Effects of smooth random surface on fluid monolayer thermodynamics

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Abstract. We consider the lattice gas approach to statistical mechanics of fluid adsorbed on random surfaces with fluid–fluid and fluid–surface potentials. It was shown that effective Hamiltonian contains quenched random interactions and random site fields. Their statistical features combine the properties of random geometry and fluid–fluid pair interaction potential. The high-temperature expansion leads to infinite-ranged random field model and Sherrington–Kirkpatrick spin-glass model. Thermodynamic properties are evaluated using replica theory procedure widely used to analyze quenched disorder systems. On the other hand we consider the random field model in random graph with finite connectivity instead of previous “infinite-ranged” approximations. This model has been investigated using finite connectivity technique. The replica symmetry ansatz for the order function is expressed in terms of an effective-field distribution. Analysis of random geometry effects on thermodynamic properties in such approach was done for the first time.

1. Introduction
In many physical objectives (such as adsorption, thermodynamics and transport in thin films, membranes, heterogeneous chemical reactions), there is a problem of accounting for the impact of the complex random geometry of the surface on the processes occurring in the system. The attempt to study effects of random nature of the surface on equilibrium thermodynamics of the adsorbed fluid is presented in this paper.

With the development of computer methods of research it has become possible to study a random surface geometry of the pore space of three-dimensional models, for example, by methods of fractal analysis [1,2]. Consideration of these features in the adsorption model allows to develop adsorption methods of surface area measurements in the spirit of determining the dimension of Hausdorff–Besicovitch, by precipitating the molecules of different sizes on the investigated surface and counting their number by measuring adsorption isotherms. In the fundamental works of this direction [3] surface area determined by adsorption isotherms is considered, which allows drawing a conclusion about their fractal properties.

However, discussed approaches consider the impact of random surface only by contribution to effective area without changing the specific thermodynamic quantities. It seems important to consider the impact of random geometry (described by a random field) on thermodynamics of fluids and gases, forming a monolayer. A number of authors have obtained results for the fluid
interacting on the surface in different assumptions about the heterogeneity of the surface, but all of these models describe the geometry with large simplification.

In this paper we develop an approach of using random fields generated by a random surface geometry and fluid properties in order to describe the equilibrium thermodynamics of the formed monolayer. We have considered a simple model of random surface, but this approach can be extended and applied to the analysis of complex models of random fields (at particular interest should be the study of fractal random surfaces). For the averaging of the thermodynamic quantities over the distributions of random fields we use the replica method well known in the theory of quenched disorder systems (theory of glasses, the Ising model with a random external field) [4–7]. An important feature of this approach is the consideration of random Hamiltonians generated by stochastic external fields and interparticle interactions.

It will be shown that our lattice model exhibits properties similar to those of random field Ising model in random graphs with finite connectivity which can form so called “small-world” networks. The concept of “small-world” networks was introduced as an attempt to capture and study nontrivial features observed in realistic biological, technological and social networks. The key idea is to generate a structure which interpolates between a regular finite-dimensional one and a sparse random long-range one. A family of Ising spin models defined on a lattice which, shares characteristics of a regular short-range structure in coexistence with a sparse and random range-free one was studied in [8]. Their lattice consists of a one-dimensional ring of $N$ sites occupied by Ising spins, where each site is firstly connected to its nearest neighbors, and secondly via a random Poissonian graph in which the average number of connections per site $c$ remains finite in the thermodynamic limits $N \to \infty$. Authors combined the approach developed for one-dimensional models (the transfer matrix technique) and those developed for finite connectivity models. Finite connectivity techniques have been applied to many areas, such as error correcting codes [9], theoretical computer science [10], neural networks [11] and spin glasses [12, 13].

Phase transitions in the three-state Ising spin-glass model with finite connectivity was recently studied in [14]. The replica method for disordered spin systems with finite connectivity has been extended here within the replica-symmetry ansatz. The RS ansatz for the order function that describes the behavior in this model with finite connectivity introduces a distribution of a two-component effective field that plays a crucial role in determining the relevant order parameters of the model. An iterative self-consistency relation is derived for local field distribution, an analytic solution of which does not seem possible. Instead a population dynamics numerical procedure developed to solve this equation.

Based on the finite connectivity technique the random field Ising model (RFIM) in a random graph was recently investigated in [15]. Authors focused on determining the order of the phase transition as well as the existence of a tricritical point as a function of the random graph connectivity. Their results indicate that for the Gaussian distribution of random field the phase transition is always second-order. For the bimodal distribution, there is indeed a tricritical point. However, its location is strongly dependent on connectivity. The tricritical point is suppressed below a certain minimum value of connectivity. The finite connectivity technique discussed in the present paper is based on works [16, 17]. Influence of geometry on adsorption and other thermodynamic processes is actively investigated in recent years [18]. These effects play the most important role in the nanoscale pores, where relative surface area (with respect to volume) is not small.

