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Communication: Thermodynamic analysis of critical conditions of polymer adsorption

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Polymer adsorption to solid surfaces is a ubiquitous phenomenon, which has attracted long-lasting attention. Dependent on the competition between the polymer-solid adsorption and polymer-solvent solvation interactions, a chain may assume either 3d solvated conformation when adsorption is weak or 2d adsorbed conformation when adsorption is strong. The transition between these conformations occurring upon variation of adsorption strength is quite sharp, and in the limit of "infinite" chain length, can be treated as a critical phenomenon. We suggest a novel thermodynamic definition of the critical conditions of polymer adsorption from the equality of incremental chemical potentials of adsorbed and free chains. We show with the example of freely jointed Lennard-Jones chains tethered to an adsorbing surface that this new definition provides a link between thermodynamic and geometrical features of adsorbed chains and is in line with classical scaling relationships for the fraction of adsorbed monomers, chain radii of gyration, and free energy. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4833682]

Polymer adsorption to solid surfaces is a ubiquitous phenomenon with a wide range of technological and health care applications. Behavior of chain molecules at surfaces is determined by competition between attraction due to adsorption and repulsion due to entropic penalty. Depending on the adsorption energy and temperature, the polymer assumes qualitatively different conformations: from a 3d solvated coil with one or few adsorbed monomers at weak adsorption and high temperature to a 2d chain with most monomers attached to the surface at strong adsorption and low temperature, as illustrated in Fig. 1. The transition between the regimes of weak and strong adsorption is quite sharp, and in the limit of "infinite" chain length, can be treated as a critical phenomenon.[1] The respective value of the adsorption energy U_c at given temperature T is called the critical point of adsorption (CPA). Alternatively, the critical condition of adsorption is characterized by the critical temperature T_c at given adsorption energy U.

The phenomenon of polymer adsorption attracted close attention of theoreticians starting from the 1930s when Broda and Mark[2] suggested the first statistical mechanical description of polymer adsorption. In the 1950s, Simha, Frisch, and Eirich[3] modified the ideal Gaussian chain model for polymers to describe adsorption at a planar interface. The problem was then investigated heavily in the 1960s.[4–10] One of the earliest discussions of the transition between solvated and adsorbed chains may be found in the work of Higuchi,[4] and Rubin[10] may be credited with introducing the term "critical energy" with respect to ideal and excluded volume chains. DeGennes in his landmark review[1] showed the existence of the CPA

using the self-consistent field theory.[7] Later on, there was much research to quantify the CPA using enumerative and self-consistent field theories, scaling theory, and Monte Carlo simulations,[11–17] the results of which were reviewed in Refs. 18–21. These methods were most often applied to lattice models of single chains end-tethered to a flat adsorbing surface, with notable exceptions.[22,23] The CPA for tethered chains has been defined using different geometrical and thermodynamic criteria. The geometrical approach is based on the scaling relationships for the fraction of adsorbed monomers and the chain gyration radii in normal and longitudinal directions.[14] The thermodynamic approach is based on the calculations of the chain free energy. The earliest proponents of this method were Skvortsov and Gorbunov[24] followed by Gong and Wang[25] and others.[26]

In this Communication, we present a new thermodynamic method for determining the CPA and provide a link between the thermodynamic and geometrical approaches for characterizing polymer adsorption. We propose to define the CPA from the equality of the incremental chemical potentials of adsorbed and free chains,

$$\mu_{incr}^{ad} = \mu_{incr}^{free}. \tag{1}$$

The incremental chemical potential $\mu_{incr}(N)$ is defined as the difference in the excess free energies of chains composed of N and $N + 1$ monomers, $\mu_{incr}(N) = F_{ex}(N + 1) - F_{ex}(N)$. As such, the free energy $F_{ex}(N)$ is determined by the summation of the incremental chemical potentials for each degree of polymerization from 0 (monomer) to N-1, $F_{ex}(N) = \sum_{i=0}^{N-1} \mu_{incr}(i)$. Noteworthy here is the principal difference between the definition of CPA from the condition of equality of incremental chemical potentials, $\mu_{incr}(N)$,

