Phenomenological theory of the Potts model evaporation-condensation transition

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Abstract – We present a phenomenological theory describing the finite-size evaporation-condensation transition of the $q$-state Potts model in the microcanonical ensemble. Our arguments rely on the existence of an exponent $\sigma$, relating the surface and the volume of the condensed phase droplet. The evaporation-condensation transition temperature and energy converge to their infinite-size values with the same power, $a = (1 - \sigma)/(2 - \sigma)$, of the inverse of the system size. For the 2D Potts model we show, by means of efficient simulations up to $q = 24$ and $1024^2$ sites, that the exponent $\sigma$ is compatible with $1/4$, assuming asymptotic finite-size convergence. While this value cannot be addressed by the evaporation-condensation theory developed for the Ising model, it is obtained in the present scheme if $\sigma = 2/3$, in agreement with previous theoretical guesses. The connection with the phenomenon of metastability in the canonical ensemble is also discussed.

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Introduction. – The equilibrium and dynamics of phase coexistence in first-order phase transitions is a crucial and longstanding topic in statistical physics [1–3]. Since the eighties there has been a considerable interest in the so-called micro-ensemble, in which the extensive thermodynamic variable, the magnetization in the para/ferromagnetic transition, or the particle density in the vapor/liquid case, is fixed. While systems with short-range interactions present ensemble equivalence in the thermodynamic limit, at finite sizes they exhibit a variety of equilibrium phenomenology in the micromagnetic or microcanonical ensembles, absent in the magnetic or canonical ensembles, as negative specific heat and reappearance of the entropy-temperature curve. Of remarkable relevance is the evaporation-condensation (EC) transition [4–9], that we now illustrate in the microcanonical ensemble. Consider a system presenting a first-order transition, at fixed energy density $\epsilon$ in phase coexistence $\epsilon_o < \epsilon < \epsilon_d$ ($\epsilon_o$, $\epsilon_d$ being the low and high energies at the transition in the thermodynamic limit), whose thermodynamic potential is the entropy density $s$, satisfying $ds = \beta d\epsilon$ (see fig. 1). The situation is equivalent for magnets with the free energy, the magnetization $m$ and the magnetic field $h$, or for liquids with the free energy, the intensive volume, minus the pressure, playing the role of $s$, $\epsilon$ and $\beta$, respectively. In the thermodynamic limit the phase coexistence is given by the lever rule: for $\epsilon \lesssim \epsilon_d$, the minority (low-$s$) phase condenses in a connected droplet whose volume equals a fraction $(\epsilon_d - \epsilon)/(\epsilon_d - \epsilon_o)$ of the system volume. In the presence of the droplet, the energy of the (high-$s$) bulk surrounding it is larger than the global energy $\epsilon$, hence its formation increases the entropy. This effect, however, is attenuated for finite sizes for which the droplet/bulk interface energy is not negligible and lowers the bulk energy. Through considerations on the energetics of the droplet (originally in the $m(h)$ system [4]) it results that, given a system size $N$ there is an energy $\epsilon^*(N)$ above which there is no droplet but a supersaturated (homogeneous) phase called evaporated. Below $\epsilon^*(N)$, the condensed phase is characterized by the coexistence between the droplet and the supersaturated bulk. The EC transition is such that $\epsilon^*$ and $\beta^* = \beta(\epsilon^*, N)$ converge to the phase transition values $\epsilon_d$, $\beta_d$ for large sizes, recovering the Maxwell construction (see fig. 1). The convergence is characterized by exponents that we will
call $a$ and $b$:

$$\delta e^* \equiv c_d - c^* \sim N^{-a}, \quad \delta \beta^* \equiv \beta^* - \beta_4 \sim N^{-b}. \quad (1)$$

When expressed in terms of the size-rescaled control parameter, the EC transition can be considered as a first-order phase transition under some respects, such that the discontinuity is presented by the intensive parameter [8]. According to the Ising EC theory for the $\beta \leftrightarrow h$, $\epsilon \leftrightarrow m$ system, it is $a = b = 1/(d+1)$, in $d$ dimensions. Moreover, the emerging minority phase droplet at the EC transition is known to exhibit a universal fraction of the system volume.

