Virtual clusters model on branching random graphs for confined fluid thermodynamics in heterogeneous solid geometry

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Abstract

Fluid properties near rough surfaces are crucial in both a description of fundamental surface phenomena and modern industrial material design implementations. One of the most powerful approach to model real rough materials is based on the surface representation in terms of random geometry. Understanding the influence of random solid geometry on the low temperature fluid thermodynamics is a cutting edge problem. Therefore this work extends recent studies bypassing high temperature expansion and small heterogeneity scale. We introduce random branching trees whose topology reflects the hierarchical properties of random solid geometry. This mathematical representation allows to obtain averaged free energy using novel statistical model of virtual clusters interacting through random ultrametric pairwise potentials. Excellent agreement with direct Monte Carlo calculations is obtained. Moreover, we find that this model leads to interesting features of fluid-solid interactions that have not been discussed in the literature. Our results demonstrate that at low temperature a significant impact to fluid-solid interface energy is induced by hierarchical structure of random geometry. Due to the interdisciplinary nature of the study, our approach can be generalized and applied to a wide range of quenched disorder systems on random graphs. Cooperative phenomena in biological populations and social networks seem most attractive.

I. INTRODUCTION

The study of molecular fluid thermodynamic properties near solid surfaces with a nanoscale geometric heterogeneity is an urgent problem in modern physics. Despite the fact that thousands of works are devoted to the study of confined molecular systems, most of them consider the solid surface model to be smooth on a nanometer scale. However, in recent years, more and more publications demonstrate the significant effect of nanoroughness on a wide class of physical and chemical phenomena: adsorption of simple and chain fluids for materials characterization and optimal storage design \[1-7\], thin film thermodynamics and wetting transition on atomic scale roughness substrates \[8-12\], friction properties of superhydrophobic surface for liquid lubrication design \[13\], molecular surface modifiers for Electric Double Layer supercapacitors \[14\], heterogeneous catalysis \[15\], thermal conduc-
tivity at interfaces and confinement [16, 17] and even geometric control of bacterial surface accumulation [18].

The key element in a description of the fluid properties near the rough surfaces is effective interaction potential between a fluid molecule and solid media. The development of an accurate theoretical model of such potential taking into account both the properties of heterogeneous surface geometry and temperature fluctuations is a cutting edge problem. It is highly desirable since full atomistic methods like Grand Canonical Monte Carlo or Molecular Dynamics are mostly restricted to small geometric defects in the top solid layer due to the high computational cost of simulations [19–21].

The study of rough surfaces has a long history and various mathematical approaches from fractals to random process theory were used. As was demonstrated in [3, 4, 11, 22] the most appropriate model for description of real heterogeneous materials requires random geometry approaches. The theoretical result accounting the random correlated geometry was obtained in our work [22]. More specifically we calculated free-energy-averaged (FEA) effective interaction potentials using analogy with the First Passage Time Probability Theory for Markov random processes. However, this base model is limited to the leading-order term in the high temperature expansion of the FEA potential, which is known to be inaccurate at low temperatures. The effect of an anomalous temperature dependence of the effective fluid-solid potential in the case of geometrically rough surfaces has been discovered by Grand Canonical Monte Carlo GCMC simulations [19]. Deviations from the smooth case are more pronounced at large roughness and low temperatures. Recently Shi, Santiso and Gubbins in [21] pointed out the limitations of our model and emphasized the need for potential that would work well for surfaces with large geometrical defects. Also more accurate temperature dependence is needed for calculations of isosteric heat of adsorption, where influence of surface heterogeneity is crucial [23].

In our current work, we have developed a theoretical model based on statistical physics approach to expand the FEA fluid-solid interaction potential calculations in the field of low temperatures and a wide range of geometric heterogeneity scales. In this study, we go beyond the usual random process model and introduce an ensemble of branching graphs that reflect the hierarchical structure of random solid geometry (see Fig 1). We find that these can lead to interesting features in the potentials that have not been discussed in the literature.
From the physics point of view the roughness is a relative characteristic and the influence of the geometry is defined by the size of a fluid particle. For example a particle with the size a much larger than roughness scale does not interact with heterogeneity and surface can be considered as smooth. The more interesting case corresponds to molecules much smaller than the roughness that can penetrate the free space of solid matter. The central object of our research is a probe molecule located within significantly rough solid media. Figure 1 illustrates the fluid available space which is free of the solid molecules. Let us consider

