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.

Formation of a solid layer at the surface of a liquid entails creation of solid-liquid and solid-vapor interfaces, with energy cost $\gamma_{sl} + \gamma_{sv}$, and the elimination of a liquid-vapor interface with an energy gain of γ_{lv}. This will occur only if a net energy gain is realized, i.e., $\gamma_{lv} - (\gamma_{sl} + \gamma_{sv} - \Delta_N) > 0$. The γ, which include an entropic component, are defined for surfaces of semi-infinite bulk. Therefore, for the above condition to be rigorously correct, the finite thickness (N layers) of the surface crystal requires that a term Δ_N be included to account for any enthalpic or entropic interactions of the two interfaces ($\Delta_N \rightarrow 0$ as $N \rightarrow \infty$). As pointed out by TR, the observation [2] of only a single monolayer ($N = 1$) implies that $\Delta_1 \geq 0$. In the simple approximation of surface-localized interactions, $\Delta = 0$. While not all of these surface energies may be easily accessible experimentally, they are, in principle, "experimental observables."

From Wu's data [2] one can obtain $\gamma_{sv} + \gamma_{sl} = \gamma_{lv} - \Delta T(\Delta S + S_l)$, where ΔS is the surface entropy reduction from that of the bulk liquid upon surface freezing and S_l is the liquid surface-excess entropy. Zisman [4] finds $\gamma_{sv} - \gamma_{sl} = 19.2$ for a liquid C_{16} drop on a single crystal C_{36}, whose surface is $-CH_3$ terminated, i.e., the same geometry as the surface-crystal/melt interface of Wu [2]. This is important, since Zisman [4] finds a CH_2-terminated surface to have a significantly higher γ_{sv}. Approximating Zisman's value to apply for pure C_{16} (C_{36}) and using the corresponding $\gamma_{sv} + \gamma_{sl} = 26.93$ (23.19) from Wu [2], we obtain $\gamma_{sv} = 23.07$ (21.20) and $\gamma_{sl} = 3.87$ (2.00). Since [2,5] $\gamma_{lv}(T_m) \approx 28$ for all relevant n, we have $\gamma_{sv}(T_m) < \gamma_{lv}(T_m)$. It is this lower surface tension of the solid, which is a necessary condition for surface crystallization. Mitchell and Elton [6] also measure $\gamma_{sv} < \gamma_{lv}$ for C_{16} and C_{18}. Mach [7] measures $\gamma_{sv} \approx 20$ for smectic-A, CH_3-terminated films of liquid crystals. Hoffman [8] claims an extremely small $\gamma_{sl} \approx 0.3$ for C_{94} in his growth rate study. These data, while not for the exact conditions under consideration, should nevertheless be very close and are the best available. These obviously conflict with TR's assumptions that $\gamma_{sv} > \gamma_{lv}$, $\gamma_{sv} \approx 35$, and $\gamma_{sl} \approx 8$. Their assumptions are not based on experiment, but on a model where $\gamma \propto \rho^2$ (ρ is the electron density), 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 the liquid phase. TR computed only the first, thus overestimating Δ_1. Much of their calculated Δ_1 is therefore the surface excess entropy for the solid-liquid and solid-vapor interfaces which are already included in γ_{sl} and γ_{sv}. This, combined with unrealistically high values of γ_{sv} and γ_{sl}, coincidentally predict the surface crystallization.

We have shown that the low energies of the CH_3-terminated crystal face can cause surface crystallization, and demonstrated a need, and a new method, for a more complete chain-length and temperature determination of the individual γ_{sv}, γ_{sl}, and Δ_1. The recognition by TR of the importance of longitudinal freedom and their calculation is an important step along that road.

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Received 15 January 1997 [S0031-9007(97)03344-9]
PACS numbers: 68.10.–m, 61.25.Em, 64.70.Dv

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0031-9007/97/79(3)/531(1)$10.00