Surface partition of large clusters

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The surface partition of large clusters is derived analytically for a simple statistical model by using the Laplace-Fourier transformation method. In the limit of small amplitude deformations, a suggested "hills and dales model" reproduces the leading term of the Fisher result for the surface entropy to within a few percent. The model also gives the degeneracy prefactor of large clusters. The surface partition of finite clusters is also discussed.

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I. INTRODUCTION

During last forty years, the Fisher droplet model (FDM) [1] has been used to analyze the condensation of a gaseous phase (droplets of all sizes) into a liquid. The systems analyzed with the FDM are many and varied, including nuclear multifragmentation [2], nucleation of real fluids [3], the compressibility factor of real fluids [4], clusters of the Ising model [5], and percolation clusters [6]. In FDM, the surface free energy F_A of a cluster of A-constituents can be represented as

$$F_A = \sigma(T) A^{2/3} + \tau T \ln A. \qquad (1)$$

Here, $\sigma(T)$ is the temperature-dependent surface tension which in the vicinity of the critical temperature T_c is parametrized in the following form: $\sigma(T)|_{\rm FDM} = \sigma_{\rm o}[1 - T/T_c]$. The last contribution in Eq. (1) generates the Fisher power law with dimensionless parameter τ.

From the study of the combinatorics of lattice gas clusters in two dimensions, Fisher postulated Eq. (1) and its specific temperature dependence of the surface free energy, which gives naturally an estimate of T_c. He argued that the temperature-independent part of $\exp[-F_A/T]$, i.e., $A^{-\tau}\exp[\sigma_{\rm o} A^{2/3}/T_c]$, is nothing else but a surface entropy or, in other words, it is a surface degeneracy factor for the cluster of given volume. The Fisher parametrization of the surface free energy is, of course, not unique. The statistical multifragmentation model (SMM) [7] commonly used in the study of nuclear multifragmentation, for instance, successfully employs another one [7] with $\sigma(T)|_{\rm SMM} = \sigma_{\rm o}[(T_c^2 - T^2)/(T_c^2 + T^2)]^{5/4}$ and neglects altogether the logarithmic term $\tau T \ln A$. However, in contrast to FDM, the SMM describes not only the gaseous phase of nuclear clusters, but the nuclear liquid phase as well on the same footing [8,9]. Since both models are successful in nuclear multifragmentation, we are confronted with an evident question: "Which parametrization is correct?"

Moreover, since the FDM is successfully used in many different fields, we are faced with a few simple, but quite fundamental questions related to any discrete clusters: "What is the origin of the Fisher parametrization for the temperature dependent surface free energy? Is there any general reason why in many applications the surface entropy of large clusters grows as $\exp[\sigma_{\rm o} A^{2/3}/T_c]$?" This work is devoted to these questions.

II. HILLS AND DALES MODEL

To answer these questions we consider a statistical model of surface deformations. We impose a necessary constraint that the deformations conserve the volume of the cluster of A-constituents. The model-independent results correspond to the deformations of vanishing amplitude. Thus, the shape of the deformation cannot be important to our result and we can therefore choose one that is regular to simplify our presentation. For this reason, we shall consider cylindrical deformations of positive height $h_k > 0$ (hills) and negative height $-h_k$ (dales), with k-constituents at the base. For simplicity, it is assumed that the top (bottom) of the hill (dale) has the same shape as the surface of the original cluster of A-constituents. We also assume that (i) the statistical weight of deformations $\exp(-\sigma_{\rm o}|\Delta S_k|/s_1/T)$ is given by the Boltzmann factor due to the change of the surface $|\Delta S_k|$ in units of the surface per constituent s_1; (ii) all hills of heights $h_k \le H_k$ (H_k is the maximal height of a hill with a base of k-constituents) have the same probability dh_k/H_k besides the statistical one; and (iii) assumptions (i) and (ii) are valid for the dales. These assumptions are not too restrictive and allow us to simplify the analysis.