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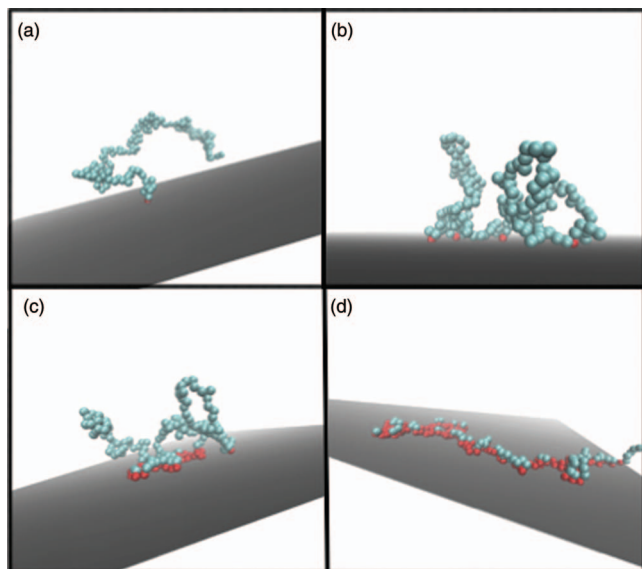
FIG. 1. Characteristic conformations of tethered chains. Adsorbed monomers are marked in red, solvated – in blue. Snapshots from MC simulations of freely jointed chains composed of 200 Lennard-Jones particles. (a) reduced adsorption energy, $U = 0$ (fully solvated coil at non-adsorbing wall), (b) -5.4 (CPA), (c) -7 (moderate adsorption), (d) -10 (strong adsorption).

that we use in (1), and the condition of equality of the chain chemical potentials or the excess chain free energy, $F_{ex}(N)$, used in the previously published papers.[24–26] The proposed thermodynamic method is based on the experimental definition of the CPA in polymer chromatography, where the CPA separates the regimes of so-called size exclusion chromatography (SEC) and liquid adsorption chromatography (LAC).[27–29] The elution time at the CPA is chain length independent. This property is utilized in the so-called liquid chromatography at critical conditions (LCCC) for separation of polymers by their functionalities and morphology rather than by the molecular weight. To fulfill this requirement, the partition coefficient, which is determined by the difference of the chain free energies in adsorbed and free states, $K(N) \propto \exp(-\beta(F_{ex}^{ad}(N) - F_{ex}^{free}(N)))$, must be chain length independent.[20, 24] Thus, the condition (1) of the equality of the incremental chemical potentials is equivalent to the condition, $\partial K/\partial N = 0$.

Moreover, the "chain increment *ansatz*"[30] implies that the incremental chemical potential $\mu_{inc}(N)$ for sufficiently long chains is constant and does not depend on the chain length N. This *ansatz* holds for ideal chains. However, its extension to real chains has been a subject of intense discussions.[30, 31] Our recent detailed MC study[31] confirmed that the chain increment *ansatz* holds for free chains ($N \gg 10$) with Lennard-Jones non-bonded monomer-monomer interactions at good solvent conditions, which are considered in this paper. Below, we show that this *ansatz* holds also for tethered chains, and the proposed CPA definition (1) can be read as the equality of two length independent constants. The critical value of adsorption energy U_c can be determined by calculating the incremental chemical potential μ_{incr}^{ad} for different values of N and U and utilizing the fact that the plots μ_{incr}^{ad} versus U at different N should intersect at $U = U_c$, as shown in Fig. 2(a).

The proposed method is illustrated drawing on the classical case study example of polymer chains tethered at the adsorbing plane surface. We performed MC simulations of freely joined chains of Lennard-Jones (LJ) particles of LJ diameter σ_{ff} bound by harmonic bonds. Non-bonded interactions were modeled with LJ potential with the cutoff distance of $r_c = 10\sigma_{ff}$ and no shift or tail correction added to the potential. The monomers interacted with the surface via the square well potential of width σ_{ff} and depth $- U$ measured in the units of the LJ interaction energy ϵ_{ff}. The chain terminal bead was tethered at the surface at the distance of 0.5 σ_{ff}, in the center of the adsorption well. The simulation box dimensions are of sufficient size, such that it is impossible for the polymer chain to "wrap around" the box and interfere with itself. In this way, we ensure we are examining the dilute solution limit, with no influence from neighboring polymers. Equilibration of the system included displacement, configurational bias regrowth,[32] and particle insertion/deletion moves.