2. The model and replica procedure

We will consider a monolayer of adsorbed gas molecules on random surface (figure 1). Even in their classical work Lee and Young [18] have considered the model of lattice gas, which is obtained when the volume is divided into $N$ equal parts. The pair interaction potential in this
Figure 1. Schematic illustration of molecular adsorption on the surface. Simulated random surface with adsorbed molecules is presented as a function of dimensionless axes \(D\)—molecular diameter). In a separate inset on the figure normalized radial surface correlation function is presented as a function of the reduced distance \(\tau = \tau / D\).

model (in the case of fast damped tail) can be approximated by the following potential on the lattice:

\[
    u(i, j) = \begin{cases} 
        \infty, & \rho(i, j) = 0, \\
        -\varepsilon, & 0 < \rho(i, j) \leq r_{\text{int}}, \\
        0, & \text{else}. 
    \end{cases}
\]

(1)

Such interaction potential corresponds to the condition of the repulsion between particles at short distances and attraction at the intermediate ones and the absence of the interaction at the large distances (see more [8]).

In order to define pairs of interacting molecules on a random surface we introduce the adjacency matrix \(a_{ij} = 1\), if the distance between the positions \(i, j\) on the surface is less \(r_{\text{int}}\) (but greater than 0) and \(a_{ij} = 0\) otherwise. Thus \(a_{ij}\)—symmetric random matrix with values from \{0, 1\} and dimension \(N \times N\), where \(N\)—total number of possible positions for the gas molecules on the surface. Let introduce to each cell scalar function \(\phi(i) = 1\), if the cell is occupied by a gas molecule and \(\phi(i) = 0\) otherwise. Not more than one atom can be located in each cell (because in this case \(u = \infty\)). We denote the potential of the gas molecules interaction with the wall \(-h_{s}\), then the Hamiltonian of the system with a fixed number of particles \(K\) on the surface
has the form:

$$H_K(\phi) = \left\{ \begin{array}{l}
\frac{\varepsilon}{2} \sum_{i,j} a_{ij} \phi(i) \phi(j) - \sum_{i=1}^{N} h_i \phi(i), \\
\sum_{i=1}^{N} \phi(i) = K.
\end{array} \right. \quad (2)$$

Then the partition function for a variable number of particles on the surface (in the grand canonical ensemble) in the equilibrium with gas in the closed pore with a chemical potential $\mu$:

$$\Xi = \sum_{K} \sum_{\phi(1)} \cdots \sum_{\phi(n)} \exp \{-\beta [-\mu K + H_K(\phi)]\}. \quad (3)$$

Making a linear transform $\phi(i) = (s_i + 1)/2$ one consider the Hamiltonian with a scalar field $s_i = \pm 1$. For an arbitrary distribution of $s$ total number of particles $K = 1/2 \sum_{i=1}^{N} (1 + s_i)$. This conversion allows to represent the partition function in the canonical ensemble for the field $s$, that simplifies the calculations:

$$\Xi = \sum_{s_1} \cdots \sum_{s_N} \exp \left\{ -\beta \left[ -\mu \sum_{i=1}^{N} \frac{s_i + 1}{2} - \frac{\varepsilon}{8} \sum_{i,k=1}^{N} a_{ik} (s_i + 1)(s_k + 1) - \frac{h_s}{2} \sum_{i=1}^{N} (s_i + 1) \right] \right\}. \quad (4)$$

Thus partition function can be represented as $\Xi = \text{Tr} e^{-\beta H^{\text{eff}}(s)}$ with the effective Hamiltonian:

$$H^{\text{eff}}(s) = -\frac{J}{2} \sum_{i,k=1}^{N} a_{ik}s_is_k - J \sum_{i=1}^{N} s_i \sum_{k=1}^{N} a_{ik} - \frac{\mu}{2} \sum_{i=1}^{N} s_i - \frac{J}{2} \sum_{i,k=1}^{N} a_{ik} - N \left( \frac{\mu + h_s}{2} \right). \quad (5)$$

Where we have done substitution $J = \varepsilon/4$. Random variables $\xi_i = \sum_k a_{ik}$ on the one hand represent the sum of the elements in the $i$-th row of the adjacency matrix, and on the other hand determine the number of positions (with the characteristic size of the molecule) on the random surface lying within the interaction radius ($r_{\text{int}}$) from the fixed $i$-th, i.e. the number of particles interacting with it (figure 2). We consider rather simple and natural model and assume that all $\xi_i$ are independent random variables with the same Gaussian distribution $f_\xi(x) = 1/(\sqrt{2\pi}\sigma) \exp \left( -\frac{(x - \alpha)^2}{2\sigma^2} \right)$. Knowing the random surface probability distributions and interaction potential one may obtain such distribution $f_\xi(x)$ by numerical simulations.