After the seminal work [4], there has been a quite intense research activity concerned with the topic. The EC transition and its finite-size rounding have been rigorously characterized [5,6,8,10,11]. Numerical tests of the EC theory have been performed for different systems in two and three dimensions: the lattice gas at fixed temperature [6,7,12] and density [13,14]; the Ising model in the micromagnetic ensemble [10,15,16]; the Lennard-Jones gas at fixed temperature [17–19] and density [14]. The general outcome is that the theory provides an accurate description of the EC transition and its finite-size rounding in the Ising-liquid/vapor paradigm.

There has also been a variety of studies concerning the Potts model (PM) first-order transition in the microcanonical ensemble, although the situation in this case is much less clear. Differently from the Ising case, the transition is order/disorder, temperature (not field)-driven. In the nineties, the transition temperatures and interface tension [21,22] were analyzed in 2D with the Metropolis algorithm. Using multicanonical simulations, these quantities were also studied in 3D, up to linear sizes $L = 30$ and for $q$ up to 10 [23] and, for the first time, they estimated the “spinodal” interval $\delta \beta^*$, claimed to shrink as $N^{-1/4}$ compatible with $b = 1/(d+1)$. In 2007, an efficient cluster algorithm was developed and tested in 2D for $q = 10$ up to $L = 1024$ [24] (we analyze this data in the present work). Reference [25] focuses on the calculation of the interface free energy in the EC transition, and on the related exceptionally large finite-size effects. Finally, in refs. [26,27], the Wang–Landau algorithm was applied in 2D with $q = 8$ and 20, up to $L = 1024$ and 512, respectively. By scaling of the quantity $\delta \beta^*$ vs. $\delta e^*$, the validity of the Ising EC exponents $a = b = 1/3$ was proposed [26]. Moreover, the fraction of system volume occupied by the droplet at the transition was claimed to be $f = 2/3$, again in agreement with the Ising theory.

We will show, however, that both the outcome of novel simulations for a larger value of $q$, and the data of ref. [24], seem to be incompatible with the exponent $b = 1/3$. Motivated by such a controversy, we discuss a possible alternative to the Ising EC exponents for the 2D PM. We first expose simple arguments to describe the EC phenomenology in terms of Potts quantities and of an exponent $\sigma$ relating the droplet volume and its interface area. We claim how, in 2D, $\sigma$ may not assume its geometrical value, 1/2, but rather 2/3. Finally we analyze the numerical data and show how, up to the simulated sizes, it is compatible with $\sigma = 2/3$ and incompatible with $\sigma = 1/2$ and hence with the Ising EC scaling. The relationship of the EC phenomena with metastability in the canonical ensemble will be finally discussed.

**Model and notations.** We consider the $q$-color Potts model in a $d$-dimensional lattice with $N$ sites. It is defined by the Hamiltonian $H = \frac{1}{2} \sum_{\langle i,j \rangle} (1 - \delta_{c_i c_j})$, where the sum is over the bonds of the lattice, and the degree of freedom $\tau_i$ takes one out of $q$ values. The intensive entropy $s$, inverse temperature $\beta$, and the finite-size energy probability density (EPD) at the transition, $P_{\beta s}$, as functions of $\epsilon, N$, are related in the following way: $\ln P_{\beta s} = - \beta \epsilon + s \beta = \partial_s s$. For a sufficiently high value of $q > q_c(d)$, the transition is first order [28]; the quantities $P, s, \beta$ behave in the coexistence interval qualitatively as sketched in fig. 1. We will also consider the order and disorder entropies at the transition, $s_o, s_d = s(\epsilon, \epsilon_o, N)$. The quantities $\beta_o, c_d, c_o, \epsilon_o, s_o, s_d$ are $q, d$, and lattice dependent.

**Evaporation-condensation in the Potts model.** Our arguments are very similar to that describing the EC transition in the Ising/Lattice gas model, in the spirit of that of ref. [7]. We will focus on the disordered phase, $\epsilon \lesssim \epsilon_d$.