FIG. 1. Illustration of 3D solid surface geometry with a slice at level z (A). Configuration space $\Omega_T = \cup_i \Omega_i$ is available for fluid molecule at z-slice (B). Colors reflect fluctuations of the external field in each closed region ("islands") $\Omega_i$. Excluded volume that determines the interaction of a fluid particle with a solid (C). Illustration of a hierarchical surface of a solid phase and a branching random graph that reflects the structural features of such random geometry (D).
a probe molecule at the distance $z$ from the average level of the roughness region. The partition function of the molecule interacting with solid media by potential $U(\vec{r})$ is defined by the integration over the configuration space $\Omega_T (z)$ available at the $z$ level:

$$\Theta = \int_{\Omega_T} d\vec{r} e^{-\beta U(\vec{r})} \quad (1)$$

Figure 1.B illustrates the slice of the solid media at the level $z$, where the total configuration space can be split into separated islands $\Omega_T = \bigcup_i \Omega_i$. Thus, the partition function can be represented as the sum:

$$\Theta = \sum_i \int_{\Omega_i} d\vec{r} e^{-\beta U(\vec{r})} \quad (2)$$

For the sake of simplicity assume that all the islands have the same average size $|\Omega_i| = |\Omega|_z$ depending on the slice level $z$. Wherein the random surface properties are conserved and taken into account by the random values of the mean field external potentials $U_i$ corresponding to the island $\Omega_i$. Following the Free Energy Averaging procedure [19, 22] to obtain the effective fluid-solid interaction potential at each slice $z$, it is necessary to calculate free energy which depends on certain realization of quenched random fields $U_i$ and then to obtain the averaging using joint probability distribution $P(U_1, U_2, ..., U_N)$ of random fields as:

$$-\beta F = \langle \log \Theta \rangle_P = \int dU_1...dU_N P(U_1, ..., U_N) \log \Theta(U_1, ..., U_N) \quad (3)$$

where $F$ is the Helmholtz free energy of the probe particle interacted with the rough surfaces. Thus, physical properties of the system are mostly defined by random fluctuations of fields $U_i$ and their correlations. Therefore, a deep analysis of their joint probability distribution is necessary.

To build a theoretical model avoiding the high-temperature approximation we introduced random branching trees whose topology reflects the hierarchical properties of random solid geometry with large scale heterogeneity (see Fig 1.D). The joint probabilistic model $P(U_1, ..., U_N)$ should correctly describe correlations between random fields taking into account such hierarchical structure of rough solid. To meet these requirements, the simple model of summation of random variables on the random graph branches was introduced in this work. We showed that such model leads to the ultrametric properties of fields due to the random trees nature.
Proposed probabilistic model of random fields on random branching trees allows to link the calculation of averaged free energy with the statistical model of virtual clusters that interact through random pairwise potentials. The problem of calculating the free energy averaged over the probability measure of random fields or random pair interactions naturally arises in the theory of systems with frozen or quenched disorder: spin glass theory [24–27], theory of spin systems on random graphs [28–30], spectral theory of random matrices and graph Laplacian [31–34]. Thus to solve the model of virtual clusters, we developed a method based on the finite-connectivity technique for calculating the partition function of spin systems in random small-world networks and applied this method to study fluid behavior for the first time. Excellent agreement of the developed theoretical model with Monte Carlo simulation was obtained for different cases of geometry representations. Moreover, we found that at low temperatures a significant contribution to free energy comes from the hierarchical structure of random geometry. For example, two solid surfaces with the same roughness affect the fluid molecule differently due to the different topology of their graph representation. This effect has not been previously discussed in the literature.

The article is organized as follows: a description and derivation of the probabilistic model for the joint distribution of fields is given in the Section II. Also in this section we show how the proposed probabilistic model helps to calculate the desired thermodynamic properties via replica technique. Section III is devoted to solution for partition function of our quenched disorder system. A nonlinear integral equation is obtained for the probability density of effective local fields, which determines the free energy of the system in the framework of a replica-symmetric ansatz. A numerical analysis of these equations is carried out by population dynamics algorithms. A discussion of numerical results is given in Section IV. Also in this section, the results of comparing the obtained model with numerical simulation by the Monte Carlo method are considered; In conclusion, we discuss the applications and future development of our statistical model on branching random graphs both in problems of fluid physics and in contemporary topical bioinformatics problems associated with random graphs, problems of cooperation in stochastic complex social networks, swarms and populations. Thus our model demonstrates a good example of interdisciplinary research and unexpected correspondence between the modern statistical physics models.
II. MODEL