The fourth term in the expression for the effective potential is the sum of a large number of independent random variables $\sum_{i=1}^{N} \xi_i$ and in the thermodynamic limit it converges to $Na$. Representing random variables through the normal ones $\xi_i = a + \sigma h_i$, $h_i \sim N(0,1)$ and transforming some constants for convenience: $h_0 = Ja + (h_s + \mu)/2$, $c = (h_s + \mu + Ja)/2$ we obtain the final expression for the Hamiltonian containing random field $h$ and the matrix $a_{ij}$:

$$H^{\text{eff}}(s) = -\frac{J}{2} \sum_{i,k=1}^{N} a_{ik}s_is_k - h_0 \sum_{i=1}^{N} s_i - J\sigma \sum_{i=1}^{N} s_i h_i - Nc. \quad (6)$$

Random Hamiltonians of this type naturally arise in the theory of glass (see the classic works [4, 5]), where Hamiltonian with random interaction between particles is considered:

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} s_i s_j, \quad P(J_{ij}) \sim N(J_0, J). \quad (7)$$

And also in the Ising model with a random external field [6]:

$$H = -\frac{J}{N} \sum_{i,j} s_i s_j - \sum_{i} h_i s_i, \quad P(h_i) \sim N(0, \sigma). \quad (8)$$
Random Hamiltonian in our model is an association of previous; it contains both a term responsible for the random interactions (elements of the adjacency matrix) and random external field. The main goal is the calculation of the grand potential averaged over the distribution of random fields $\xi$:

$$\Omega \equiv \langle \tilde{\Omega} \rangle_\xi = \int \tilde{\Omega}(\xi) \rho(\xi) d\xi = -kT \int d\xi \rho(\xi) \left[ \log \left( \prod ds \right) e^{-\beta H(s,\xi)} \right].$$ (9)

Since the integration over the distribution of random fields often leads to the Gaussian integrals (random fields are included in the exponent linearly in Gibbs ensemble) and the exact calculation of the partition function is possible only for a narrow range of tasks, then it makes sense to change the order of integration of random fields and internal degrees of freedom $s$. For the implementation of this procedure, the replica technique is applied. This technique is based on the following representation of the logarithm:

$$\log Z = \lim_{n \to 0} \frac{Z^n - 1}{n}. \quad (10)$$

Introducing $n$ independent replicas of the system it becomes possible to average their partition function $\langle Z^n \rangle$ and calculate the grand potential taking the linear term in $n$ of the expansion for disorder-averaged replicated partition function $\langle Z^n \rangle$. Our Hamiltonian contains two types of randomness, we make calculations on the assumption of their independence, i.e. their joint probability density is factorized:

$$\langle Z^n \rangle_{\xi,\eta} = \int \int d\xi d\eta \rho_1(\xi) \rho_2(\eta) \int \prod_{\alpha=1}^n \left( \prod_{i=1}^N ds_i^\alpha \right) e^{-\beta[H(\xi,s) + H(\eta,s)]} \right]$$

$$= \text{Tr}_\alpha \left\{ \int d\xi \rho_1(\xi) e^{-\beta H(\xi,s)} \int d\eta \rho_2(\eta) e^{-\beta H(\eta,s)} \right\}, \quad (11)$$

where $\alpha$—index of the replica. The replicated partition function for $n$ replicas of the system has the form

$$Z^n = \text{Tr}_\alpha \exp \left\{ \sum_{\alpha=1}^n \left[ \frac{J}{2} \sum_{i,j} a_{ik} s_i^\alpha s_j^\alpha + h_0 \beta \sum s_i^\alpha + \beta J \sigma \sum h_i + \beta Nc \right] \right\}$$

$$= e^{Nn\beta c} \text{Tr}_\alpha \left\{ \exp \left[ \sum_{\alpha} \frac{J}{2} \sum_{i,j} a_{ik} s_i^\alpha s_j^\alpha \right] \exp \left[ \beta J \sigma \sum s_i^\alpha h_i \right] \right\}. \quad (12)$$
Since the matrix $a_{ij}$ has a complicated structure and we know a priori only the distribution of the sum of its elements in each row ($\xi_i$), we suggest simple probabilistic model for distribution of its elements which is equal to random graph approximation:

$$
\rho(\|a\|) = \prod_{i,j} [\delta(a_{ij} - 1)p + \delta(a_{ij})(1-p)], \quad p = \frac{a}{N}.
$$

### 3. Finite connectivity technique. Replica symmetric solution

After integration the first term in the replicated partition function over this distribution one may obtain

$$
\int \exp \left[ \sum_{\alpha} \frac{J^2}{2} \sum_i a_{ik} s_i^\alpha s_j^\alpha \right] \prod_{i,j} d\rho(a_{ij}) = \prod_{i \neq j} \left( p \exp \left[ \frac{J^2}{2} \sum_i s_i^\alpha s_j^\alpha \right] + 1 - p \right) = \prod_{i \neq j} \exp \left( 1 + p \sum_{k=1} \left[ \frac{J^2}{2} \sum_i s_i^\alpha s_j^\alpha \right]^k \right). \quad (14)
$$