With these assumptions, it is possible to find the one-particle statistical partition of the deformation of the k-constituent base as a convolution of the two probabilities discussed above:

$$z_k^{\pm} \equiv \int_0^{\pm H_k} \frac{dh_k}{\pm H_k} e^{-\sigma_{\rm o} P_k |h_k|/T s_1} = T s_1 \frac{[1 - e^{-\sigma_{\rm o} P_k H_k/T s_1}]}{\sigma_{\rm o} P_k H_k}, \qquad (2)$$

where the upper (lower) sign corresponds to hills (dales). Here, P_k is the perimeter of the cylinder base.

Now we have to find a geometrical partition (degeneracy factor) or the number of ways to place the center of a given deformation on the surface of the A-constituent cluster that is occupied by the set of $\{n_l^{\pm} = 0, 1, 2, \ldots\}$ deformations of the l-constituent base. Our next assumption is that the desired geometrical partition can be given in the excluded volume approximation

$$\mathcal{G}=\left[S_A-\sum_{k=1}^{K_{max}}k(n_k^+ + n_k^-)s_1\right]s_1^{-1}, \tag{3}$$

where s_1k is the area occupied by the deformation of k-constituent base ($k=1,2,\ldots$), S_A is the full surface of the cluster, and $K_{max}(S_A)$ is the A-dependent size of the maximal allowed base on the cluster. The first term in the right-hand side (r.h.s.) of (3) corresponds to the surface available to place the center of each of $\{n_k^{\pm}\}$ deformations that exist on the cluster surface. It is necessary to impose the condition $\mathcal{G}\geqslant 0$, which ensures that the deformations do not overlap. Equation (3) is the van der Waals excluded volume approximation usually used in statistical mechanics for low particle densities [7,8,10], and can be derived for objects of different sizes in the spirit of Ref. [11].

According to Eq. (2), the statistical partition for the hill with a k-constituent base matches that of the dale; i.e., $z_k^+=z_k^-$. Therefore, the grand canonical surface partition (GCSP)

$$Z(S_A)=\sum_{\{n_k^{\pm}=0\}}^{\infty}\left[\prod_{k=1}^{K_{max}}\frac{[z_k^+\mathcal{G}]^{n_k^+}}{n_k^+!}\frac{[z_k^-\mathcal{G}]^{n_k^-}}{n_k^-!}\right]\Theta(s_1\mathcal{G}) \tag{4}$$

corresponds to the conserved (on average) volume of the cluster because the probabilities of hill and dale of the same base are identical. The $\Theta(s_1\mathcal{G})$-function in (4) ensures that only configurations with a positive value of the free surface of the cluster are taken into account. However, this makes the calculation of the GCSP rather difficult. In addition, the standard method to deal with the excluded volume partitions, the Laplace transform [8,10] in S_A, cannot be applied because of the explicit dependence of K_{max} (maximal base of deformations) on S_A. However, the GCSP (4) can be solved via the Laplace-Fourier technique [12]. The latter employs the identity

$$G(S_A)=\int_{-\infty}^{+\infty}d\xi\int_{-\infty}^{+\infty}\frac{d\eta}{2\pi}e^{i\eta(S_A-\xi)}G(\xi), \tag{5}$$

which is based on the Fourier representation of the Dirac δ-function. The representation (5) allows us to decouple the additional S_A dependence in $K_{max}(S_A)$ and reduce it to the exponential one, which can be integrated by the Laplace transform [12]:

$$\begin{aligned}\mathcal{Z}(\lambda)&\equiv\int_0^{\infty}dS_A e^{-\lambda S_A}Z(S_A)\\ &=\int_0^{\infty}dS'\int_{-\infty}^{+\infty}d\xi\int_{-\infty}^{+\infty}\frac{d\eta}{2\pi}e^{i\eta(S'-\xi)-\lambda S'}\sum_{\{n_k^{\pm}=0\}}^{\infty}\\ &\quad\times\left[\prod_{k=1}^{K_{max}(\xi)}\frac{[z_k^+S'e^{ks_1(i\eta-\lambda)}]_{n_k^+}}{n_k^+!s_1^{n_k^+}}\frac{[z_k^-S'e^{ks_1(i\eta-\lambda)}]_{n_k^-}}{n_k^-!s_1^{n_k^-}}\right]\Theta(S')\\ &=\int_0^{\infty}dS'\int_{-\infty}^{+\infty}d\xi\int_{-\infty}^{+\infty}\frac{d\eta}{2\pi}e^{i\eta(S'-\xi)-\lambda S'+S'\mathcal{F}(\xi,\lambda-i\eta)}.\end{aligned} \tag{6}$$

After changing the integration variable $S_A\to S'=S_A-\sum_{k=1}^{K_{max}(\xi)}k(n_k^++n_k^-)s_1$, the constraint of Θ-function has disappeared. Next, all n_k were summed independently, leading to the exponential function. Now the integration over S' in (6) can be done, giving

$$\mathcal{Z}(\lambda)=\int_{-\infty}^{+\infty}d\xi\int_{-\infty}^{+\infty}\frac{d\eta}{2\pi}\frac{e^{-i\eta\xi}}{\lambda-i\eta-\mathcal{F}(\xi,\lambda-i\eta)}, \tag{7}$$

where the function $\mathcal{F}(\xi,\tilde{\lambda})$ is defined as follows:

$$\mathcal{F}(\xi,\tilde{\lambda})=\sum_{k=1}^{K_{max}(\xi)}\left[\frac{z_k^+}{s_1}+\frac{z_k^-}{s_1}\right]e^{-ks_1\tilde{\lambda}}. \tag{8}$$

As usual, in order to find the GCSP by the inverse Laplace transform, it is necessary to study the structure of singularities of the partition (7). Hereafter, we will call (7) an isochoric partition, or an isochoric ensemble, since the hills and dales model (HDM) requires the cluster volume conservation.

III. ISOCHORIC ENSEMBLE SINGULARITIES

For a finite cluster surface, the structure of singularities of the isochoric partition (7) can be complicated. To see this, let us first make the inverse Laplace transform

$$\begin{aligned}Z(S_A)&=\int_{\chi-i\infty}^{\chi+i\infty}\frac{d\lambda}{2\pi i}\mathcal{Z}(\lambda)e^{\lambda S_A}\\ &=\int_{-\infty}^{+\infty}d\xi\int_{-\infty}^{+\infty}\frac{d\eta}{2\pi}\int_{\chi-i\infty}^{\chi+i\infty}\frac{d\lambda}{2\pi i}\frac{e^{\lambda S_A-i\eta\xi}}{\lambda-i\eta-\mathcal{F}(\xi,\lambda-i\eta)}\\ &=\int_{-\infty}^{+\infty}d\xi\int_{-\infty}^{+\infty}\frac{d\eta}{2\pi}e^{i\eta(S_A-\xi)}\sum_{\{\tilde{\lambda}_n\}}e^{\tilde{\lambda}_nS_A}\left[1-\frac{\partial\mathcal{F}(\xi,\tilde{\lambda}_n)}{\partial\tilde{\lambda}_n}\right]^{-1},\end{aligned} \tag{9}$$

where the contour integral in λ is reduced to the sum over the residues of all singular points $\lambda=\tilde{\lambda}_n+i\eta$ with $n=0,1,2,\ldots$, since this contour in the complex λ-plane obeys the inequality $\chi>\max(\mathrm{Re}\{\tilde{\lambda}_n\})$. Now all integrations in (9) can be done, and the GCSP acquires the form

$$Z(S_A)=\sum_{\{\tilde{\lambda}_n\}}e^{\tilde{\lambda}_nS_A}\left[1-\frac{\partial\mathcal{F}(S_A,\tilde{\lambda}_n)}{\partial\tilde{\lambda}_n}\right]^{-1}, \tag{10}$$

i.e., the double integral in (9) simply reduces to the substitution $\xi\to S_A$ in the sum over singularities. This remarkable answer is a partial example of the general theorem on the Laplace-Fourier transformation properties proved in [12].