A. Probability model for Random Fields on Branching Random Graphs

Let us consider the field $U_i$, which corresponds to the Lennard-Jones interaction of a particle located in the island $\Omega_i$ in the solid media. Considering the space above and below the particle at level $z$ the islands form the volume $\Sigma_i = \int dz \Omega_i(z)$, where integration corresponds to the normal direction. Then the solid-fluid interaction $U_i$ can be found as the integral over the solid media $V_s$ without excluded volume $\Sigma_i$

$$U_i = \int_{V_s \setminus \Sigma_i} d\vec{r}_s U_{LJ}(|\vec{r} - \vec{r}_s|)$$ (4)

where $U_{LJ}$ is the Lennard-Jones potential between the particle and solid molecules. Due to the rapidly decreasing Lennard-Jones potential, the contribution from each layer to (4) is mainly determined by the geometric properties of the islands $\Omega_i(z)$ (the size $|\Omega|_z$ and shape), which are random parameters and vary for each realization of a rough solid geometry. Thus, the external field in each $\Omega_i(z)$ at level $z$ is determined by all solid media layers and the islands in such the hierarchical structure Fig. [1]. This hierarchical structure of the rough surfaces imposes certain requirements on the fluctuations of the fields $U_i$. Thus, the joint probabilistic model $P(U_1, \ldots, U_N)$ should correctly describe the correlations between random fields fluctuations taking into account the hierarchical structure of the islands in normal $z$-direction.

In our proposed model each realization of a random geometry of a solid with such hierarchical structure of $\Omega_i(z)$ is represented in the form of a Branching Random Tree, where the vertices reflect islands $\Omega_i$. Let us consider the layer $z$ of the solid media and a set of islands $\Omega_i(z)$. The contribution to the fields $U_i$ from each layer at level $h$ depends on the random geometry of the islands $\Omega_i(h)$. As one can see from Figure [2] the contribution of each vertex $i$ in the graph is denoted by the random variable $\xi_i$. In our model all $\xi_i$ are independent random variables with a certain expectations and a variances. Therefore, one can replace the integration over the layers in (4) by summation over the vertices in Random Tree, which contribute to the external field $U_i$. Thus, in the present model, for a fixed realization of a random graph, field $U_i$ is defined as the sum of the random variables $\xi_k$ on the vertices of the graph that lie on the branch connecting the root of the tree and the final vertex $i$. 
\[ U_i = \sum_{k \in Br(i)} \xi_k \]  

(5)

where branch \( Br(i) \) is unique due to tree structure of the random graph. Graphs with large number of layers in hierarchical structure are of interest. So the use of a multivariate Gaussian model to describe the joint probability distribution of fields \( U_i \) is justified. Without loss of generality, one can consider normalized random fields \( U_i = U_i - U_0 \), where \( U_0 = E(U_i) \) is the expected value. The most important part of the model is the correlation matrix \( C_{ij} \), which determines the fluctuations of the fields. Assuming pairwise independence of random variables \( \xi_k \) correlations can be written as:

\[ C_{ij} = E(U_i U_j) = E \sum_{k \in Br(i)} \sum_{s \in Br(j)} \xi_k \xi_s = \sum_{k \in Br(i) \cap Br(j)} E\xi_k^2 \]  

(6)

As one can see from (6) the correlation between two fields \( U_i \) and \( U_j \) in islands \( \Omega_i \) and \( \Omega_j \) is defined not by the Euclidean distance between them \(|\vec{r}_i - \vec{r}_j|\), but by the common path in the Branching Tree for branches \( Br(i) \cap Br(j) \). In this case the distance between the vertices induces the ultrametric space with unusual for Euclidean space properties [24].

We introduce the intersection \( Q_{ij} \) which denotes the depth in the graph where branches \( Br(i) \) and \( Br(j) \) start to diverge. Using this definition one can rewrite expression (6) as the follows: \( C_{ij} = C(Q_{ij}) \). For a specific realization of a random graph with fixed intersections \( Q_{ij} \), the conditional probability of random fields \( U_i \) has the form of multivariate normal distribution:

\[ P(U_1, ..., U_N|Q_{ij}, ..., Q_{kl}) = \frac{1}{A} \exp\left( -\frac{1}{2} \sum_{ij} U_i C^{-1}(Q_{ij}) U_j \right) \]  

(7)

where \( A \) denotes the normalization constant. Each realization of a random geometry of the solid surface has its own realization of random graph. Thus, to obtain the final probability measure for fields \( U_i \), it is necessary to average the conditional probability (7) over an ensemble of random graphs. This ensemble defines the joint probability of all intersections \( P(Q_{ij}, ..., Q_{kl}) \). We assume the simple model of this joint probability \( P = \prod \rho(Q_{ij}) \), where each \( Q_{ij} \) is chosen according to the same discrete multimodal distribution \( \rho(Q_{ij}) \):

\[ \rho(Q_{ij}) = \sum_k p_k \delta(Q_{ij} - q_k) \]  

