Surface freezing of alkane
(entropy & surface tension)

A. V. Tkachenko and Y. Rabin, *Phys. Rev. Lett.* **76**, 2527 (1996)

comment : B. Ocko and coworkers, *Phys. Rev. Lett.* **79**, 531 (1997)

reply : A. V. Tkachenko and Y. Rabin, *Phys. Rev. Lett.* **79**, 532 (1997)
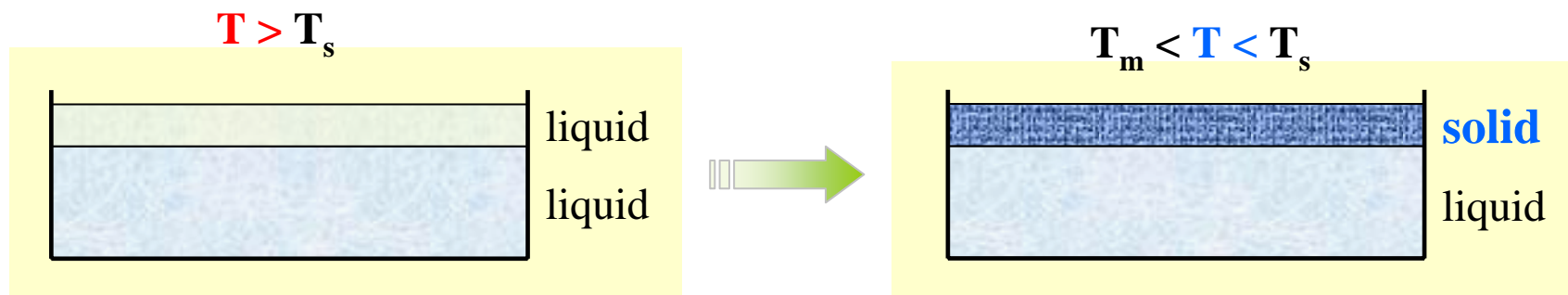
presenter : Yoonnam Jeon (31th Oct. 2009)

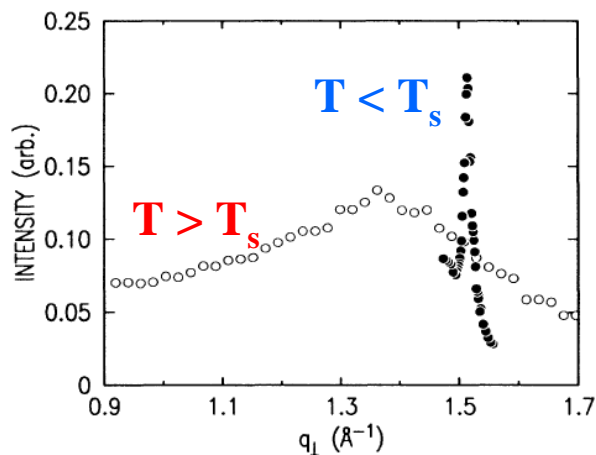# Surface freezing

Surface freezing

From Wikipedia, the free encyclopedia

Surface freezing is the appearance of long-range crystalline order in a near-surface layer of a liquid. The surface freezing effect is opposite to a far more common surface melting, or premelting. Surface Freezing was experimentally discovered in melts of alkanes and related chain molecules in the early 1990's independently by two groups. John Earnshaw and his group (Qeen's University of Belfast) used light scattering, which did not allow a determination of the frozen layer's thickness, and whether or not it is laterally ordered. A group led by Ben Ocko (Brookhaven National Laboratory), Eric Sirota (Exxon) and Moshe Deutsch (Bar-Ilan University, Israel) discovered independently the same effect, using x-ray reflectivity which allowed them to show that the frozen layer is a crystalline monolayer, with molecules oriented roughly along the surface normal, and ordered in an hexagonal lattice. A related effect, the
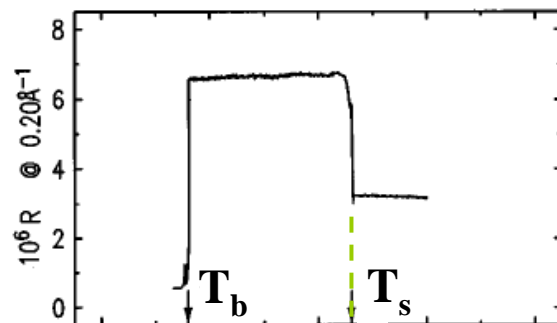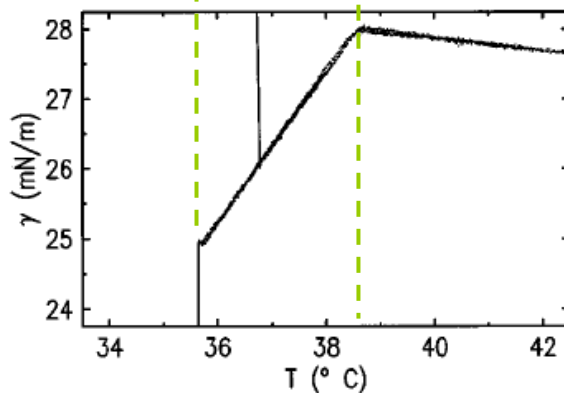
$T > T_s$