In the small $a/N$ limit, the connectivity-average replicated partition function become, to the leading order in $N$

$$
\langle Z^n \rangle = \text{Tr}_\alpha \left\langle \exp \left[ \beta \sum_{\alpha} \sum_i s_i^\alpha \theta_i \right] \right\rangle_{\theta} \exp \left[ \frac{a}{N} \sum_{i \neq j} \left( \exp \left[ \frac{J^2}{2} \sum_i s_i^\alpha s_j^\alpha \right] - 1 \right) \right], \quad (15)
$$

where $\theta = \{\theta_1, \ldots, \theta_N\}$, $\theta_i = J \sigma h_i + h_0$. To extract the variables under summation from the inner exponential term, one introduces the identity

$$
1 = \sum_{\sigma} \delta_{\sigma \sigma_i} \equiv \sum_{\sigma} \prod_{a=1}^n \delta_{\sigma^a \sigma_i^a}, \quad (16)
$$

where $\sigma$, $\sigma_i$ are $n$-component vectors representing replica states. Thus, the replicated partition function could be rewritten in the following form

$$
\langle Z^n \rangle = \sum_{s^1 \ldots s^n} \left\langle \exp \left[ \beta \sum_{\alpha} \sum_i s_i^\alpha \theta_i + \frac{a}{N} \sum_{i \neq j} \sum_{\sigma \tau} \delta_{\sigma \sigma_i} \delta_{\tau \sigma_j} \left( \exp \left[ \frac{J^2}{2} \sum_i \sigma^\alpha \tau^\alpha \right] - 1 \right) \right] \right\rangle_{\theta}. \quad (17)
$$

Let introduce the order parameter distribution $P(\sigma) = N^{-1} \sum_i \delta_{\sigma \sigma_i}$, which represents the fraction of sites with a given configuration $\sigma \in \{-1, 1\}^n$ of replicated spin variables. Partition function can be transformed into an integral representation to be calculated by steepest descent by making use of the following decomposition

$$
1 = \int \prod_{\sigma} \left\{ dP(\sigma) \delta \left[ P(\sigma) - N^{-1} \sum_i \delta_{\sigma \sigma_i} \right] \right\} = \int \prod_{\sigma} \left\{ dP(\sigma) d\hat{P}(\sigma) \right\} \exp \left[ i \sum_{\sigma} \hat{P}(\sigma) \left( P(\sigma) - N^{-1} \sum_i \delta_{\sigma \sigma_i} \right) \right], \quad (18)
$$
where \( \hat{P} \) is an auxiliary field. Changing the order of summation and integration and using

\[
\sum_{s^1,\ldots,s^n} \left\langle \exp \left[ \beta \sum_{\alpha} \sum_i s_i^a \theta_i - \frac{i}{N} \sum_{\alpha} \sum_{i} \hat{P}(\sigma) \delta_{\sigma s_i} \right] \right\rangle_{\theta}
\]

\[
= \left\{ \sum_{s} \left\langle \exp \left[ \beta \sum_{\alpha} s^\alpha - \frac{i}{N} \hat{P}(s) \right] \right\rangle_{\theta} \right\}^N,
\]

(19)

what means that random field is assumed to be the set of independent identically distributed random variables. Performing the trace and changing \( \hat{P} \) to \( \hat{N} \) one may obtain the following expression

\[
\langle Z^n \rangle = \int \prod_{\sigma} d\hat{P}(\sigma) \hat{P}(\sigma) e^{N \Psi(P,\hat{P})},
\]

(20)

\[
\Psi(P,\hat{P}) = i \sum_{\sigma} \hat{P}(\sigma) P(\sigma) + a \sum_{\sigma} P(\sigma) P(\tau) \left( \exp \left[ \frac{J}{2} \sum_{\alpha} \sigma^\alpha \tau^\alpha \right] - 1 \right)
\]

\[+
\log \sum_{s} \left\langle \exp \left[ \beta \sum_{\alpha} s^\alpha - i \hat{P}(s) \right] \right\rangle_{\theta}
\].

(21)

In the large-\( N \) limit the integral is dominated by the stationary point of \( \Psi(P,\hat{P}) \), leading to the extremum representation for disorder-averaged grand potential per site

\[
\omega = - \lim_{N \to \infty} \left( \beta N \right)^{-1} \lim_{n \to 0} \log \langle Z^n \rangle = - \lim_{n \to 0} \left( \beta n \right)^{-1} \text{Extr}_{P,\hat{P}} \Psi(P,\hat{P}).
\]

Working out its saddle-point equations \( \text{tial} \Psi/\text{tial} P(s) = 0 \) and \( \text{tial} \Psi/\text{tial} \hat{P}(s) = 0 \), for all \( s \), gives respectively

\[
\hat{P}(\sigma) = ia \sum_{\tau} P(\tau) \left( \exp \left[ \frac{J}{2} \sum_{\alpha} \sigma^\alpha \tau^\alpha \right] - 1 \right),
\]

(22)

\[
P(\sigma) = \frac{\left\langle \exp \left[ \beta \sum_{\alpha} s^\alpha \right] - i \hat{P}(\sigma) \right\rangle_\theta}{\sum_s \left\langle \exp \left[ \beta \sum_{\alpha} s^\alpha - i \hat{P}(s) \right] \right\rangle_\theta}.
\]

(23)