The simple poles in (9) are defined by the condition $\tilde{\lambda}_n=\mathcal{F}(S_A,\tilde{\lambda}_n)$, and the latter can be cast as a system of two coupled transcendental equations

$$R_n=\sum_{k=1}^{K_{max}(S_A)}[z_k^++z_k^-]e^{-kR_n}\cos(I_nk), \tag{11}$$

$$I_n = - \sum_{k=1}^{K_{max}(S_A)} [z_k^+ + z_k^-] e^{-kR_n} \sin(I_n k), \qquad (12)$$

for dimensionless variables $R_n = s_1 \mathrm{Re}(\tilde{\lambda}_n)$ and $I_n = s_1 \mathrm{Im}(\tilde{\lambda}_n)$.

To this point, Eqs. (11) and (12) are general and can be used for particular models which specify the height of hills and depth of dales. However, there exists an absolute supremum for the real root $(R_0; I_0 = 0)$ of these equations. It is sufficient to consider the limit $K_{max}(S_A) \to \infty$, because for $I_n = I_0 = 0$ the r.h.s. of (11) is a monotonically increasing function of $K_{max}(S_A)$. Since $z_k^+ = z_k^-$ are the monotonically decreasing functions of H_k, the maximal value of the r.h.s. of (11) corresponds to the limit of infinitesimally small amplitudes of deformations $(H_k \to 0)$. Then, for $I_n = I_0 = 0$, Eq. (12) becomes an identity and Eq. (11) becomes

$$R_0 \to 2 \sum_{k=1}^{\infty} e^{-\sigma_o P_k H_k / 2T s_1} e^{-kR_0} = 2[e^{R_0} - 1]^{-1}, \qquad (13)$$

and we have $R_0 = s_1 \tilde{\lambda}_0 \approx 1.060\,09$. Since for $I_n \neq 0$ defined by (12), the inequality $\cos(I_n k) \leqslant 1$ cannot become the equality for all values of k simultaneously, it follows that the real root of (11) obeys the inequality $R_0 > R_{n>0}$. The last result means that in the limit of infinite cluster $(S_A \to \infty)$, the GCSP is represented by the farthest-right singularity among all simple poles $\{\tilde{\lambda}_n\}$:

$$Z(S_A)|_{S_A \to \infty} \approx \frac{e^{R_0 S_A / s_1}}{1 + \dfrac{R_0(R_0+2)}{2}} \approx 0.3814 e^{R_0 S_A / s_1}. \qquad (14)$$

There are two remarkable facts regarding (14): first, this result is model independent because in the limit of vanishing amplitude of deformations all model-specific parameters vanish; second, in evaluating (14) we did not specify the shape of the cluster under consideration, but only implicitly required that the cluster surface together with deformations is a regular surface without self-intersections. Therefore, for vanishing amplitude of deformations the latter means that Eq. (14) should be valid for any non-self-intersecting surfaces.

For spherical clusters, the r.h.s. of (14) becomes familiar $(0.3814 e^{1.06\,009 A^{2/3}})$, which, combined with the Boltzmann factor of the surface energy $e^{-\sigma_o A^{2/3}/T}$, generates the following temperature-dependent surface tension of the large cluster:

$$\sigma(T) = \sigma_o \left[1 - 1.06\,009 \frac{T}{\sigma_o} \right], \qquad (15)$$

which means that the actual critical temperature of the three-dimensional Fisher model should be $T_c = \sigma_o / 1.06009$, i.e., 6.009% smaller in σ_o units than Fisher originally supposed. This equation for the critical temperature remains valid for the temperature-dependent σ_o as well. Our result, given in Eq. (15), agrees with Fisher estimate of $\sigma(T)$. Agreement between our result and $\sigma(T)|_{\mathrm{SMM}}$ occurs, if $\sigma_o = \sigma(T)|_{\mathrm{SMM}} + 1.06009\, T$.