liquid
liquid

$T_m < T < T_s$

solid
liquid

XRD

X-ray
reflectivity

surface
tension

How can we observe
'surface freezing' with
surface tension ?

$$\gamma = (G_{surf} - G_{bulk}) / A$$

$$G = H - TS$$
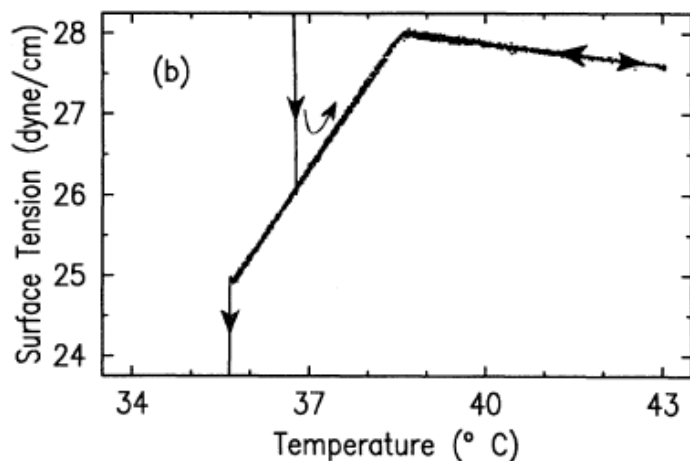
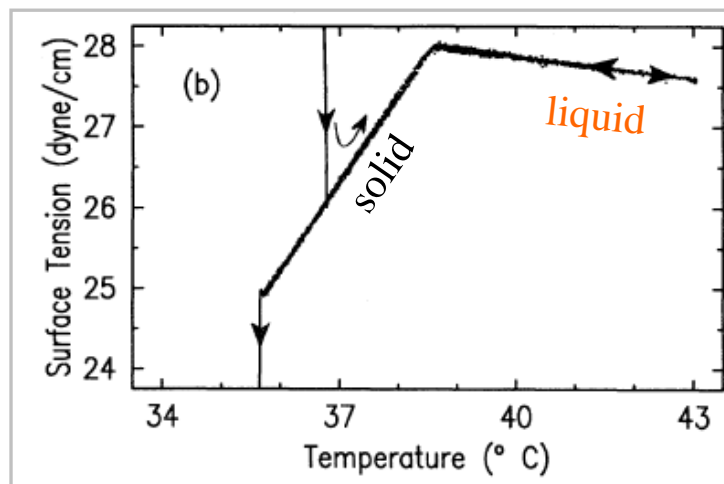$$\gamma = \varepsilon' - T(S_{surf} - S_{bulk})$$