(8)

where discrete values \( p_k \) denote the probabilities that an arbitrary pair of branches \( i, j \) has intersections \( Q_{ij} \) at depth level \( q_k \). These probabilities are \( \sum p_k = 1 \) and \( p_k \) could be
FIG. 2. Schematic illustration of a branching random graph and the process of summing random variables $\xi_i$ along branches to generate random external fields $U_k$. The blue solid line indicates a common path in the graph from the root to leafs $i$ and $j$.

calculated for each graph ensemble as relative number of pairs which satisfy the required property:

$$p_k = \frac{\#\{(i, j) : Q_{ij} = q_k\}}{N^2} = \frac{a_k}{N} \tag{9}$$

The numbers $a_k$ depend on random graph generation patterns and can be calculated numerically by the Monte Carlo simulations or analytically using the Parisi matrix representation of such graph structure. Summing all the above together, the desired general probability model for the distribution of random fields has the following form:

$$P(U_1, ..., U_N) = \frac{1}{A} \int \prod_{ij} dQ_{ij} \rho(Q_{ij}) \exp\left(-\frac{1}{2} \sum_{ij} U_i C^{-1}(Q_{ij}) U_j\right) \tag{10}$$

Obtained probability distribution for fields $U_i$ allows to consider averaged over random surface geometry partition function as $\langle \Theta \rangle_P$. According to equation (3) direct calculation is complicated by the presence of logarithm in the subintegral expression. We have used replica technique as a standard tool for quenched disorder systems [24].

However, as will be shown below, the standard replica equations are not suitable for our problem and the replica technique will be modified. Expression (2) for partition function
can be rewritten in the following form: \( \Theta = \sum_i q_i \), where auxiliary variable \( q_i = e^{-\beta U_i} \) is introduced for convenience. To calculate the free energy of the system \( \beta F = -\log \langle \Theta \rangle_P \) averaged over the probability \( \langle \cdot \rangle_P \) we start from the replica trick as follows

\[
- \beta F = \lim_{m \to 0} \frac{\partial \langle \Theta(m) \rangle_P}{\partial m}
\]  

(11)

where we introduce the partition function of \( m \) identical replicas of the system. Using multinomial formula one can obtain the following expression for replicated partition function:

\[
\Theta(m) = \left( \sum_i^N q_i \right)^m = \sum_{\phi_1 \ldots \phi_N} m! q_i^{\phi_i} \delta(m - \sum \phi_i)
\]  

(12)

Further analysis faces two challenges. The first is the presence of a Kronecker delta in the calculation of the sum that constrains the possible configurations of clusters \( \phi_i \). The second is the presence of factorial term \( m! \). To obtain the replica limit \( \langle \Theta(z) \rangle_P \) can be represented in the integral form using Gamma function representation for \( m! \) as follows:

\[
- \beta F = \frac{1}{2\pi i} \lim_{m \to 0} \frac{\partial \langle \Theta(z) \rangle_P}{\partial m} \frac{dz}{z} = \frac{1}{2\pi i} \int \log z \langle \Theta(z) \rangle_P dz
\]  

(13)

where the integration is performed along a counterclockwise closed path encircling the origin and entirely in the region of convergence.

In our study we demonstrate that \( \langle \Theta(z) \rangle_P \) can be represented in the integral form using Gamma function representation for \( m! \) as follows:

\[
\langle \Theta(z) \rangle_P = \int_0^\infty dt e^{-t} Z(t, z)
\]  

(14)

where the sub-integral expression on the right hand side looks similar to partition function of non-interacting clusters \( N = \sum_i^N \phi_i \) under the deterministic external field \( H_0 = U_0 - \frac{1}{\beta} \log \frac{1}{z} \) and the random fields \( U_i \) [35-38]. The next steps are devoted to free energy calculations according to the following order. Firstly, we carry out averaging over random fields \( U_i \) then over random graph typologies \( Q_{ij} \), next summation over virtual clusters \( \phi_i \) may be done, after that we integrate over auxiliary variable \( t \) and finally obtain the replica limit.
using inverse $Z$-transform. In order to simplify (14) one can use well known expression for multinomial Gaussian integral:

$$
\frac{1}{A} \int \prod_i dU_i \exp(-1/2 \sum_{ij} U_i C^{-1}_{ij} U_j + \sum_i U_i) = \exp(1/2 \sum_{ij} \phi_i C_{ij} \phi_j) \tag{15}
$$