After eliminating the auxiliary order function \( \hat{P} \) by means of this expression, one obtain the self-consistency relationship for density \( P \):

\[
P(\sigma) = \frac{\left\langle \exp \left[ \beta \sum_{\alpha} \sigma^\alpha + a \sum_{\tau} P(\tau) \left( \exp \left[ \frac{J}{2} \sum_{\alpha} \sigma^\alpha \tau^\alpha \right] - 1 \right) \right] \right\rangle_\theta}{\sum_s \left\langle \exp \left[ \beta \sum_{\alpha} s^\alpha + a \sum_{\tau} P(\tau) \left( \exp \left[ \frac{J}{2} \sum_{\alpha} s^\alpha \tau^\alpha \right] - 1 \right) \right] \right\rangle_\theta}.
\]

(24)

And by substituting saddle-point equations the potential \( \omega \) becomes

\[
\omega = - \lim_{N \to \infty} \frac{1}{\beta N} \lim_{n \to 0} \log \langle Z^n \rangle
\]

\[
= - \lim_{n \to 0} \frac{1}{\beta n} \left\{ -a \sum_{\tau} P(\sigma) P(\tau) \left( \exp \left[ \frac{J}{2} \sum_{\alpha} \sigma^\alpha \tau^\alpha \right] - 1 \right)
\]

\[+
\log \sum_{s} \left\langle \exp \left[ \beta \sum_{\alpha} s^\alpha + a \sum_{\tau} P(\tau) \left( \exp \left[ \frac{J}{2} \sum_{\alpha} s^\alpha \tau^\alpha \right] - 1 \right) \right] \right\rangle_{\theta}
\].

(25)
3.1. Replica symmetric ansatz

Our search for solution $P(\sigma)$ will be restricted to the RS ansatz [8, 14, 15]. The ergodic, or RS ansatz corresponds to the distribution $P(\sigma)$ being invariant under all permutations of the replica labels $\{1, \ldots, n\}$. Consequently, for our model Hamiltonian it should only depend on the summation $\sum_\alpha s^\alpha$ with corresponding weight. Thus, $P(\sigma)$ may always be written in the form

$$P(\sigma) = \int dh \frac{e^{\beta h \sum_\alpha \sigma^\alpha}}{[2 \cosh(\beta h)]^n},$$

(26)

where the new RS order function $W(h)$ is a normalized distribution of effective fields that has to be determined. Expanding the exponential in equation for $P(\sigma)$ and using the RS ansatz, one may obtain the self-consistency relationship for $W(h)$:

$$W(h) = \left\langle \sum_k \frac{e^{-a_k h^k}}{k!} \prod_{l=1}^k dh_l W(h_l) \delta\left(h - \theta - \frac{1}{\beta} \sum_l \arctan \left( \tanh(\beta h_l) \tan \left( \frac{\beta J}{2} \right) \right) \right) \right\rangle_{\theta}. \tag{27}$$

For each temperature $T = 1/\beta$, and connectivity $a$, this equation may be solved numerically by means of an iterative population dynamics recursive procedure for a large number of vector fields (see [8,14,15,17] for explanation in details). Knowledge of $W(h)$ allows one to determine the conventional RS scalar observables, for example

$$m = \lim_{N \to \infty} N^{-1} \sum_i \overline{s_i} = \int dh \ W(h) \tanh(\beta h), \tag{28}$$

where

$$\overline{s_i} = \lim_{n \to 0} \frac{1}{n} \sum_{\alpha} \sum_i s_i^\alpha \left[ \prod_{\gamma=1}^n e^{-\beta H(s^\gamma)} \right]. \tag{29}$$

Although for each number of thermodynamic parameters and distributions of random connectivity and random fields we may solve the self-consistency equation numerically, it spent a lot of time especially for large set of parameters. However we may obtain the high-temperature expansion which is the main objective of this work. It will be shown that this leads to infinite-ranged random field model.

4. High-temperature expansion. Infinite-ranged random field model

Expanding the exponential in the replicated partition function in the high-temperature limit $(kT \gg J)$ and making use of the following integration over random field $h$ distribution

$$\int \prod_i \left( dh_i \frac{1}{\sqrt{2\pi}} \exp \left[ -\frac{h_i^2}{2} \right] \right) \exp \left[ \beta J \sigma \sum_\alpha \sum_i s_i^\alpha h_i \right]$$

$$= \prod_i \int dh_i \frac{1}{\sqrt{2\pi}} \exp \left[ -\frac{h_i^2}{2} + h_i \beta J \sigma \sum_\alpha s_i^\alpha \right] = \exp \left[ \sum_i \frac{\gamma_i^2}{2} \left( \sum_\alpha s_i^\alpha \right)^2 \right], \tag{30}$$
where we make substitution $\gamma = J\beta \sigma$ for further simplification. Thus, the averaged (over all randomness) replicated partition function has the

$$
\langle Z^n \rangle = e^{N n \beta c} \text{Tr}_\alpha \left\{ \exp \left[ \frac{J\beta p}{2} \sum_i \sum_{i \neq j} s_i^\alpha s_j^\alpha + O \left( J^2 \beta^2 \right) \right] \right. \\
\times \left. \exp \left[ \sum_i \left( h_0 \beta \sum_\alpha s_i^\alpha + \frac{\gamma^2}{2} \left( \sum_\alpha s_i^\alpha \right)^2 \right) \right] \right\}. \tag{31}
$$