(energy density per unit area)

$$d\gamma/dT = - (S_{surf} - S_{bulk}) / A$$

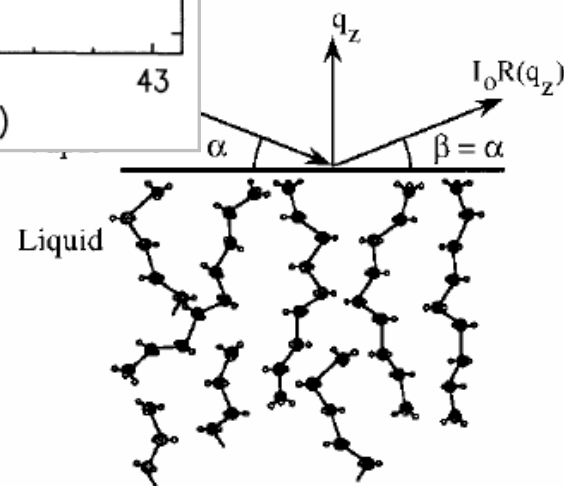ε' *: excess surface energy per unit area*
S : entropy density

Surface tension & entropy
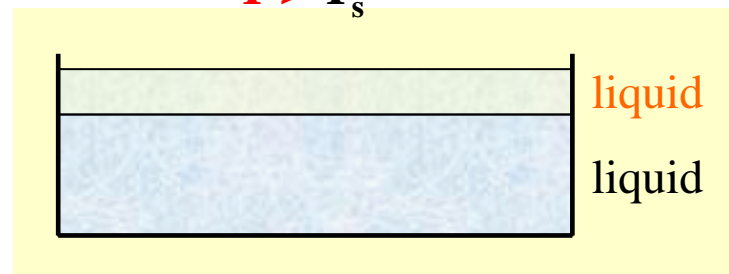
$$d\gamma/dT = -(S_{surf} - S_{bulk})/A$$

$$\boxed{S_{surf} \geq S_{bulk}}$$

surface molecule : less constrained

$T > T_s$

liquid

liquid

Surface tension & entropy

(b)

liquid

solid

Crystalline Monolayer

CH$_3$ Layer

Liquid
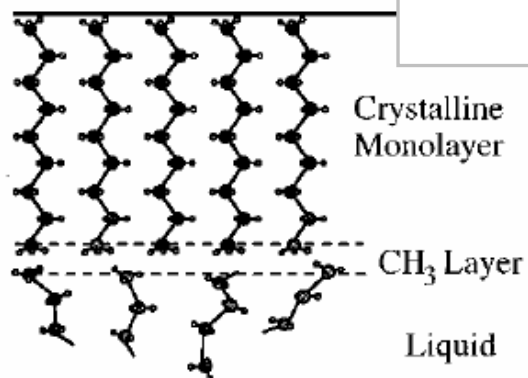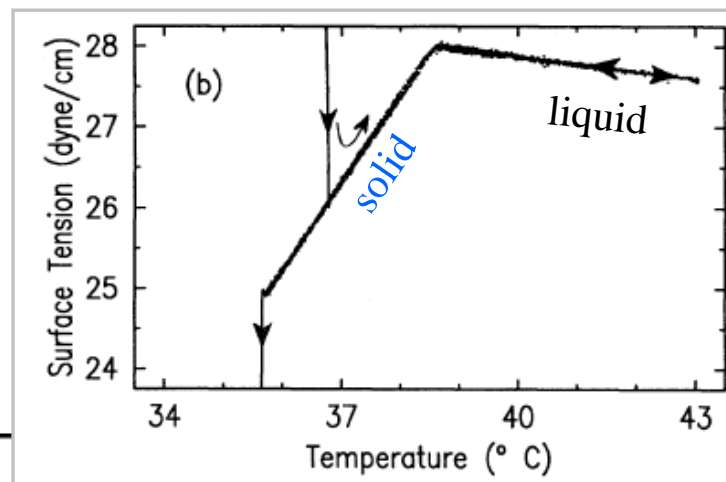
$$d\gamma/dT = - (S_{surf} - S_{bulk}) / A$$