Substituting expression (15) one can rewrite (14) as follows:

$$
Z(t, z) = \left\langle \sum_{\phi_1 \ldots \phi_N} \prod_{i=1}^N \frac{1}{\phi_i!} e^{-\beta H} \right\rangle_{\{Q_{ij}\}} \tag{16}
$$

$$
H = H_0 \sum_i \phi_i - \beta \sigma^2/2 \sum_i \phi_i^2 - \beta/2 \sum_{i \neq j} \phi_i C_{ij}(Q_{ij}) \phi_j \tag{17}
$$

Where the replicated partition function (16) is expressed in terms of the effective Hamiltonian $H$ of interacting cluster systems with self-action $\sigma^2$ which stands for diagonal elements of the correlation matrix $C_{ij}$. The couplings $C_{ij} \in \mathbb{R}$ are independent identically distributed random variables as a decreasing functions of ultrametric distance $Q_{ij}$ in random trees. These couplings are drawn from discrete multimodal distribution:

$$
\rho(C_{ij}) = \sum_{l=1}^k a_l \frac{1}{N} \delta(C_{ij} - c_l) + (1 - \sum_{l=1}^k \frac{a_l}{N}) \delta(C_{ij}) \tag{18}
$$

At this step, the model can be considered as the union of $k$ disjoint random networks (small world random networks with finite connectivity). In the $l$-th network a given pair of clusters are connected with probability $a_l/N$ where the connectivity $a_l$ is the average number of connections per cluster (see Fig. 3 for illustrative explanation). The values $a_l$ remain finite in the thermodynamic limit $N \to \infty$.

In the thermodynamic limit, the connectivity-averaged replicated partition function becomes to the leading order in $N$:

$$
Z(t, z) = \left\langle \sum_{\phi_1 \ldots \phi_N} \prod_{i=1}^N \frac{1}{\phi_i!} \exp(-\beta H_0 \sum_i \phi_i + \beta \sum_i \theta_i \phi_i + 1/N \sum_{i \neq j} J(\phi_i, \phi_j)) \right\rangle_{\{\theta_i\}} \tag{19}
$$

where we use the Hubbard-Stratonovich transform and introduce effective random fields $\theta_i$ with identical probability distribution $\rho(\theta) = \frac{1}{\sqrt{2\pi\sigma}} \exp \left( -\frac{\theta^2}{2\sigma^2} \right)$. Given pair of clusters $\phi_i, \phi_j$ interacts via pair potential of the form:

$$
J(\phi_i, \phi_j) = \sum_{l=1}^k a_l (e^{\beta^2 \phi_i \phi_j c_l} - 1) \tag{20}
$$
FIG. 3. Schematic illustration of the different distances between the vertices of the graph - euclidean and ultrametric (A). From the graph one can see that the common path in tree for vertices \( l \) and \( m \) is greater than that for vertices \( l \) and \( k \). The correlation analysis shows that \( U_l, U_m \) are strongly correlated and \( U_l, U_k \) are almost non-correlated fields, despite the fact that the Euclidean distance \( R(l,m) \) is greater than \( R(l,k) \). This is contrary to the usual decay of correlations with distance in space. Schematic representation of the union of random networks with different connectivity (B).

III. ANALYTICAL CALCULATIONS: REPLICA SYMMETRIC ANSATZ

A. Finite Connectivity Technique for Union of Random Networks

Since the connectivities are finite, one cannot expand the inner exponential and introduce the order parameters, like in standard infinite-connectivity calculations \[24, 26\]. Instead, to extract the variables into summation from the inner exponential, we provide finite connectivity technique. Expression (19) for replicated partition function can be transformed into an integral to be calculated by steepest descent as \( N \to \infty \), via the introduction of the order parameter distribution \( P(\sigma) = 1/N \sum_i \delta_{\sigma \phi_i} \) which represents the fraction of clusters \( \phi_i \) of the size \( \sigma \) (see Supplementary Materials for details):

\[
Z(t, z) = \int \prod_{\sigma} \left[ dP(\sigma) d\hat{P}(\sigma) \right] e^{N\Psi(P, \hat{P})}
\]

\[
\Psi(P, \hat{P}) = i \sum_{\sigma} \hat{P}(\sigma) P(\sigma) + \sum_{\sigma \tau} P(\sigma) P(\tau) J(\sigma, \tau) + \log \sum_{s} \left\{ \frac{1}{s!} \exp \left[ -\beta H_0 s + \beta \theta s - i \hat{P}(s) \right] \right\}_{\{\theta\}}
\]
where $\hat{P}$ is the auxiliary distribution. In the large-$N$ limit the integral is dominated by the stationary point of $\Psi(P, \hat{P})$. After eliminating the auxiliary order function by means of saddle-point equations $\frac{\partial \Psi}{\partial \hat{P}} = 0$ and $\frac{\partial \Psi}{\partial P} = 0$, the self-consistency equation for density has the form:

$$P(\sigma) = \frac{1}{\Gamma!} \left[ - \beta H_0 \sigma + \beta \theta \sigma + 2 \sum_{\tau} P(\tau) J(\sigma, \tau) \right]_{\{\theta\}}$$