Our first working hypothesis is that the energy difference $\epsilon_d - \epsilon$ in the coexistence region can be split into two main contributions: one coming from a single, connected droplet of the ordered phase with energy $\epsilon_o$ and extensive
mass $\lambda N$, $\lambda \in [0 : 1]$; the second one comes from a disordered, supersaturated fraction of the system, the bulk, which surrounds the droplet. The equivalent assumption in the Ising case has been rigorously proven [5]. In the 2D Potts model case, the snapshots of the (thermalized) condensed phase configurations reveal the existence of a single connected droplet (as can also be seen in refs. [24, 26]), suggesting the validity of the hypothesis. Our second crucial hypothesis is that the average interface energy between the droplet and the disordered bulk, proportional to the droplet interface perimeter, is in its turn proportional to a power of the droplet volume fraction $\lambda N$, $\lambda$ being proportional to the droplet interface, the proportionality constant, and $\sigma$ being a $d$-dependent exponent, of possible non-geometrical nature [1, 29]:

$$\frac{d-1}{d} \leq \sigma < 1$$  \hspace{1cm} (2)

In this circumstance, the conservation of energy is expressed as

$$\epsilon = \lambda \epsilon_b + (1 - \lambda) \epsilon + \epsilon_{\text{int}},$$  \hspace{1cm} (3)

where $\epsilon_b$ is the energy of the disordered bulk, depending on the droplet volume fraction $\lambda$, with $\epsilon \leq \epsilon_b \leq \epsilon_d$ (the bulk energy decrement is due to the increase of the correlation length with respect to that at $\epsilon_d$). Due to the presence of the droplet, the bulk energy $\epsilon_b$ is larger than the global energy $\epsilon$; such an energy excess decreases with decreasing size, when the relative contribution of the interface perimeter increases.

The total entropy presents contributions from the droplet, bulk and droplet surface, $S_\lambda(\epsilon) = S_{\text{int}} + S_{\text{ba}} + S_{\text{sur}}$. The droplet entropy is simply $S_{\text{int}} = \lambda N s_\lambda$. The surface entropy is proportional to the droplet perimeter (the contour entropy $s_\lambda$ being the proportionality constant), with a logarithmic correction that we neglect [30–32], hence $S_{\text{sur}} = s_\lambda (\lambda N)^\sigma$. The bulk entropy takes the form $S_{\text{ba}} = N \{ s_d(1 - \lambda) + \beta d (\beta - \beta_d^2)/(2c_d \Delta)^2 \}$, with $\zeta = (1 - \lambda) (\epsilon_b - \epsilon_d)$. It is obtained by expanding up to second order in $\epsilon_d - \epsilon$ around the disordered state at $s_0$, where $c_d$ is the specific heat at the transition $c_d = -\beta \beta_d^2 / \partial^2 s_d / \partial \epsilon^2$. Finally, using $s_d = -\Delta d_\lambda$, where $\Delta = \epsilon_d - \epsilon$ and, eq. (3), the total $\lambda$-dependent intensive entropy reads:

$$s_\lambda(\epsilon) = s_d - \beta_d \epsilon + C \lambda^\sigma N^{\sigma - 1} - \frac{1}{2} \frac{\beta_d^2}{c_d} \Delta^2 \left[ \lambda - \epsilon_d / \Delta - \frac{w}{\Delta} \lambda^\sigma N^{\sigma - 1} \right]^2,$$  \hspace{1cm} (4)

with $C \equiv s_\lambda - \beta_d w$.

We will call $\lambda_m(\epsilon, N)$ the value maximising $s_\lambda$, such that $s_{\lambda m}$ and $P_{\lambda m}$ become the thermodynamic functions, $s$ and $P$. $\lambda_m$ is expected to be a solution of $\partial_\lambda s_\lambda(\epsilon, N) = 0$ in the condensed phase for $\epsilon$ below a threshold $\epsilon^*(N)$, and $\lambda_m = 0$ in the evaporated phase for $\epsilon > \epsilon^*(N)$, where no real solution of $\partial_\lambda s_\lambda = 0$ exists [7].

**Thermodynamic limit.** Maximizing $s_\lambda$ in eq. (4) with $N = \infty$, one gets $s(\epsilon) = s_d - \beta_d (\epsilon - \epsilon_d)$, i.e., the Maxwell construction, required by van Hove’s theorem. The maximizing $\lambda$ corresponds to the lever rule expected in the thermodynamic limit: $\lambda_m = (\epsilon_d - \epsilon) / \Delta$.

