was found also for ΔT. We conclude from both the quality of the fits in Fig. 2 and the resultant values in Table I that in contrast with alkanes, for dry alcohols the vdW interaction is significant and cannot be neglected. Also, the positive values obtained in the fit for $\Delta\gamma^{(0)}$ and χ_2 indicate, as for alkanes, a partial wetting of the bulk liquid by the crystalline bilayer, in agreement with the experimental observations [5,8].

D. Hydrated alcohol melt

We now discuss the effect of long- and short-range forces on the surface freezing of hydrated alcohol. SF in hydrated alcohols is similar to that in dry alcohol, the only difference being a uniform swelling of ~ 2.5 Å due to water intercalation at the center of the bilayer. This water layer should show a short-range repulsive interaction with the hydrophobic chains. Accordingly, we consider the bilayer to consist of two monolayer separated by a water slab of thickness $a = 2.5$ Å. The total interaction energy per unit area consists, therefore, of two terms, a long-range vdW one and a short-range hydration one, and can be written as

$$V(l,a) = V_W(l) + V_H(a). \tag{12}$$

The vdW interaction energy results from interactions between the two interfaces of each layer and also from those of the bilayer. Assuming a common Hamaker constant for both we have

$$V_W(l) = -\chi_3\{2/[12\pi l^2] + 1/[12\pi(2l+a)^2]\}, \tag{13}$$

where $l = 1.27 \times n$ Å is the monolayer's thickness and $(2l+a) = (2.54 \times n + 2.5)$ Å is the total bilayer thickness including the water slab thickness a. Here the vdW interaction is attractive due to the presence of water. The second term in Eq. (12) is the short-range repulsion due to the water layer, and has the empirical form

$$V_H(a) = S\exp(-a/r), \tag{14}$$

where a is the water layer thickness, $r \sim 1$–3 Å is the interaction's decay length, and S is its amplitude. The excess surface free energy per unit area due to the creation of the crystalline bilayer for the hydrated alcohol can then be written as

$$\delta\gamma = \overline{\delta\gamma -}\, \chi_3\{2/[12\pi l^2] + 1/[12\pi(2l+a)^2]\} + S\exp(-a/r). \tag{15}$$

The temperature range over which the crystalline bilayer exists is

$$\Delta T = A_0\{\delta\gamma_1 + \chi_3(2/[12\pi(1.27n)^2] + 1/[12\pi(2.54n+2.5)^2]) - S\exp(-a/r)\}/\Delta S_b(n). \tag{16}$$

The surface tension difference between the liquid surface and the solid-bilayer-covered surface is

$$\Delta\gamma = \delta\gamma_1 + \chi_3\{2/[12\pi(1.27n)^2] + 1/[12\pi(2.54n+2.5)^2]\} - S\exp(-a/r). \tag{17}$$

The measured [7,8] ΔT is shown in Fig. 3(a) (circles) along with fits of Eq. (16), including (solid line) and excluding (dashed line) the vdW term. We used $\Delta\gamma^{(0)}$, χ_3, S, and w as the fit parameters, keeping $r = 1.56$ Å constant [20]. The fitted values are listed in Table I, and $S = 32.95$ mN/m. Note that the hydration term is independent of chain length, as it should be since it only concerns the water layer, whose thickness is n independent. Thus, its inclusion in or exclusion from the fit will only modify the value of the n-independent $\Delta\gamma^{(0)}$ term in $\delta\gamma_1$ in Eq. (3), but the sum $\Delta\gamma^{(0)} - S\exp(-a/r)$ remains unchanged. As Fig. 3(a) shows, the data now clearly prefers the fit which includes the vdW term over that without this term. The χ_3 value is smaller than that of dry alcohols, but still larger than that of alkanes, while $\Delta\gamma^{(0)}$ is about the same for all three to within ±10% when the vdW term is included. The value of the mismatch repulsion parameter of adjacent molecules, w, is found to be

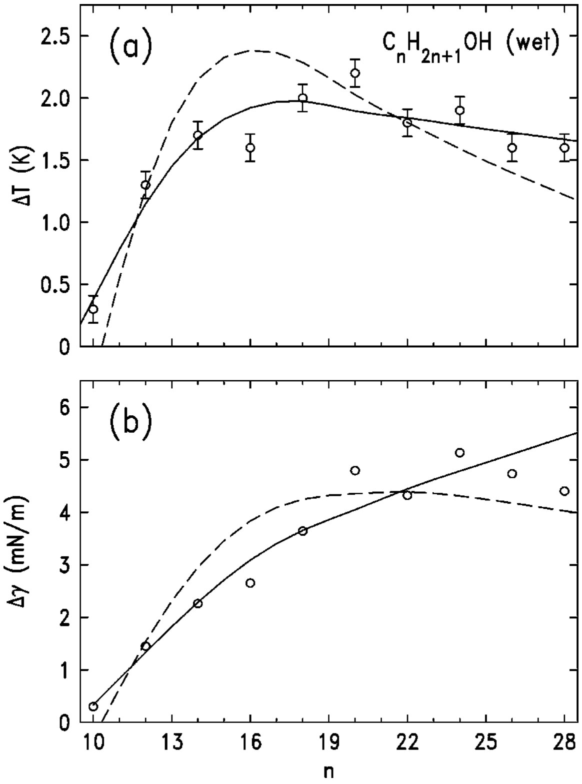

FIG. 3. (a), (b) Same as Fig. 1, but for hydrated alcohols. The relevant equations are Eqs. (16) and (17).