This relation is similar to those in Schneider–Pytte random field Ising model [6].

$$
\langle Z^n \rangle = \exp \left[ N n \beta \left( c - \frac{p J}{2} \right) \right] \times \text{Tr}_\alpha \left\{ \exp \left[ \frac{J\beta p}{2} \sum_\alpha \left( \sum_i s_i^\alpha \right)^2 + h_0 \beta \sum_\alpha s_i^\alpha + \sum_i \frac{\gamma^2}{2} \left( \sum_\alpha s_i^\alpha \right)^2 \right] \right\}. \tag{32}
$$

The averaged grand potential per unit site may be obtained by saddle point. The details of the calculation are outlined in appendix:

$$
\frac{\Omega}{N} = \frac{t^2 a J}{2} - \frac{J a + h_s + \mu}{2} - \frac{1}{\beta \sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} \right] \ln 2 \cosh \left( \beta \left[ J \sigma x + taJ + Ja + \frac{h_s + \mu}{2} \right] \right), \tag{33}
$$

where $t$ is the solution of the following self consistency equation

$$
t = \frac{1}{\sqrt{2\pi} \sigma} \int dx \exp \left[ -\frac{x^2}{2\sigma^2} \right] \tanh \beta \left[ J x + taJ + Ja + \frac{h_s + \mu}{2} \right]. \tag{34}
$$

We are studying the equilibrium thermodynamics of absorbed fluid monolayer on stochastic surface so we are interested in average density per unit site of the lattice in the monolayer

$$
\rho = \frac{\langle \phi (i) \rangle}{N} = -\frac{1}{N} \frac{\text{tial} \Omega}{\text{tial} \mu} = \frac{1}{2} + \frac{1}{2 \sqrt{2\pi} \sigma} \int dx \exp \left[ -\frac{x^2}{2\sigma^2} \right] \tanh \beta \left[ J x + taJ + Ja + \frac{h_s + \mu}{2} \right] = \frac{1}{2} (1 + t). \tag{35}
$$

What corresponds to the making transformation $\phi (i) = (s_i + 1)/2$. Knowing grand potential all thermodynamics functions may be obtained in the analytic form [19].

5. Results and discussion

Classical Langmuir adsorption model explains adsorption by assuming an adsorbate behaves as an ideal gas at isothermal conditions. By assuming $J = 0$ in the self-consistency equation for $t$, specific density has the form

$$
\rho = \frac{1}{2} + \frac{1}{2 \sqrt{2\pi} \sigma} \int dx \exp \left[ -\frac{x^2}{2\sigma^2} \right] \tanh \beta \left[ \frac{h_s + \mu}{2} \right] = \frac{1 + \tanh \beta \left[ \frac{h_s + \mu}{2} \right]}{2} = \frac{e^{\beta (h_s + \mu)}}{e^{\beta (h_s + \mu)} + 1}. \tag{36}
$$
Figure 3. Influence of relative randomness $\sigma/a$ on adsorption isotherms. Reduced density of adsorbed fluid per unit site versus reduced pressure for different values of temperature. Very far from criticality $kT = 3Ja$ (A). Far from criticality $kT = 2Ja$ (B) and near the criticality $kT = Ja$ (C). The intermolecular interaction potential energy $J$ can be very different for various fluids (that will influence on the critical temperature). Characteristic values for $J$ are discussed in the text.

If we define the partition function for one molecule $j = e^{\beta h}$, one may obtain usual Langmuir adsorption isotherm: $\rho = (je^{\beta \mu}/kT)/(1 + je^{\beta \mu}/kT)$.

For interacting fluid particles ($J \neq 0$) on random surface ($\sigma > 0$) the transcendental saddle-point equation for $t$ may be solved numerically for any set of desired parameters. Particularly, we are interested to study impact of surface randomness on adsorption isotherms for different temperatures around and far from criticality (figure 3).

By analyzing bifurcations of solutions of saddle-point equation one may obtain the equation for determination of critical temperature $T_c$.

$$\frac{\partial}{\partial t} \left( \frac{1}{\sqrt{2\pi}\sigma} \int dx \exp \left[ -\frac{x^2}{2\sigma^2} \right] \tanh \beta [Jx + taJ] \right) \bigg|_{t=0} = 1,$$

(37)

$$\Theta \equiv kT_c = \frac{aJ}{\sqrt{2\pi}\sigma} \int dx \exp \left[ -\frac{x^2}{2\sigma^2} \right] \frac{1}{\cosh^2 \left( \frac{Jx}{kT_c} \right)}.$$  

(38)

Then, if we define $\tau = \sigma/a$, what represents the measure of randomness, the equation for $T_c$ has the form

$$\Theta = \frac{J}{\sqrt{2\pi}\tau} \int dx \exp \left[ -\frac{x^2}{2a^2\tau^2} \right] \frac{1}{\cosh^2 \left( \frac{Jx}{kT_c} \right)}.$$  

(39)

This equation may be solved numerically for different values of $J$. By analyzing the solutions (figure 4) we may observe the shifting of critical temperature with increasing of $\tau$. The intermolecular interaction potential energy $J$ may be very different for various fluids (what will influence on the critical temperature). For example for argon (Ar) $J/k = 120$ K, for methane
Figure 4. Reduced critical temperature as a function of randomness parameters \( \sigma, a \) for reduced pair interaction potential \( J = -0.8 \) (A) and two different \( J = -0.8 \) (blue) and \( J = -1.6 \) (red) (B). If random field variation \( \sigma = 0 \) (classical case) then \( kT_c \approx Ja \). The intermolecular interaction potential energy \( J \) can be very different for various fluids (that will influence on the critical temperature). Characteristic values for \( J \) and \( T_c \) are discussed in the text.