$$\boxed{S_{surf} << S_{bulk}}$$

surface molecule : more constrained

$T_m < T < T_s$

solid

liquid
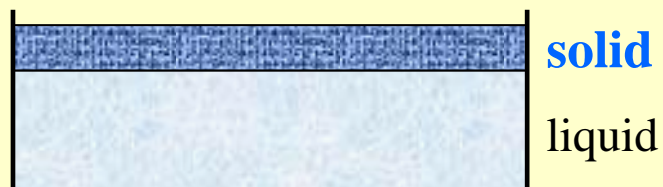
Surface tension & entropy
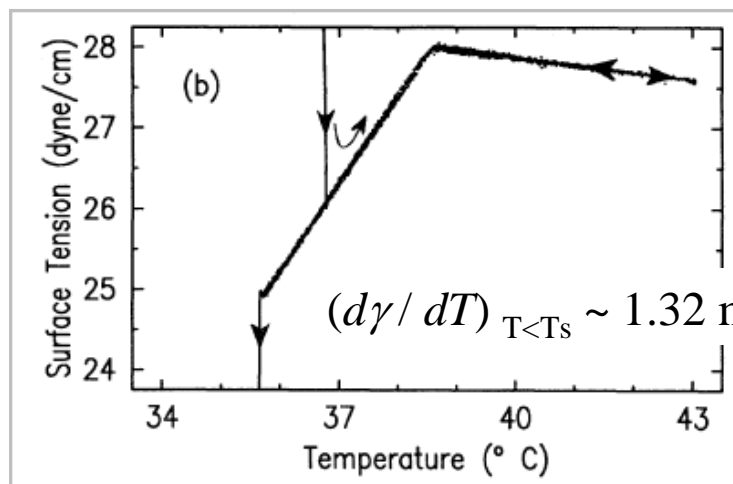
$(d\gamma / dT)_{T>Ts} \sim -0.088 \text{ mN/m} \cdot \text{K}^{-1}$

$-(S^l_{surf} - S^l_{bulk})$

$(d\gamma / dT)_{T<Ts} \sim 1.32 \text{ mN/m} \cdot \text{K}^{-1}$
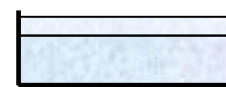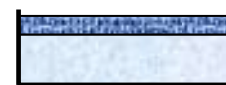
$-(S^s_{surf} - S^l_{bulk})$

* from ref : S_r (rotator phase) $= 1.41 \text{ mN/m} \cdot \text{K}^{-1} \sim S_s$

$S_r - 0.088 = 1.33 \text{ mN/m} \cdot \text{K}^{-1} \sim S_s - S_b$

* **rotator phase** : crystals with 3D <u>long-range positional order</u> of their centers of mass, <u>but no long-range in the rotational degree of freedom</u> of a molecule about its long axis
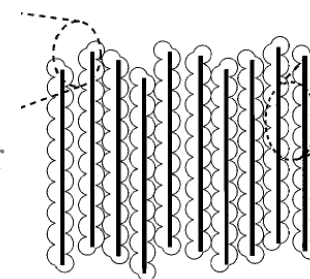
Fluctuation-Stabilized Surface Freezing of Chain Molecules

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(Received 26 October 1995)

We propose a fluctuation-based entropic scenario for the explanation of surface freezing in alkanes and other liquids of chain molecules. Our model is based on the notion that strong fluctuations along the molecular axis of uniaxially ordered stretched chains can exist in a solid monolayer on top of a liquid phase, and provide sufficient entropy to stabilize it against the formation of a bulk rotator phase. We show that the phenomenon can exist only in a restricted range of molecular weights, and calculate the molecular weight dependences of the temperature range in which it is observed and of the correction to the surface tension.

energy density per unit area

$$\gamma$$

$$\gamma_l$$

(bare liquid surface)

$T^b < T < T^s$
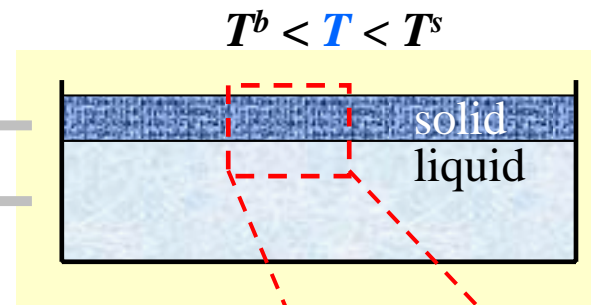
solid

liquid

excess surface free energy per unit area

$$\delta\gamma \equiv \gamma - \gamma_l = \delta\gamma^{(0)} + N(T - T^b)\frac{\delta S_{sl}}{A_0} - \Delta_s$$