(22)

where $\Gamma$ remains a normalization factor, so $\sum_{\sigma} P(\sigma) = 1$. Substituting saddle-point equations the potential $\Psi$ becomes

$$\Psi(P) = - \sum_{\sigma \tau} P(\sigma) P(\tau) J(\sigma, \tau) + \log \sum_{s} \left\{ \frac{1}{s!} \exp \left[ - \beta H_0 s + \beta \theta s + 2 \sum_{\tau} P(\tau) J(s, \tau) \right] \right\}_{\{\theta\}}$$

(23)

Here $\Psi(P)$ has energetic and entropic contributions, $\Psi = \Psi_{en} + \Psi_{entr}$, that are, respectively, the first and the second terms of the right-hand side of (23).

**B. Integral equation for local fields distribution**

In work [28] the system of spins interacting via one small world random network is considered using replicated transfer matrix technique. Despite significant differences some steps of our calculations are based on the model presented in this paper. To simplify the mathematical calculations, we leave only the principal (leading) term in the expression for the pair potential (20) $J(\sigma, \tau) = c(e^{\beta \alpha \sigma \tau} - 1)$, where $\alpha = \beta c_{max}/2$. The solution $P(\sigma)$ is restricted to the so-called Replica Symmetric (RS) ansatz [28–30]. The ergodic, or RS ansatz corresponds to the distribution $P(\sigma)$ in the following form:

$$P(\sigma) = \frac{1}{\sigma!} \int dh W(h)e^{\beta \sigma h}/\chi_0(h)$$

(24)

where $W(h)$ is the normalized distribution of local complex fields $h = h_1 + i h_2$ ($dh = dh_1 dh_2$), and $\chi_0(h)$ is an auxiliary partition function

$$\chi_\tau(h) = \sum_{s} \frac{1}{s!} e^{\beta s(h + \alpha \tau)}$$

(25)

Introducing RS ansatz (24) into equation (22) one can obtain the following self-consistent equation for local fields distribution $W(h)$ (see Supplementary Materials for details):

$$W(h) = \chi_0(h)e^{-\tau} \sum_{k \geq 0} \frac{c^k}{k!} \left\{ \int \prod_{l=1}^{k} dh_l W(h_l) \delta \left( h + H_0 - \theta - \frac{\alpha}{\beta} \sum_{l=1}^{k} \partial_{dh} \log \chi_0(h_l) \right) \right\}_{\{\theta\}}$$

(26)
Numerical algorithm for solving this self-consistent equation for local fields distribution is presented below.

C. Averaged Free Energy in replica limit

Using RS representation (24) one can obtain from (23) energetic and entropic contributions \( \Psi = \Psi_{en} + \Psi_{entr} \)

\[
\Psi_{en} = - \sum_{\sigma, \tau} P(\sigma) P(\tau) J(\sigma, \tau) = (27)
\]

after linearization one can obtain the following expression:

\[
\Psi_{en}(P) = - \frac{1}{\beta} \sum_{l=1}^{k} a_l \alpha_l \left( \int dh W_0(h) \frac{\partial}{\partial h} \log \chi_0(h) \right)^2 (28)
\]

The last term of \( \Psi \) in (23) corresponds to the entropy contribution \( \Psi_{entr}(P) \). By substituting the RS solution it becomes:

\[
\Psi_{entr}(P) = \log \left\langle \exp \left( - \beta U_0 + \beta \theta + 2 \sum_{l=1}^{k} a_l \alpha_l \int dh W_0(h) \frac{\partial}{\partial h} \log \chi_0(h) \right) \right\rangle_{\theta} (29)
\]

We observe that the distribution \( W(h) \) can be represented by the shifting \( W(h) = W_0(h - \frac{1}{\beta} \log \frac{t}{z}) \), where \( W_0 \) is the solution of self-consistent equation with \( t/z = 1 \). In thermodynamic limit we are interested in the case \( z \sim N \), so expressions (28) and (29) can be approximated by the following leading terms:

\[
\Psi_{en}(P) = - \frac{t^2}{z^2 \beta} \sum_{l=1}^{k} a_l \alpha_l \left( \int dh W_0(h) \frac{\partial}{\partial h} \log \chi_0(h) \right)^2 (30)
\]

\[
\Psi_{entr} = \frac{t}{z} Z_0 e^{-\beta^2 \sigma^2 / 2} + 2 \frac{t^2}{z^2} Z_0 e^{-\beta^2 \sigma^2 / 2} \sum_{l=1}^{k} a_l \alpha_l \int dh W_0(h) \frac{\partial}{\partial h} \log \chi_0(h) (31)
\]