The free energies were calculated with the incremental gauge cell method (IGCM) proposed by our group recently.[30] The IGCM is based on the gauge cell methodology,[33, 34] and assumes that a system cell of volume V_P containing a polymer chain of length N_P is in thermodynamic equilibrium with a finite-volume "gauge cell" of volume V_G with N_G monomers which behave as ideal gas. Gauge cell monomers may be added to/removed from the free end of the chain, and the
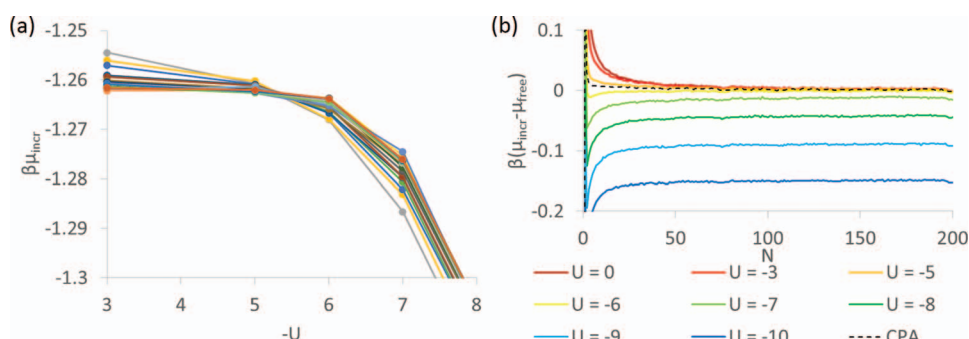

FIG. 2. (a) Dependence of the incremental chemical potential on the adsorption energy U for tethered chains of different length N from 25 to 200. The intersection point corresponds to the CPA at $U_c = -5.4$ +/− 0.05. Calculations performed with the IGCM. (b) Chain length dependence of the incremental chemical potential.

composite system ($V_P + V_G = V$ and $N_P + N_G = N$) is kept at a constant temperature T. Making use of the equilibrium between the gauge and system cells, the incremental chemical potential is determined from the average number of monomers in the gauge cell, and the ratio $P(N)$ of the probabilities to observe N_G and N_G-1 monomers in the gauge cell over the course of a simulation,[30] $\mu_{incr}(N_P) = kT\ln(\frac{P_{N_G}}{P_{N_G-1}}) - kT\ln(\frac{V_G}{\Lambda^3 N_G})$.

Figure 2(a) shows the IGGC incremental chemical potential obtained in simulations for the chains of different lengths for N varying from 30 to 200 in multiples of 10. The CPA of $U_c = -5.4 +/- 0.05$ is determined from the point of intersection, which is clearly defined. Noteworthy, we define here the CPA not from the condition of intersection of the free energies $F_{ex}(N)$, as was done in earlier works,[24–26] but from the condition of intersection of the incremental chemical potentials $\mu_{incr}(N)$ in accord with Eq. (1). Additional calculation data are presented in the supplementary material.[38] The chain length dependence of the incremental chemical potential (reduced by the respective free chain incremental chemical potential) is shown in Fig. 2(b). In the repulsion and weak adsorption regime, $U > U_c$, the chains are extended and the difference $\mu_{incr}^{ad} - \mu_{incr}^{free}$ vanishes for large N (>100). At the CPA, $U = U_c = -5.4$, the equality (1) holds starting from the chain length of $N = 25$. In the adsorption regime, the asymptotic value of the incremental chemical potential is constant in conjunction with chain increment *ansatz*, but it depends progressively on U. The linearity of the length dependence of the chain free energy is also demonstrated, and the reader is directed to the supplementary material[38] for details.

The proposed thermodynamic definition of the CPA complies with the geometrical definitions employed in earlier works. DeGennes defined the CPA from the criterion that below the CPA, the probability P_a of adsorption for a monomer distanced from the tethered end by n monomers decreases to 0 as n increases. Above the CPA, this probability approaches a finite limit as $n \to \infty$. Furthermore, it was suggested and confirmed in lattice and off-lattice simulations[14,22] that the chain adsorption behavior near the CPA is determined by a scaling relationship between the number of adsorbed monomers M, chain length N, and dimensionless deviation of the adsorption energy U from the CPA energy U_c, $\tau = \frac{U-U_c}{U_c}$ in the form