$$\gamma_s$$

$$\gamma_{sl}$$

$$\gamma_l$$
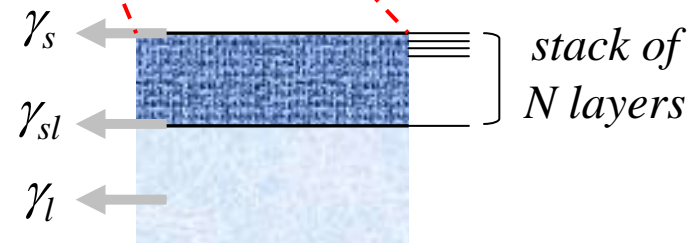
stack of N layers

$\delta\gamma^{(0)} \equiv \gamma_s + \gamma_{sl} - \gamma_l$

δS_{sl} : entropy gain per molecule
(associated with the solid-to-liquid bulk transition)

→ second term : free energy penalty for the creation of a stack of N ordered layers

Δ_s : free energy difference of N layers between in the surface and in the bulk solid phase

Soft-Matter Optical Spectroscopy

Surface freezing condition

$$\delta\gamma \equiv \gamma - \gamma_l = \delta\gamma^{(0)} + \boxed{N(T-T^b)\frac{\delta S_{sl}}{A_0}} - \Delta_s < 0 \quad \Longrightarrow \quad \text{surface freezing at } T > T^b$$

positive

$$\Delta_s - \delta\gamma^{(0)} > 0 \quad \Longleftrightarrow \quad \text{surface freezing at } T > T^b$$

$$\begin{cases} \delta\gamma^{(0)} \equiv \gamma_s + \gamma_{sl} - \gamma_l : \text{independent with } N \\[2mm] \Delta_s : \text{decreasing function of } N \\[2mm] \delta\gamma > \delta\gamma^{(0)} + (T-T^b)\frac{\delta S_{sl}}{A_0} - \Delta_s \quad : \text{global minimum, at } N = 1 \end{cases}$$

$$\gamma_{sl} \approx \gamma_s - \gamma_l$$

$$\delta\gamma^{(0)} \equiv \gamma_s + \gamma_{sl} - \gamma_l \quad \longrightarrow \quad \delta\gamma^{(0)} = 2\,\gamma_l\,(\gamma_s / \gamma_l - 1)$$

$$\gamma_s / \gamma_l \approx (\rho_s / \rho_l)^2$$

(ρ : electron density)

$$\delta\gamma^{(0)} = 2\,\gamma_l\,[(\rho_s / \rho_l)^2 - 1]$$

for alkane
$$\left[\begin{array}{l} \gamma_l = 27 \text{ ergs/cm}^2 \\ \rho_s / \rho_l = 1.15 \end{array} \right.$$

$$\delta\gamma^{(0)} \sim 18 \text{ ergs/cm}^2$$

$$\Delta T(n) \equiv T^s - T^b = \frac{A_0}{\delta S_{sl}(n)}[\Delta_s(n) - \delta\gamma^{(0)}]$$

$$\Delta\gamma \equiv \delta\gamma(T^b) = \Delta_s(n) - \delta\gamma^{(0)}$$

Consistent with above rough estimate

Soft-Matter Optical Spectroscopy

E. B. Sirota,[1] X. Z. Wu,[2] B. M. Ocko,[3] and M. Deutsch[4]

What Drives the Surface Freezing in Alkanes?