**Finite sizes.** When the system size $N$ is finite, the entropy gets maximized creating a droplet of size smaller than $(\epsilon_d - \epsilon) / \Delta$ due to the $N^{\sigma - 1}$ term in the square bracket in (4), and to a further penalization for large $\lambda$'s in the $\lambda^\sigma$ term (since $C < 0$, as we will see). Looking for the solution of $\partial_\lambda s = 0 $ one obtains, to second order in $N^{\sigma - 1}$, the equation:

$$\lambda - x + n \lambda^{\sigma - 1} [\sigma \gamma x - D] - \lambda^{\sigma - 1} \gamma n(1 + \sigma) = 0,$$  \hspace{1cm} (5)

where we have defined shortcuts for our variables, $\gamma = w/\Delta$, $D = |C| s_d / (\beta_d^3 \Delta^2)$, and:

$$x = \frac{\epsilon_d - \epsilon}{\Delta}, \hspace{1cm} n = N^{\sigma - 1}.$$  \hspace{1cm} (6)

At fixed $x$, there is a value of $n$ (a sufficiently small value of $N$) above which there is no real solution; in other words, for $x < x^*(n)$ (the evaporated phase), $\lambda_m = 0$. Conversely, for $x > x^*(n)$ (the condensed phase), $\lambda_m \sim x$ is a solution of (5). The reduced EC transition energy $x^*$ vanishes for vanishing $n$, reflecting the absence of evaporated phase for $N \rightarrow \infty$. From now on, we will refer to $\lambda_m$ and to $x^*$ and $\lambda^*$ as functions of the reduced energy and size variables, $(x, n)$.

In the evaporated phase with $\lambda = 0$, there is no macroscopic droplet and the EPD is entirely composed by Gaussian thermal fluctuations. In the condensed phase for $x > x^*$ one has $\lambda_m \sim r_{n, x} x$, being $r_{n, x} < 1$ a function of $n, x$ approaching one for large $x$ or low $n$; the EPD presents in this regime a stretched exponential extra term which dominates for large $N$. From eq. (4):

$$\frac{\ln P_{\beta \lambda}}{N} \sim \begin{cases} -\beta \beta_d^2 \Delta^2 x^2 / (2c_d \Delta) & x < x^*(n) \text{ (ev.)} \\ -|C| (r_{n, x} x) \sigma n & x > x^*(n) \text{ (co.)} \end{cases},$$  \hspace{1cm} (7)

An estimation of the $N$-dependence of the reduced EC transition energy $x^*$ is obtained equating $\ln P$ in both regimes and, neglecting terms of $O[N^{2 \sigma - 2}]$, one gets $x^* \sim N^{-1/\sigma}$ (the proportionality constant includes $-C^{-1}$, so that it must be $C < 0$ for a solution to exist), which gives the exponent $a$ in eq. (1). $b$ is obtained inserting $x^*$ in the expression of $\beta_\lambda$ (derivating $\ln P(\beta_\lambda, \lambda_m)$ with respect to $\epsilon$). In substantially,

$$a = b = \frac{1 - \sigma}{2 - \sigma},$$  \hspace{1cm} (8)
or \( a = b = 1/3 \) for \( \sigma = 1/2 \) and \( a = b = 1/4 \) for \( \sigma = 2/3 \), which is our main prediction. Taking the geometrical value, \( \sigma = (d-1)/d \), one recovers the standard Ising EC exponents \( a = b = 1/(d+1) \). There is, indeed, essentially the same nucleation-like competition in both cases, between (higher) bulk fluctuations, and (lower) bulk fluctuations plus droplet fluctuations [7].