$$M = N^\phi f(\tau N^\phi). \tag{2}$$

Most of the published values of the crossover exponent ϕ fall into the interval between 0.52 and 0.48.[14,15,22,25,35–37] As determined in MC simulations of self-avoiding chains,[22] the crossover exponent $\phi = 0.5 +/- 0.02$, which coincides with its mean field value of 0.5.[19,22] In the following scaling analysis, we adopt the value of $\phi = 0.5$ that is sufficient with respect of the statistical accuracy of our simulation data. To secure that the fraction of adsorbed monomers M/N does not depend on N in the limit of large N, the scaling equation (2) implies that in the limit of $x = \tau N^\phi \to -\infty$, the scaling function $f(x) \propto |x|^{\frac{1}{\phi}-1}$. As such, assuming $\phi = 0.5$, $M/N \propto |\tau|^{\frac{1}{\phi}-1} = |\tau|$, provided that $N \gg |\tau|^{-2}$. At the CPA in the limit of $|\tau| \ll N^{-1/2}$, the fraction of adsorbed monomers decreases with the chain length as $\frac{M}{N} \propto N^{\phi-1} = N^{-1/2}$. Based on this scal-

ing *ansatz* (2), the CPA and crossover exponent can be evaluated from simulations by counting the fraction of adsorbed monomers and fitting the results to Eq. (2). Extrapolation of the linear asymptote in the adsorption regime gives the CPA of $U_c = -5.4 +/- 0.05$ in compliance with the proposed thermodynamic method. DeGennes' method and that of Eq. (2) are illustrated for chains of length $N = 200$ in the supplementary material,[38] and show clear correspondence with the IGCM value of the CPA.

The scaling ansatz implies also that the chain gyration radii in the normal $R_\perp$ and parallel $R_\parallel$ directions to the surface scale as[14]

$$R_\perp = N^{\nu_3} h_\perp(\tau N^\phi) \quad \text{and} \quad R_\parallel = N^{\nu_3} h_\parallel(\tau N^\phi). \tag{3}$$

Here and below, $\nu_3 = 0.588$ and $\nu_2 = \frac{3}{4}$ are the 3d and 2d Flory exponents for polymer chains[22] and $x = \tau N^\phi$. The scaling functions $h_\perp$ and $h_\parallel$ fulfill the following asymptotes. In the adsorption limit at $x = \tau N^\phi \to -\infty$, $R_\perp$ does not depend on N, while $R_\parallel$ scales as N^{ν_2}. These conditions require that $h_\perp \propto |x|^{-\frac{\nu_3}{\phi}}$ and $h_\parallel \propto |x|^{\frac{\nu_2-\nu_3}{\phi}}$, and, respectively,

$$R_\perp \propto |x|^{-\frac{\nu_3}{\phi}} N^{\nu_3} = |\tau|^{-\frac{\nu_3}{\phi}},$$
$$R_\parallel \propto |x|^{\frac{\nu_2-\nu_3}{\phi}} N^\nu = |\tau|^{\frac{\nu_2-\nu_3}{\phi}} N^{\nu_2} \quad \text{at } x \to -\infty. \tag{4}$$

The geometrical scaling is illustrated in Fig. 3(a), where the gyration radii $R_\perp$ and $R_\parallel$ calculated for chains of different lengths and surfaces of different adsorption energy are presented using the scaling coordinates of (3). The slopes of linear asymptotes in the adsorption regime correspond to the predicted values of $-\frac{\nu_3}{\phi} \approx -1.176 =$ for $R_\perp$ and $\frac{\nu_2-\nu_3}{\phi} \approx 0.324$ for $R_\parallel$.

In the repulsion limit at $x = \tau N^\phi \to \infty$, both $R_\perp$ and $R_\parallel$ scale as N^{ν_3}, and, respectively, $R_\perp/R_\parallel \sim 1$. At the very CPA in the limit of $|\tau| \ll N^{-1/2}$, $h_\perp$, and $h_\parallel$ approach certain constants, $h_\perp(0)$ and $h_\parallel(0)$. Thus, this scaling *ansatz* (4) implies that $R_\perp/R_\parallel$ is independent of N at $\tau \to 0$. This conclusion was used[14,15,22] for the practical calculation of the CPA from the point of intersection of $R_\perp/R_\parallel$ versus U plots for the chains of different length N. However, since the scaling *ansatz* holds only with the provision of large N, such a geometrical method applied for finite length chains may overestimate the critical point, as shown in the supplementary material.[38]