In a recent letter [1] Tkachenko and Rabin (TR) suggested that the crystalline monolayer observed [2] to form at the surface of molten alkanes at a temperature $T_m + \Delta T$, of up to a few °C above bulk melting (T_m), is entropically stabilized by fluctuations along the axis of the molecules. Such fluctuations are indeed significant in the bulk rotator phases [3], and probably represent the entropic component of its interfacial tensions neglected by TR. We show here that some of TR's assumptions are incorrect and surface crystallization is expected purely on the basis of the interfacial tensions (γ, in units of mN/m) of semi-infinite bulk.
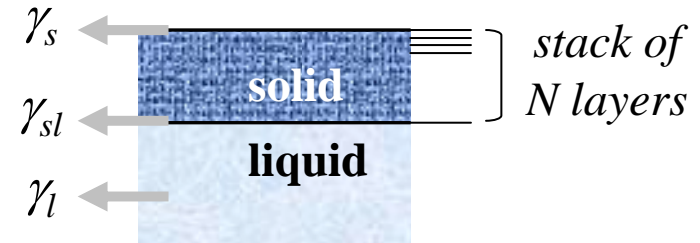
a relation found to correlate nicely with the Hamaker constant for various small molecule liquids [9]. However, this has never been shown to hold for the *ordered* phases of the alkanes and, in fact, the electron-poor "depletion region" between the layers [3] should *reduce* the Van der Waals attraction in the crystal phases relative to the uniform-density liquid state. Furthermore, even $\gamma_{lv}(T)$ does not scale with ρ^2, since its significant entropic component is comparable to its enthalpic component [5].

The finite thickness correction Δ_1 is the difference between two quantities: (1) the disorder of a single monolayer in contact with vapor and liquid and (2) the sum of the disorder of an outermost layer of a semi-infinite crystal in contact with the vapor phase and one in contact with

Tkachenko and Rabin (TR)

$$\delta\gamma \equiv \gamma_s + \gamma_{sl} - \gamma_l + N(T-T^b)\frac{\delta S_{sl}}{A_0} - \Delta_s < 0$$

γ_s

γ_{sl} **solid**   *stack of N layers*

γ_l **liquid**

: global minimum, at $N = 1$ ⟶   surface freezing at $T > T^b$

Ocko group

$\gamma_{sv} + \gamma_{sl} - \gamma_{lv} + \underline{\Delta_N} < 0$ ⟶   only single monolayer ($N = 1$) implies $\Delta_1 \geq 0$

to account for any enthalpic or entropic interactions of the two interfaces
($\Delta_N \rightarrow 0$ as $N \rightarrow \infty$)

Soft-Matter Optical Spectroscopy

Surface freezing condition

$$\gamma_{sv} + \gamma_{sl} = \gamma_{lv} - \Delta T (\Delta S + S_l) = 26.93 \text{ (for } C_{16}) \quad \textit{by ref. Phys. Rev. E } 55, 3164 (1997)$$

ΔS : surface entropy reduction

S_l : liquid surface-excess entropy

$\gamma_{lv} (T_m)$ ~28 for all relevant n

ref : W. A. Zisman, in *Contact Angle, Wettability and adhesion*, edited by F. M. Fowkes (ACS, Washington, DC., 1994)

C_{16} liquid drop

C_{36} single crystal
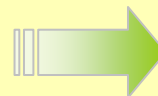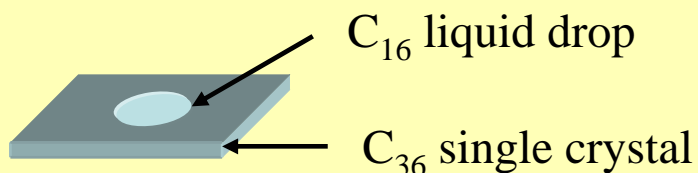
$$\gamma_{sv} - \gamma_{sl} = 19.2$$
for $-CH_3$ terminated

same geometry with Ocko's
(surface crystal/melt interface)

$$\gamma_{sv} = 23.07 \ \& \ \gamma_{sl} = 3.87$$

$\gamma_{sv} (T_m) < \gamma_{lv} (T_m)$: necessary condition for surface crystallization

$\gamma_{sv}(T_m) < \gamma_{lv}(T_m)$: necessary condition for surface crystallization

$$\sigma^2 = \sigma_0^2 + \frac{k_B T}{2\pi\gamma} \ln\frac{q_{max}}{q_{min}} \quad \Longrightarrow \quad \gamma_s / \gamma_l \approx (\sigma_s / \sigma_l)^2$$

TR

assumptions : $\gamma_{sv} > \gamma_{lv}$, $\gamma_{sv} \sim 35$, and $\gamma_{sl} \sim 8$
(based on a model where $\gamma \propto \rho^2$)

Obviously conflict !