For example, for \( \text{CH}_4 \) \( J/k = 148 \) K, for ethane \( \text{C}_2\text{H}_6 \) \( J/k = 243 \) K, for hydrogen \( \text{H}_2 \) \( J/k = 29.2 \) K, for carbon dioxide \( \text{CO}_2 \) \( J/k = 189 \) K. Thus the critical temperature varies from 20 K (for inert gases) to 500 K (acyclic hydrocarbons, alkanes).

We have studied the impact of random geometry of the surface on the thermodynamic properties of fluid monolayer. The finite connectivity technique was discussed and self-consistency equation for effective field distribution was obtained. Using this distribution one may calculate grand potential of the system and for example average specific density. In the case of high temperatures (or low interaction potential) the grand potential was calculated providing the transcendent equation for specific density. Impact on adsorption isotherms and critical temperature shifting effect was discussed. Analysis of random geometry effects on thermodynamic properties in such approach was developed for the first time.

However it seems that the surfaces of many real substances can be described using random fields, the probability distributions of which are not invariant with respect to changes in scale. Parameters of such complex geometry can significantly affect the thermodynamic properties of the monolayer interacting on the surface especially for highly inhomogeneous random surfaces. In the case of multiple characteristic scales or absence of scale invariance of the distributions describing the surface, influence of the geometry can be different depending on the size of the fluid molecules.

The used model can quite well describe certain types of prepared surfaces, but it needs to be expanded for description of stochastic fractal surfaces, namely, we should consider in more detail the joint distributions of the field \( \xi \), determined by the surface and the fluid properties. Despite the rather simple and natural look of the distribution functions appearing in the model, it seems possible to generalize this approach to more complex models of random fields describing the surface. Especially the model should be extended do deal with correlated random fields.
Appendix

Let us consider the following replicated partition function

\[
\langle Z^n \rangle = \exp \left[ N n \beta \left( c - \frac{pJ}{2} \right) \right] \times \text{Tr}_\alpha \left\{ \exp \left[ \frac{J \beta p}{2} \sum \alpha \left( \sum_i s_i^\alpha \right)^2 + h_0 \beta \sum \alpha s_i^\alpha + \sum_i \frac{\gamma^2}{2} \left( \sum \alpha s_i^\alpha \right)^2 \right] \right\}. \quad (A.1)
\]

Making use of Hubbard–Stratonovich transformation introduce effective fields \(x_\alpha\)

\[
\exp \left[ \frac{J \beta p}{2} \sum \alpha \left( \sum_i s_i^\alpha \right)^2 \right] = \prod_{\alpha=1}^n \exp \left[ \frac{J \beta p \left( \sum_i s_i^\alpha \right)^2}{2} \right] = \prod_{\alpha=1}^n \int \frac{1}{\sqrt{2\pi}} \, dx_\alpha \exp \left[ -\frac{x_\alpha^2}{2} + (pJ\beta)^{1/2} x_\alpha \sum_{i=1}^n s_i^\alpha \right] = \int \prod_{\alpha=1}^n \left( \frac{1}{\sqrt{2\pi}} \, d x_\alpha \right) \exp \left[ -\sum_\alpha \frac{x_\alpha^2}{2} + (pJ\beta)^{1/2} \sum_{i=1}^n \sum_\alpha s_i^\alpha x_\alpha \right]. \quad (A.2)
\]

And obtain the partition function representation in terms of integration over effective fields

\[
\langle Z^n \rangle = \exp \left[ N n \beta \left( c - \frac{pJ}{2} \right) \right] \prod_{\alpha=1}^n \left( \int \frac{1}{\sqrt{2\pi}} \, d x_\alpha \right) \exp \left[ -\sum_\alpha \frac{x_\alpha^2}{2} \right] \times \text{Tr}_\alpha \prod_{i=1}^N \exp \left[ (pJ\beta)^{\frac{1}{2}} \sum_\alpha s_i^\alpha x_\alpha + h_0 \beta \sum_\alpha s_i^\alpha + \frac{\gamma^2}{2} \left( \sum_\alpha s_i^\alpha \right)^2 \right]. \quad (A.3)
\]

Making use of the identity

\[
\text{Tr} \left( \prod_{i=1}^N \exp \left[ \ldots \right] \right) = \prod_{i=1}^N \text{Tr} \exp \left[ \ldots \right] = (\text{Tr} \exp \left[ \ldots \right])^N = \exp \left[ N \ln \text{Tr} \exp \left[ \ldots \right] \right]. \quad (A.4)
\]