Finally, the geometrical scaling can be extended to the scaling of the chain free energy found by Gong and Wang.[25] For sufficiently long chains, the difference in free energy (approximated by the difference in incremental chemical potential times the degree of polymerization, $\beta\mu \cdot N$) between the chain at one value of the incremental chemical potential and the corresponding value at the CPA may be described as a scalable function,

$$\beta\Delta\mu \cdot N = \beta(\mu_{incr} - \mu_{incr}^{CPA}) \cdot N \sim f(|\tau|N^\phi), \tag{5}$$

where the function $f(|\tau|N^\phi)$ in the limit of strong adsorption fulfills a power law with an exponent α, $f(|\tau|N^\phi) = A(|\tau|N^\phi)^\alpha$, so that $\beta\Delta\mu \sim |\tau|^\alpha N^{\alpha\phi-1}$. As the degree of polymerization approaches infinity, we assume as above, that the difference in chemical potential becomes negligible and independent of the degree of polymerization, i.e., $N^{\alpha\phi-1} = 1$. For the mean-field
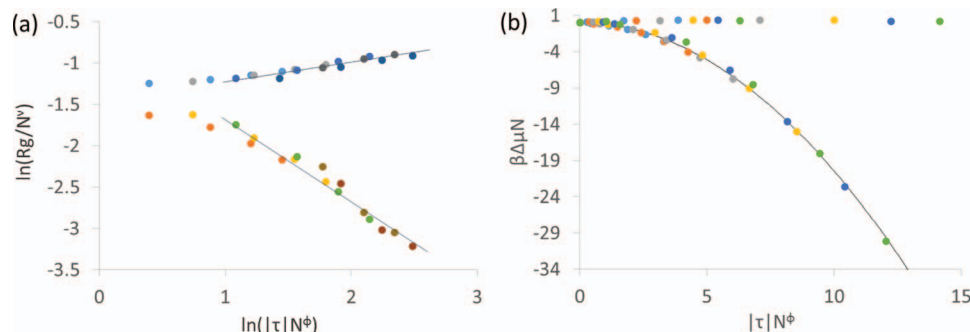
FIG. 3.   (a) Scaling of the gyration radii in the adsorption regime. Linear asymptotes correspond to the theoretical slopes of $-\frac{\nu_3}{\phi} \approx -1.176 =$ for $R_\perp$ (descending upper branch) and $\frac{\nu_2-\nu_3}{\phi} \approx 0.324$ for $R_\parallel$ (ascending branch). The plot is based on the CPA of $U_c = -5.4$ determined by the thermodynamic method. (b) Parabolic scaling of the incremental chemical potential, multiplied by N.

crossover exponent, $\phi = \frac{1}{2}$ this implies $\alpha = 2$. As such, we conclude that for large N, the difference in chemical potential scales with the deviation from the critical point quadratically, as $\Delta\mu \sim |\tau|^2$, $N \to \infty$. Figure 3(b) illustrates the collapse of the incremental chemical potential data onto a master curve. For the case of strong adsorption, the curve is given by the parabola $\beta\Delta\mu N = A(|\tau|N^{0.5})^2$, which follows from Eq. (5) above. The degree with which this scaling law applies to finite size chains, such as those considered here, gives credence to the mean field value of $\phi = 0.5$, and corroborates the similar findings for the scaling of free energy by others[25] despite the disparity in computational approaches.

In conclusion, we have proposed a new thermodynamic method for determining the CPA of polymer chains from the equality of the incremental chemical potentials of adsorbed and free chains and demonstrated its abilities with off-lattice MC simulations of freely jointed chains of LJ particles. For the chemical potential calculations we employed the incremental gauge cell method suggested earlier.[30] We found that the proposed method provides a consistent description of the critical behavior in line with the classical scaling approach with the crossover exponent of $\phi = 0.5$. The established scaling relationships for the density of adsorbed monomers, chain radii of gyration and free energy provide a detailed description of the transition from the 3d conformations at weak adsorption to the 2d conformations at strong adsorption. The proposed method can be extended from the surface-tethered chains considered here to polymer adsorption in more complex geometries, including porous substrates, and with various types of adsorption interactions. The proposed method is directly related to the experimental definition of the CPA in chromatographic experiments from the chain length independence of the partition coefficient.[20] As such, this method is expected to provide a rationale for modeling the polymer partitioning, especially in the regime of liquid chromatography at critical conditions.[27–29]

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[38]See supplementary material at http://dx.doi.org/10.1063/1.4833682 for the content of the three sections: A, B, and C. Section A outlines the computational and simulation methods utilized by the authors and provides additional information on the chain free energy. Section B provides background about the geometrical scaling methods mentioned in this Communication. Section C offers an alternative consideration of the scaling behavior at the CPA.