

Entropy Contribution to the Line Tension: Insights from Polymer Physics, Water String Theory and the Three-Phase Tension

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Abstract

The notion of the three-phase (line) tension remains one of the most disputable notions in the surface science. A very broad range of its values has been reported. Experts even do not agree on the sign of the line tension. The polymer-chain-like model of the three-phase (triple) line enables the rough estimation of the entropic input into the value of the line tension, estimated as $\Gamma_{en} \cong \frac{k_B T}{d_m} \cong 10^{-11} N$, where d_m is the diameter of the liquid molecule. The introducing of the polymer-chain-like model of the triple line is justified by the “water string” model of the liquid state, predicting strong orientation effects for liquid molecules located in the vicinity of hydrophobic moieties. The estimated value of the entropic input into the line tension is close to experimental findings, reported by various groups.

Keywords: line tension; entropic contribution; entropic force; orientation effect; hydrophobic substrate.

1. Introduction

Surface tension is due to the special energy state of the molecules at a solid or liquid surface [1-4]. Molecules located at the triple (three-phase) line where solid, liquid, and gaseous phases meet are also in an unusual energy state [1-4]. The notion of line (three-phase) tension has been introduced by Gibbs. Gibbs stated: "These (triple) lines might be treated in a manner entirely analogous to that in which we have treated surfaces of discontinuity. We might recognize linear densities of energy, of entropy, and of several substances which occur about the line, also a certain linear tension" [5]. Consider, that Gibbs emphasized the role of the entropy density, which will play the main role in our approach to the problem of line tension.

In spite of the fact that the concept of line tension is intuitively clear, it remains one of the most obscure and disputable notions of the surface science [6-8]. Researchers disagree not only on the value of the line tension but even on its sign.

Experimental values of a line tension Γ in the range of $10^{-5} - 10^{-12}$ N were reported [6-11]. Very few methods allowing experimental measurement of line tension were developed [9-14]. A. Marmur estimated a line tension as $\Gamma \cong 4d_m \sqrt{\gamma_{SA}\gamma} \cot \theta_Y$, where d_m is the molecular dimension, γ_{SA}, γ are surface energies of solid and liquid correspondingly, and θ_Y is the Young angle. Marmur concluded that the magnitude of the line tension is less than $5 \cdot 10^{-9}$ N, and that it is positive for acute and negative for obtuse Young angles [15-16]. However, researchers reported negative values of the line tension for hydrophilic surfaces [14]. As to the magnitude of the line tension the values in the range $10^{-9} - 10^{-12}$ N look realistic. Large values of Γ reported in the literature are most likely due to contaminations of the solid surfaces [3].

Let us estimate the characteristic length scale l at which the effect of line tension becomes important by equating surface and "line" energies: $l \cong \Gamma/\gamma = 1-100$ nm. It is clear that the effects related to line tension can be important for nano-scaled droplets or for nano-scaled rough surfaces. However, these effects also may be important for design of microfluidics circuits [6] and stabilization of the Cassie air-trapping wetting regime, enabling manufacturing of superhydrophobic and superoleophobic surfaces [17]. The notion of the line tension remains highly controversial at least due to the conceptual difficulties, which arise because the interfaces between two phases are always diffuse and never sharp [18]. In the present article we try to estimate the role of the entropy contributions in constituting the line (three-phase) tension.

2. "Water String Theory", Insights from Polymer Physics and Entropy Contribution into the Line Tension.

It should be mentioned that calculation of the line tension from the first principles by MD and DFT simulations is not a trivial task [19-20]. Nosonovsky in his recent article shown that both energy and entropy contribution should be considered for predicting surface and line tensions [21]. However, the entropy input is usually neglected within the reported MD and DFT calculations of the three-phase tension [19-20]. We'll try to perform a rough estimation of input of the entropy factors in the entire value of the line tension. We restrict our treatment by then most controversial case, when a sessile drop sits on hydrophobic (say polymer) surface, and the three-

phase tension at the solid/liquid/vapor boundary appears. The line tension is also inherent for so-called liquid lens, but it seems to be more studied and less controversial [12, 18].

Let us start from the unobvious assumption that the line tension Γ may be split into “interactional” (denoted Γ_{int}) and entropy-inspired (denoted Γ_{en}) contributions:

$$\Gamma = \Gamma_{int} + \Gamma_{en}, \quad (1)$$

where Γ_{int} is due to the interaction of molecules located at the triple line with surrounding ones, and Γ_{en} is the entropy input into the three-phase tension. In order to estimate Γ_{en} , assume that molecules constituting the triple line form the quasi-polymer chain, as depicted in Figure 1. This idea is inspired by the “water-string theory” presented and discussed in Refs. 22-24. X-ray absorption spectroscopy and x-ray Raman scattering demonstrated that water, consists of structures with two strong H-bonds, one donating and one accepting, thus promoting formation of chain-like structures [22-24]. There is much theoretical and experimental evidence that water molecules are strongly oriented in the vicinity of hydrophobic moieties [25-27], and this is the case in our treatment (recall, that we restricted our consideration by sessile droplets, placed on hydrophobic surfaces). The authors of ref. 27 exploited the intensity vibrational sum-frequency generation (VSFG) technique pointing to an enhanced ordering of the water molecules surrounding the hydrophobic groups; in particular, the orientation was demonstrated for water molecules at the water/polydimethylsiloxane interfaces, thus justifying the chain-like model of the triple line, shown in Figure 1.