Where \( Z_0 = e^{-\beta U_0} \). As results after substitution (30) and (31) to (13) one can obtain desired average free energy for the first order expansion in fields correlation. Following the Free Energy Averaging technique [19, 22], we equate the obtained free energy with the energy of the reference system in the effective field \( U_{eff} \):

\[
U_{eff}(\beta) = U_0 + U_{fluct} + U_{topology} = U_0 - \frac{\beta \sigma^2}{2} + \frac{\alpha}{\beta} \left( 2 \frac{m_0}{Z_0} e^{-\beta^2 \sigma^2 / 2} - \frac{1}{\beta} \frac{m_0^2}{Z_0^2} e^{-\beta^2 \sigma^2} \right) (32)
\]
m_0 = \int dh W_0(h) \frac{\partial}{\partial h} \log \chi_0(h)

where \( \bar{\alpha} = \sum a_t \alpha_t / \sum a_t \) is averaged value of \( \alpha \) via knowledge of random graph generation pattern. Thus the effective external potential is explicit function of the density distribution \( W(h) \) which can be obtained numerically using self-consistent equation (26) for certain temperature \( \beta \) and the random branching graph statistics. For qualitative analysis \( U_{\text{topology}} \) may be approximately simplified for the case of \( U_0 = 0 \) with \( Z_0 = \exp(-\beta U_0) = 1 \):

\[
U_{\text{topology}} = \frac{\bar{\alpha}}{\beta} e^{-\frac{\beta^2 \sigma^2}{2}} \int dh W_0(h) \frac{\partial}{\partial h} \log \chi_0(h)
\] (33)

IV. RESULTS AND DISCUSSION

A. Numerical solution of self-consistent equation

To solve the self-consistent integral equation (26) for local fields density \( W(h) \) we have proceeded numerically by means of population dynamics with large number of fields updated by an iterative method [27, 29]. At the initial moment, the ensemble of fields is determined independently based on a uniform distribution. In this paper, we performed a simulation on the size of the ensemble \( N = 10^5 \). For each iteration a number \( k \) is chosen randomly from a Poisson distribution with mean . Then elements \( h_l \) with \( l \) running from 1 to \( k \) are chosen at random from the population. Considering the local fields, the summation of terms on the argument of delta function in the right-hand side of (26) is calculated. Next, one selects at random a new element \( h \) from the population and sets

\[
h = \theta - H_0 + \frac{\alpha}{\beta} \sum_{l=1}^{k} \frac{\partial}{\partial h} \log \chi_0(h_l)
\] (34)

the procedure converges to a limiting distribution \( W(h) \). Since this distribution is the main parameter that determines the behavior of the system, it is extremely important to study the properties of solutions for different variations of parameters. Several factors affect the solution: temperature \( T \), mean connectivity \( c \), external field \( H_0 \) and random fluctuations \( \theta \). Thus, to investigate the behavior of the solution, we performed a series of calculations fixing some parameters and varying others. The results of numerical calculations are presented in Fig. 4 and Fig. 5. To study the dependence on temperature and constants of connectivity, we consider the case when the external field and fluctuations are turned off. From the results
it follows that the distribution is sensitive to both temperature and topological features of the graph (see Fig. 4). With temperature increasing and small connectivity, the distribution becomes narrow and demonstrates multimodal structure, turning into a discrete spectrum. On the contrary, with temperature decreasing and increasing of connectivity, the distribution covers a wider range of field values and becomes smooth, approaching the normal distribution (see Fig. 4a,f). In the second series of calculations, we have fixed temperature $T = 80$ K, connectivity $c = 5$ and included random fluctuations $\theta$ with standard deviation $\sigma = 10$ K and zero mean. In this case, the discrete distribution structure disappears. When the external field is switched on, a distribution shift is observed depending on the values of the external field, and the shape of the distribution varies slightly (see Fig. 5).