**Analysis of the solution in two dimensions.**

**The value of the exponent \( \sigma \).** Reference [29] presents an effective droplet (Fisher) series for the 2D PM disordered phase. The results suggest that the exponent \( \sigma \) could be different from its geometrical value, at least in two dimensions. In the series, the free energy of clusters of area \( \ell \) is assumed to be proportional to \( \omega^{\sigma \ell^d} \), with \( \sigma_3 = 2/3 \), and \( \omega \) being an effective surface tension. The value of \( \sigma_3 \) is obtained requiring the matching with exact results on the free energy cumulants for \( q_4 = 4 \), or fitting it from the numerical free energy cumulants for high \( q \), and the resulting Fisher series accurately describes the energy histograms at \( \beta_0 \) (see [33–35]). The success of the hypothesis \( \sigma_3 = 2/3 \) motivates the study of the case \( \sigma = 2/3 \) in the present formalism. A posteriori, considering the \( \sigma = 2/3 \) case is justified by our numerical results for \( \delta \beta^* \) and those of refs. [24,36], as we explain in the next section. Droplets in the Ising model at low temperatures are compact since their free energy is minimized by minimizing the droplet/bulk interface perimeter. In the Potts model, droplets of the ordered phase at fixed energy, i.e., at fixed perimeter interface, are those maximizing the entropy. It is known that the average area of self-avoiding lattice polygons and loops with perimeter \( p \) is \( A \sim p^{3/2} \) [37,38]. If also the most probable two-dimensional lattice polygon with fixed perimeter \( p \) exhibited an area proportional to \( p^{3/2} \), this would provide a hint for a microscopic explanation of the emergence of \( \sigma = 2/3 \).

**The EC transition for \( \sigma = 1/2 \) and \( \sigma = 2/3 \).** For \( \sigma = 1/2 \), eq. (5) becomes a third-order equation in terms of \( \mu = \lambda^{1/3} \). There is no real solution for \( x < x^*(n) = 3(Dn/2)^{2/3} + O[n] \), and \( x^*(n) = (Dn/2)^{2/3} + O[n^{1/3}] \), hence \( a = b = 1/3 \), as we anticipated. In the whole evaporated region for small enough \( n \), the scaling \( \tilde{\lambda}(\tilde{x}) = \lim_{n \to 0} \lambda_m(x,n)/x^*(n) \) holds, in terms of the scaling variable \( \tilde{x} = x/x^*(n) \). Moreover, the condensed phase fraction \( \lambda^*(n)/x^*(n) \) converges as \( n \to 0 \) to \( f_{\sigma=1/2} = \lambda(1) = 1/3 \).

In the \( \sigma = 2/3 \) case, the solution \( \lambda_m \) qualitatively identical to that of the \( \sigma = 1/2 \) case except by the values \( a = b = 1/4 \), as anticipated, and by \( f_{2/3} = 1/4 \). Equation (5) takes the form of a fourth-order equation in \( \mu = \lambda^{1/3} \). Numerically finding the solution of \( \text{Im}[\lambda(n)] = 0 \), one finds \( x^*(n) \sim k(nD)^{2/3} + O[n] \), with \( k \approx 1.7547 \ldots \). The discontinuity of the droplet volume fraction turns out to be \( f_{2/3} = 1/4 \) (see the scaling function \( \tilde{\lambda}(\tilde{x}) \) in fig. 2).

We note that both \( f_{1/2} \) and \( f_{2/3} \) are different from the value of the equivalent quantity in the Ising case, \( 2/(d+1) \).

**Comparison with numerical data in the microcanonical ensemble.** We have simulated the 2D PM in the microcanonical ensemble with the algorithm presented in ref. [24] (a Monte Carlo cluster algorithm based on the Fortuin-Kasteleyn representation, with Metropolis acceptance probability), for systems with \( q = 4 \), and up to \( L = 1024 \). The details of our numerical methods will be presented in [39]. We also analyze the data from ref. [24] for \( q = 10 \) up to \( L = 1024 \). For \( q = 10,12 \) we have detected the position of the EC transition point \( (\epsilon^*(N),\beta^*(N)) \) as the maximum of a c-spline fitting the data. For \( q = 24 \), for which the EC transition becomes sharp, with the prominence of strong metastable phenomena, we have estimated the lower (upper) bound for \( \epsilon^* \) as the highest (lowest) \( \epsilon \) at which one observes the condensed (evaporated) phase in a simulated annealing decreasing (increasing) \( \epsilon \), and \( \beta^*(N) \) as the \( \beta(\epsilon \downarrow \epsilon^*(N),N) \) value in the evaporated phase. Plotting the quantity \( N^2 \delta \beta^* \) vs. \( N \), we observe (see fig. 3) that it stays constant for the three largest sizes for \( b = 1/4 \), while it systematically increases with \( N \) for \( b = 1/3 \). The behavior for \( q = 12 \) is qualitatively identical [39], and also that of ref. [26] for \( q = 20 \) [40]. Up to the sizes at hand, and assuming that the finite-size asymptotic convergence has been achieved for the largest ones, the data for \( \delta \beta^* \) exclude the value \( b = 1/3 \), and are compatible with \( b = 1/4 \). The quantity \( \delta N \) reveals more ambiguous results, yet a slight preference for \( a = 1/4 \) is observed [39]. More precise estimations are needed to safely estimate the value of \( b \) from the data, and to verify their asymptotic convergence in \( N \).
We have also analyzed the statistics of Fortuin-Kasteleyn cluster areas and perimeters in the condensed phase, where the last quantity is defined as the Potts interface energy of each Wolff cluster [41] (both quantities are naturally accessed in the cluster algorithm). The area-perimeter dependence (shown in fig. 4 for \(q = 24\), \(L = 1024\)) provides a more direct indication that the value \(\sigma = 1024\) is suited for an effective description, while \(\sigma = 1/2\) is not. This point deserves a systematic analysis, that will be presented in a forthcoming communication.