Equation (14) also allows us to find the exact value of the degeneracy prefactor (0.3814), which was unknown in the FDM and its extensions.

For large but finite clusters, it is necessary to take into account not only the farthest-right singularity $\tilde{\lambda}_0 = R_0 / s_1$ in (10), but all other roots with positive real part $R_{n>0} > 0$. In this case for each $R_{n>0}$ there are two roots $\pm I_n$ of (12) because the GCSP is real by definition. The roots of Eqs. (11) and (12) with largest real part are insensitive to the large values of $K_{max}(S_A)$; therefore, it is sufficient to keep $K_{max}(S_A) \to \infty$. For the limit of vanishing amplitude of deformations, Eqs. (11) and (12) can be, respectively, rewritten as

$$\frac{2R_n}{R_n^2 + I_n^2} = e^{R_n} \cos(I_n) - 1, \qquad (16)$$

$$\frac{2I_n}{R_n^2 + I_n^2} = - e^{R_n} \sin(I_n). \qquad (17)$$

After some algebra the system of (16) and (17) can be reduced to a single equation for R_n

$$\cos\left[\left(\frac{4(1+R_n)}{e^{2R_n} - 1} - R_n^2 \right)^{1/2} \right] = \cosh R_n - \frac{\sinh R_n}{1 + R_n}, \qquad (18)$$

and the quadrature $I_n = \sqrt{4(1+R_n)/(e^{2R_n} - 1) - R_n^2}$. It can be shown that, besides the opposite signs, there are two branches of solutions, I_n^+ and I_n^-, for the same n value:

$$|I_{n\geqslant 1}^{\pm}| \approx 2\pi n \pm \frac{1}{\pi n}, \qquad (19)$$

$$R_{n\geqslant 1} \approx \pi^2 n^2 + 1 - \pi n \sqrt{\pi^2 n^2 + 2}. \qquad (20)$$

The exact solutions $(R_n; I_n^{\pm})$ for $n > 1$ which have the largest real part are shown in Fig. 1 together with the curve parametrized by functions I_x^+ and R_x taken from Eqs. (19) and (20), respectively. From Eq. (20) and Fig. 1, it is clear that the largest real part $R_1 \approx 0.0582$ is about 18 times smaller than R_0. Therefore, for a cluster of a few constituents, the correction to the leading term (14) is exponentially small. Using the approximations (19) and (20), for $n > 2$ one can estimate

$$\left| e^{\tilde{\lambda}_n S_A} \left[1 - \frac{\partial \mathcal{F}(S_A, \tilde{\lambda}_n)}{\partial \tilde{\lambda}_n} \right]^{-1} \right| \leqslant e^{S_A / 2\pi^2 n^2 s_1} / (2\pi^2 n^2), \qquad (21)$$

the upper limit of the $(R_n; I_n^{\pm})$ root contribution into the GCSP (10). This result shows that the total contribution of all complex poles in (10) is negligibly small compared to the leading term (14) for a cluster of a few constituents or more. The latter, however, requires a more careful accounting for the volume conservation of a cluster.