B. Comparison with Monte-Carlo simulation

To validate the final theoretical predictions of the effective potential, we have performed a series of numerical experiments based on Monte Carlo simulation of random branching graphs. The following algorithm was used to generate a graph ensemble: starting from the
FIG. 5. Different solutions of the integral equation for the distribution function of local fields for \( \theta \neq 0 \). Calculations were performed for the same coupling constants and temperatures (\( T = 80 \) K, \( C = 5 \)) and different values of the external field (a, b, c).

root of the tree, for each parent node, number of child nodes was created according to the Poisson distribution with a mean value determined by a specific generating pattern. Each node of the graph contributes to the field according to the normal distribution with zero mean and variance \( \Delta: \mathbb{E}\xi^2 = \Delta^2 \). This process continues until the required depth of the graph is reached. Recall that a random external field is created in the process of summing random variables along the branches of the graph from root to leaf. Then, for each graph realization, free energy has been directly calculated and global averaging has been performed over the entire ensemble according to equation (3).

In the current work, the size of the ensemble is \( N = 10^5 \). Results of the comparison between theoretical calculations according to (32) with Monte Carlo simulation carried out on an ensemble of graphs with different generating patterns are shown in Fig. 6 and Fig. 7. In the first series of experiments, we have investigated the effect of random field fluctuations on the effective potential. Based on the same generating pattern, cases with different values of the standard deviation of the fields at the nodes of the graph have been compared (\( \Delta = 5 \) K and \( \Delta = 10 \) K). The results demonstrate a good agreement between the theory and the numerical experiment. Fig. 6 shows that the temperature dependence is particularly strong at low temperatures and large fluctuations of random fields.

Of greatest interest is the influence of the topology of random graphs on the free energy averaged potential. Therefore, in the second series of experiments, the simulation was carried out for two different generating patterns (see Fig. 7) with equal standard deviation of local fields fluctuations at the nodes \( \Delta = 10 \) K. For both patterns, the fluctuation part of the potential \( U_{\text{fluct}}(T) \) is the same (depicted by a gray dashed line) and by itself cannot predict...
the differences observed in the simulation. However, the results of the theory demonstrate good agreement with experiment by taking into account the last term in the expression for the effective potential \( U_{\text{topology}}(T) \).

V. SUMMARY AND CONCLUSION

In the current work study of molecular fluid thermodynamic properties near solid surfaces with a nanoscale geometric heterogeneity in wide range of temperatures and heterogeneity scales via novel theoretical model. Excellent agreement with Monte Carlo simulations was demonstrated on several cases with different graph patterns reflecting the hierarchical properties of the solid geometry. Thus, the proposed model looks promising for the further construction of effective fluid-solid interaction potentials. These potentials are highly desirable in Molecular Dynamics or DFT modeling of wide class of interface thermodynamic

FIG. 6. The temperature dependence of the effective potential is presented for different variances of random variables at vertices of random graphs \( \bar{E}\xi^2 = \Delta^2 \) for \( \Delta_1 = 5 \text{ K} \) and \( \Delta_2 = 10 \text{ K} \). The external field is turned off. The inset schematically shows the structural generation pattern of the graph ensemble.
FIG. 7. The dependence of the effective potential on temperature is presented for graphs with different structural patterns. The external field is turned off. Schematic representations of patterns (A). Temperature dependence of the effective potential for given generation patterns at $\Delta = 10$ K and comparison with Monte Carlo simulations (B). The dashed line indicates only the contribution from the $U_{\text{fluct}}$ term.

In a recent series of works DFT-based models have been developed for the fluid interaction with geometrically heterogeneous surfaces. More specifically in [3, 4] we proposed Random Surface Density Functional Theory (RS-DFT) and Random Surface Statistical Associating Fluid Theory (RS-SAFT) to describe the adsorption of simple and chain fluids on various modern carbon materials with nanoscale heterogeneity. Our main important result is novel approach to inverse design of such rough surfaces of real materials based on experimental adsorption data. Results of current research expand the boundaries of it’s applicability to low temperatures and large geometric defects and constitute a significant step forward in understanding the influence of random geometry on fluid thermodynamics.

On the other hand, we believe that the statistical model on random graphs and theoretical methods proposed in this paper may be interesting for studying cooperative phenomena in biological populations and social networks. The application of statistical physics methods in the study of complex systems dynamics, social behavior and cooperation in populations and swarms is a hot topic of research [39–43]. For example in work [40] authors study ”thermodynamics” of evolutionary games to answer the question how cooperation can evolve between players. They use Hamiltonian dynamics of models of the Ising type to describe
populations of cooperating and defecting players to show that the equilibrium fraction of cooperators is given by the expectation value of a thermal observable akin to a magnetization. Also, statistical models on graphs have modern applications in Computer Vision and Bayesian Networks for reconstruction of images with defects [44], analysis of computational complexity and neural networks [45, 46].

However classical models work well for pairwise interactions depending on the Euclidean distance in space [47], while social interactions in network or in a swarm are much more complex. In our proposed model, the distance is defined in terms of the topological structure of a random graph, which opens up new possibilities for research applications.

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