Now the following representation consist the trace over \(n\) replicas at a single spin site

\[
\langle Z^n \rangle = \exp \left[ N n \beta \left( c - \frac{pJ}{2} \right) \right] \prod_{\alpha=1}^n \left( \int \frac{1}{\sqrt{2\pi}} \, d x_\alpha \right) \exp \left[ -\sum_\alpha \frac{x_\alpha^2}{2} \right] + N \ln \text{Tr} \left( \exp \left[ \left( pJ\beta \right)^{\frac{1}{2}} \sum_\alpha s_i^\alpha x_\alpha + h_0 \beta \sum_\alpha s_i^\alpha + \frac{\gamma^2}{2} \left( \sum_\alpha s_i^\alpha \right)^2 \right] \right) = \exp \left[ N n \beta \left( c - \frac{pJ}{2} \right) \right] \prod_{\alpha=1}^n \left( \int \frac{1}{\sqrt{2\pi}} \, d x_\alpha \right) \exp \left[ N \left\{ -\sum_\alpha \frac{x_\alpha^2}{2} \right\} \right] + \ln \text{Tr} \left( \exp \left[ \left( pJ\beta N \right)^{\frac{1}{2}} \sum_\alpha s_i^\alpha x_\alpha + h_0 \beta \sum_\alpha s_i^\alpha + \frac{\gamma^2}{2} \left( \sum_\alpha s_i^\alpha \right)^2 \right] \right). \quad (A.5)
\]
In the thermodynamic limit $N \gg 1$ the integrals may be evaluated by saddle-point method. We assume that at the extremum all $x_\alpha$ are equal $x_1 = x_2 = \ldots = x_n \equiv y$.

\[
\langle Z^n \rangle = \exp \left[ N n \beta \left( c - \frac{pJ}{2} \right) \right] \exp \left[ -N n \frac{y^2}{2} \right] \text{Tr}(\ldots)^N, \tag{A.6}
\]

\[
\text{Tr}(\ldots) = \text{Tr} \exp \left[ (pJ\beta N)^{\frac{1}{2}} \sum_\alpha s_\alpha y + h_0 \beta \sum_\alpha s_\alpha + \frac{\gamma^2}{2} \left( \sum_\alpha s_\alpha \right)^2 \right]. \tag{A.7}
\]

Making use of Hubbard–Stratonovich transformation once again

\[
\exp \left[ \frac{\gamma^2}{2} \left( \sum_\alpha s_\alpha \right)^2 \right] = \frac{1}{\sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} + \gamma \sum_\alpha s_\alpha x \right], \tag{A.8}
\]

\[
\text{Tr}(\ldots) = \frac{1}{\sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} \right] \text{Tr} \prod_{\alpha=1}^{n} \exp \left[ s_\alpha \left( \gamma x + h_0 \beta + (pJ\beta N)^{\frac{1}{2}} y \right) \right]
= \frac{1}{\sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} \right] \left( 2 \cosh \left[ \gamma x + h_0 \beta + (pJ\beta N)^{\frac{1}{2}} y \right] \right)^n. \tag{A.9}
\]

Now we are able to calculate the grand potential by expanding the $\langle Z^n \rangle$ up to linear term in $n$

\[
\Omega = -kT \lim_{n \to 0} \frac{1}{n} \left[ \langle Z^n \rangle - 1 \right] = -kT \lim_{n \to 0} \frac{1}{n} \left[ \exp \left[ N n \beta \left( c - \frac{pJ}{2} \right) \right] \exp \left[ -N n \frac{y^2}{2} \right] \right]
\times \exp \left[ N \ln \frac{1}{\sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} \right] \left( 2 \cosh \left[ \gamma x + h_0 \beta + (pJ\beta N)^{\frac{1}{2}} y \right] \right)^n - 1 \right]. \tag{A.10}
\]

Expanding the following integral

\[
\frac{1}{\sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} \right] \left( 2 \cosh \left[ \gamma x + h_0 \beta + (pJ\beta N)^{\frac{1}{2}} y \right] \right)^n
= 1 + n \frac{1}{\sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} \right] \ln 2 \cosh \left[ \gamma x + h_0 \beta + (pJ\beta N)^{\frac{1}{2}} y \right] + O(n^2). \tag{A.11}
\]

Then if we further define $t = y(\beta pJN)^{-1/2}$ the grand potential per site and extremum condition may be written

\[
\frac{\Omega}{N} = \gamma^2 \frac{aJ}{2} - \frac{Ja + h_s + \mu}{2}
- \frac{1}{\beta \sqrt{2\pi}} \int dx \exp \left[ -\frac{x^2}{2} \right] \ln 2 \cosh \left( \beta \left[ J\sigma x + taJ + Ja + \frac{h_s + \mu}{2} \right] \right), \tag{A.12}
\]

\[
t = \frac{1}{\sqrt{2\pi} \sigma} \int dx \exp \left[ -\frac{x^2}{2\sigma^2} \right] \tanh \beta \left[ J x + taJ + Ja + \frac{h_s + \mu}{2} \right]. \tag{A.13}
\]

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