IV. POSSIBLE ORIGIN OF LOGARITHMIC CORRECTION

The model developed here allows us to give an upper limit for the surface entropy because it corresponds to the vanishing amplitude of deformations. As we showed, this

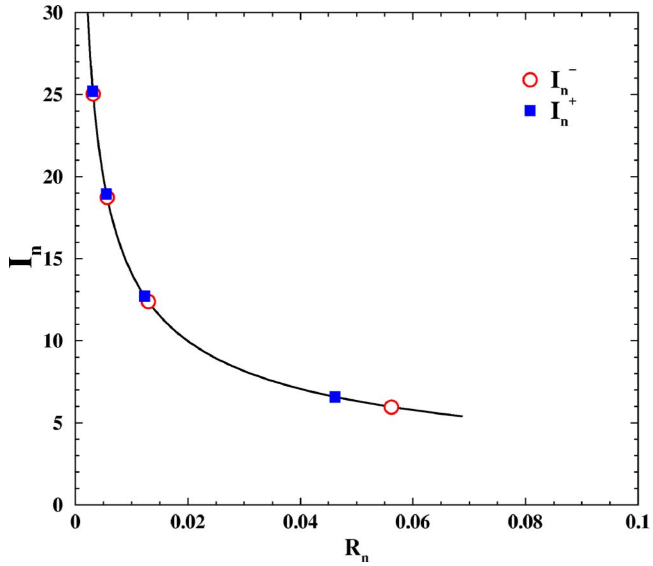

FIG. 1. (Color online) The first quadrant of the complex plane $s_1\tilde{\lambda}_n \equiv R_n + iI_n$ of the roots of the system of (16) and (17). The circles and squares represent the two branches I_n^- and I_n^+ of the roots, respectively. The curve is defined by the approximation given by (19) and (20) (see text for more details).

result is general and universal because in this limit the specific features of the model are irrelevant to our analysis. To find the next-order correction to the surface entropy one should consider the underlying model for deformations. We leave this for a later paper, but comment on how a power law may arise within the HDM.

Let us consider the left equality in Eq. (13), which is valid for small deformation heights. It can be shown that for $S_A \gg s_1$, the deformation energy

$$\frac{\sigma_o P_k H_k}{2s_1} \to -\frac{3}{2}Tk\frac{\tau}{\zeta}\frac{s_1}{S_A}\ln\left(\frac{s_1}{S_A}\right) \tag{22}$$

of a k-constituent base, indeed, generates the Fisher power law $A^{-\tau}$ for the GCSP (14) of an A-constituent cluster. Now one can see that besides the coefficient $3T\tau/(2\zeta)$ [where $\zeta^{-1} = 1 + 2/R_0(2+R_0) \approx (0.61\,861)^{-1}$], the term $-k(s_1/S_A)\ln(s_1/S_A)$ on the right-hand side of (22) is the entropy which gives an *a priori* uncertainty to measure the position of k constituents each of area s_1 on the surface of the cluster. A comparison of (22) with any $kR_n > 0$ in the left equality (13) shows that in the limit $S_A \gg s_1$, the ansatz (22) corresponds to a negligible correction compared to the exponentials $e^{R_n S_A/s_1}$. Therefore, the Fisher power law is too delicate for the present formulation of the surface partition model.

V. CONCLUSIONS

In conclusion, we developed a statistical model and derived analytically the general expression (10) for the GCSP for large clusters which are built up from any discrete constituents. This result is achieved by applying the Laplace-Fourier transformation technique to the isochoric ensemble, so named because the HDM conserves volume for the deformed cluster. The volume conservation is accounted for by the equal statistical probabilities for the hills and dales of the same base. The formalism is general and may be applied to surface deformations of any type of physical cluster, if the height and shape of deformations are known. In particular, the model allows one to consider complicated shapes of deformations, including fractals.

We analyzed the limit of vanishing deformations which allowed us to find a model-independent supremum for the surface entropy of large clusters. Remarkably, this supremum exceeds Fisher's estimate by about 6% in σ_o units. An exact value of the degeneracy prefactor of large clusters is found analytically. The analysis of the corrections to the GCSP (14) originating from the complex roots of Eqs. (11) and (12) showed that these corrections are negligible for clusters consisting of more than a few constituents. The HDM allows one to study the statistical mechanics of volume deformations of finite clusters, but this task requires further refinements of the model.

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