much smaller for hydrated alcohols than for alkanes and dry alcohols. This may be related to, or even cause, the increased stability of the surface frozen phase of hydrated alcohols [7,8], reflected in both the larger $\Delta T \approx 2\,°C$ and $10 \leqslant n \leqslant 28$ ranges of existence, as compared to dry alcohols: $\Delta T \lesssim 1\,°C$ and $16 \leqslant n \leqslant 28$. This increased stability was ascribed [7,8] to differences in hydration between the surface and bulk in the liquid phases of both, and the anomalous *increase* in hydration upon both bulk and surface freezing. In Fig. 3(b) we plot the $\Delta\gamma$ curves calculated from Eq. (17), along with the measured values (circles), using the parameters in Table I, without any adjustable parameters. As for ΔT, The agreement of the curve including the vdW term with the measured values is better than that without the vdW term, as was found also for ΔT. The positive values of $\Delta\gamma^{(0)}$ and χ_3 obtained in the fit indicates, again, a partial wetting of the bulk liquid by the crystalline bilayer, in agreement with the experimental observations [7,8].

III. CONCLUSIONS

In conclusion, our simple extension of the TR model [12] by inclusion of the long-range vdW interactions has provided a basis for describing the wetting effect of surface freezing in hydrocarbon chain systems. We find that although the effect of vdW interactions is small in alkanes, it is increasingly more important in the case of dry and hydrated alcohols. Accurate contact angle and Hamaker constant measurements in alkanes, alcohols, and other hydrocarbon chain systems would be advantageous not only to help verify the results obtained here for $\Delta\gamma^{(0)}$ but also to determine the applicability and validity range of the TR model, currently the only theory attempting to account for the surface freezing effect at the molecular level.

ACKNOWLEDGMENTS

We are grateful to Yitzhak Rabin (Bar-Ilan) for valuable discussions and Ruth Sharon (Bar-Ilan) for assistance with the computations. P.K.M. gratefully acknowledges financial support from the Faculty of Exact Sciences, Bar-Ilan University.

---

[1] J.C. Earnshaw and C.J. Hughes, Phys. Rev. A **46**, R4494 (1992); C.J. Hughes and J.C. Earnshaw, Phys. Rev. E **47**, 3485 (1993).
[2] X.Z. Wu, E.B. Sirota, S.K. Sinha, B.M. Ocko, and M. Deutsch, Phys. Rev. Lett. **70**, 958 (1993); X.Z. Wu, B.M. Ocko, E.B. Sirota, S.K. Sinha, M. Deutsch, B.H. Cao, and M.W. Kim, Science **261**, 1018 (1993).
[3] B.M. Ocko, X.Z. Wu, E.B. Sirota, S.K. Sinha, O. Gang, and M. Deutsch, Phys. Rev. E **55**, 3164 (1997).
[4] X.Z. Wu, B.M. Ocko, H. Tang, E.B. Sirota, S.K. Sinha, and M. Deutsch, Phys. Rev. Lett. **75**, 1332 (1995).
[5] M. Deutsch, X.Z. Wu, E.B. Sirota, S.K. Sinha, B.M. Ocko, and O.M. Magnussen, Europhys. Lett. **30**, 283 (1995).
[6] A. Doerr, X.Z. Wu, B.M. Ocko, E.B. Sirota, O. Gang, and M. Deutsch, Colloids Surf., A **128**, 63 (1997).
[7] O. Gang, B.M. Ocko, X.Z. Wu, E.B. Sirota, and M. Deutsch, Phys. Rev. Lett. **80**, 1264 (1998).
[8] O. Gang, X.Z. Wu, B.M. Ocko, E.B. Sirota, and M. Deutsch, Phys. Rev. E **58**, 6086 (1998).
[9] O. Gang, B.M. Ocko, X.Z. Wu, E.B. Sirota, and M. Deutsch, Phys. Rev. Lett. **82**, 588 (1999).
[10] T.K. Xia and U. Landman, Phys. Rev. B **48**, 11 313 (1993).
[11] F.A.M. Leermakers and M.A. Cohen-Stuart, Phys. Rev. Lett. **76**, 82 (1996).
[12] A.V. Tkachenko and Y. Rabin, Phys. Rev. Lett. **76**, 2527 (1996); A.V. Tkachenko and Y. Rabin, Phys. Rev. E **55**, 778 (1997).
[13] E.B. Sirota, X.Z. Wu, B.M. Ocko, and M. Deutsch, Phys. Rev. Lett. **79**, 531 (1997); A.V. Tkachenko and Y. Rabin, *ibid.* **79**, 531 (1997).
[14] M. Kawamata and T. Yamamoto, J. Phys. Soc. Jpn. **66**, 2350 (1997).
[15] A. ten Bosch, J. Chem. Phys. **108**, 2228 (1998).
[16] P. Smith, R.M. Lynden-Bell, J.C. Earnshaw, and W. Smith, Mol. Phys. **96**, 249 (1999).
[17] P.G. deGennes, Rev. Mod. Phys. **57**, 827 (1985).
[18] G.A. Sefler, Q. Du, P.B. Miranda, and Y.R. Shen, Chem. Phys. Lett. **235**, 347 (1995).
[19] W.A. Zisman, in *Contact Angle, Wettability and Adhesion*, edited by F.M. Fowkes (ACS, Washington, 1962).
[20] J.N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic, New York, 1992).
[21] M.E. Fisher, J. Chem. Soc., Faraday Trans. 2 **82**, 1569 (1986).