The use of polymer-chain model for the approximation of the triple enables the immediate estimation of the entropy contribution into the line tension, according to Eq. 2.

$$\Gamma_{en} \cong \frac{k_B T}{d_m}, \quad (2)$$

where Γ_{en} is the entropy force necessary for stretching the pseudo-polymer-chain built of liquid molecules, coinciding with the entropy input to the line tension, $k_B = 1.38 \times 10^{-23} \frac{J}{K}$ is the Boltzmann constant, T is the temperature and d_m is the diameter of the molecule, representing the characteristic dimension of the “monomer” of the “polymer chain” [28]. Assuming for the water molecule $d_m \cong 2.75 \times 10^{-10} m$ we derive from Eq. 2 for water at ambient conditions $\Gamma_{en} \cong 1.5 \times 10^{-11} N$. The calculated value of the entropy-inspired line tension Γ_{en} is comparable with the

experimentally reported values reported in Refs. [6-7, 9-11, 19]. Thus, the input of entropy factors may be at least not negligible in constituting the value of three-phase tension.

The value of Γ_{en} given by Eq. 2 supplies the upper estimation for the entropic contribution to the line tension, due to the fact that it is based on the “ideal chain approximation”, where the monomers do not interact [28]. For real chains, the interaction between monomers is not negligible and the estimation of the stretching force is supplied by Eq. 3:

$$\Gamma_{en} \cong \frac{k_B T}{\xi}, \quad (3)$$

where $\xi > d_m$ is the correlation length [28]. It is noteworthy, that the impact of the entropic term into the line tension is necessarily positive (the sign of the line tension remains debatable [6, 7, 11, 5]). It is also recognized that the value of Γ_{en} remains considerable for $\xi \cong 5 \div 10d_m$ (values of $\Gamma_{en} \cong 10^{-12}N$) have been reported [9]. This means that the entropic input into the line tension may be important even when the interaction between molecules forming the three-phase line is considered. Equation 2 also predicts the decrease of the line tension with growth of a size of a liquid molecule d_m . Regrettably, the experimental data in the field are scarce, and do not enable clear conclusion on this item.

The rough estimation of the three-phase tension, given by Eqs. 2-3 is obvious from the dimensional considerations and it appears explicitly already in Ref. 29. The new aspect strengthened in the presented paper is identification of Eq. 2 with the entropic contribution to the entire line tension seen as a sum of “interaction-” and “entropy”-inspired inputs. As any other “entropic force”, the value of Γ_{en} increases with temperature [21, 28]. The experimental observations evidence the opposite temperature trend: both surface and line tensions are decreased with temperature [4, 21, 10]. This means that the “interaction” part of the line tension in the studied systems prevails on the “entropic” one. However, the input of entropy-inspired factors into the three-phase tension may be not negligible.

Conclusions

The notion of the line (three-phase) tension (which is important for constituting apparent contact angles and stability of the Cassie wetting states [17, 31-32]) is revisited. It is suggested, that the line tension is built from “interaction” and “entropic” contribution, which is usually neglected under calculation of the three-

phase tension. For the estimation of the entropic input into the line tension the three-phase line is approximated by a polymer chain. This approximation is approximated by novel experimental data indicating strong orientation effects for liquid molecules located in the vicinity of hydrophobic moieties [22-27]. Thus, the polymer-chain model may be successful for sessile droplets placed on hydrophobic (say polymer) solid substrates. If the polymer-chain-model is adopted for the triple (three-phase) line the entropic contribution to the line tension is crudely estimated as $\Gamma_{en} \cong \frac{k_B T}{\xi}$, where ξ is the correlation length [28]. If the triple line is seen as an ideal polymer chain, the entropic input is estimated as $\Gamma_{en} \cong \frac{k_B T}{d_m}$, where d_m is the diameter of the liquid molecule, representing the characteristic dimension of the “monomer” of the “polymer chain”. Simple estimations supply for the entropic input into the line tension the value of $\Gamma_{en} \cong 1.5 \times 10^{-11} N$, which is comparable with the reported experimental data [6,7, 9, 10]. We conclude that the entropic contribution into the line tension is not negligible.

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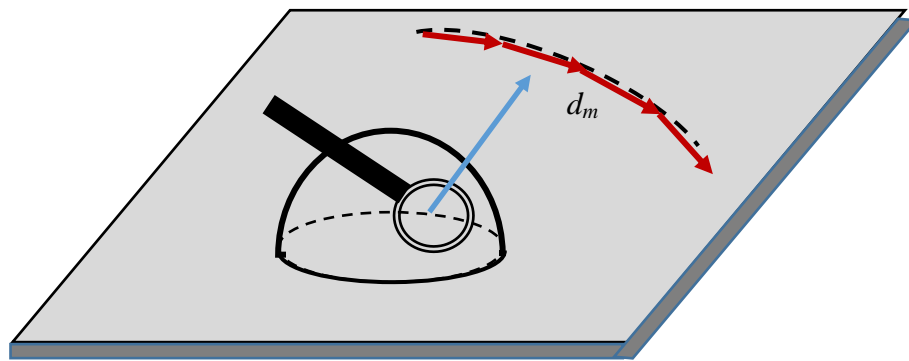


Figure 1. Three-phase line of the sessile droplet is approximated by the polymer chain with a diameter of the monomer d_m , where d_m is the diameter of the liquid molecule.