Evaporated vs. metastable. The equilibrium curve \(\beta(\epsilon)\) in the evaporated phase (illustrated in fig. 1) resembles the metastable continuation in the canonical ensemble. Nevertheless, they are, in general, different (as in the Ising model \(h\)-driven transition, whose metastable spinodal point does not vanish for large sizes [42,43]).

In the 2D Potts model, metastable states at \(\beta > \beta_\text{d}\) can be obtained from a reweighting of the disordered state at \(\beta_\text{d}\) [44]. The metastable state (for \(\beta_\text{d} \leq \beta \leq \beta^*\)) is, hence, determined by the finite-size potential, \(s(\epsilon, N)\), which fully characterizes also the evaporated phase. We consequently argue that, in this case, the thermodynamic quantities in the evaporated (microcanonical) phase and in the metastable (canonical) state coincide. Exploiting such an equivalence, one can estimate the point \((\epsilon^*, \beta^*)\) in the metastable state, if one has a method to systematically exclude out-of-equilibrium phenomena (the dynamics of the nucleating droplets), as in ref. [44]. We anticipate that, indeed, the data for \(\delta \beta^*\) computed with the present method coincides with that of ref. [44] for \(q = 12\) [39].

Conclusions and perspectives. We have presented a phenomenological theory describing the EC transition of the 2D PM. In the presence of minority phase droplets with fractal interface \((\sigma = 2/3)\), the EC phenomenon results to be different from that of the known Ising paradigm. The value \(\sigma = 2/3\), suggested by ref. [29], implies, according to the phenomenological theory, an exponent \(b = 1/4\), supported by \(\beta(\epsilon)\) data for the 2D PM up to \(q = 24, L = 1024\), that we have obtained with the help of a cluster algorithm, although the numerical evidences are still not conclusive about the precise value of \(b\). Moreover, preliminary measurements of the area/perimeter dependence of droplets suggest, again, \(\sigma = 2/3\). We propose to improve the estimation of \(b\) through a sampling of the EC transition at fixed energy, and for several values of a suitable order parameter driving the transition, fixed with the help of the Tethered Monte Carlo algorithm [39,45].

We propose some further perspectives for future work. First, a quantitative numerical test of eq. (7): in 2D the relevant quantities \(\beta_\text{d}, \Delta, \epsilon_\text{d}\) are known [28], and \(s_\epsilon, w\) could be estimated from geometrical measures of self-avoiding random walks, from measures of the cluster size distribution, or related with the known interface tension of the 2D PM. A numerical estimation of \(\lambda^*/\lambda^*\), to discriminate between the values \((1/3, 1/4, 2/3)\) (see [26]). A different challenge could be that of clarifying the nature of the 3D system [23]. It may be interesting to investigate the relevance of the phenomenon of interfacial adsorption [46] in this context, perhaps in the Hamiltonian limit for large \(q\) [46]. A final controversy: we suggest that the thermodynamic metastable spinodal [36] can be identified with the EC transition; this would contradict the results based on the pseudo-critical divergence [47–49], indicating that the spinodal does not vanish for large system sizes. A fundamental question, already put forward in ref. [27], is under what general conditions the metastable behavior of a system and its evaporated phase in the micro-ensemble coincide. In this work we have proposed (as suggested in [27]) that both coincide in the case of the Potts model.

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