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The impact of conformational fluctuations on self-assembly: Cooperative aggregation of archaeal chaperonin proteins

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Abstract

Protein complexes called rosettasomes self-assemble in solution to form large-scale filamentous and planar structures. The relative abundance of these aggregates varies abruptly with environmental conditions and sample composition. Our simulations of a model of patchy nanoparticles can reproduce this sharp crossover, but only if particles are allowed to switch between two internal states favoring different geometries of local binding. These results demonstrate how local conformational adaptivity can fundamentally influence the cooperativity of pattern-forming dynamics.

Group II chaperonin complexes from the hyperthermophilic archaeon *Sulfolobus*, called rosettasomes, spontaneously assemble *in vitro* into micron-scale structures [1,2]. Two remarkably different architectures can result from this process: bundles of filamentous chains of roughly spherical rosettasome units bound pole-to-pole, and stacks of hexagonally-packed sheets of units bound equator-to-equator. Such materials separately display great promise for nanotechnology. Sheets and strings of mutant chaperonins have been used to build ordered 2d arrays of quantum dots [2] and metallized conducting nanowires [3]. Filaments may also fulfill a biological role as components of the archaeal cytoskeleton [4]. The dual nature of rosettasome assembly offers further promise for materials science: the prospect of switching between the assembly of different structures by controlling only environmental conditions is very attractive. Conceptually, dual assembly poses new questions regarding the statistical dynamics of organized growth: How do multiple modes of assembly cooperate or interfere? Are hybrid structures an unavoidable endpoint when forces favoring different structural motifs combine?

Emulating the complex self-assembly properties of rosettasomes with synthetic particles requires interactions of a ‘patchy’ nature. It may seem sufficient to situate a strongly sticky region at each particle’s equator, and a distinct kind of stickiness at its poles. Several computer simulation studies [5-15] and a few ambitious experiments have adopted an analogous perspective, attempting to design specific aggregate geometries through anisotropy of microscopic forces. However, component design based solely on structural considerations rarely results in successful assembly. The picture emerging from these studies is one of intense

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competition between thermodynamics and kinetics: even for simple patchy nanoparticles, stochastic growth dynamics and the difficulties of defect annealing condition successful assembly on the fine-tuning of nanoparticle attraction strengths and binding geometry specificities.

In this paper we use theoretical models based on these physical perspectives to explain the dual nature of rosettasome assembly. We draw attention to a striking qualitative observation from experiments, which suggests rosettasome aggregation to be a binary rather than a hybrid process: structures intermediate in character between bundled strings and few-layered sheets are not seen in micrographs. Together with the observation that planar and filamentous structures sometimes appear in the same sample, this fact suggests a precipitous transition in aggregate geometry, from string-like to sheet-like, as control parameters (temperature, concentration, protein amino acid sequence, etc.) are changed. By contrast, our simulations of collections of patchy nanoparticles give rise to products that display a gradual transformation with model parameters from string-like to sheet-like character. We resolve this discrepancy by considering in addition a conformational flexibility of assembling units. The kinetic effects of this simple local detail are global in both space and time. Although our examination of this cooperative dynamical phenomenon is inspired by the behavior of a specific protein complex, its implications are quite general: endowing nanoscopic self-assembling components with a simple degree of conformational flexibility permits modes of assembly unattainable to components of fixed conformation [16].

The precise interactions between two rosettasome units, each comprising about 10^5 atoms, are enormously complicated. Detailed molecular dynamics simulations might accurately reproduce these solvent-mediated forces, but such an approach could scarcely be applied over time scales of milliseconds or longer that give rise to the higher-order structures considered here. Therefore, we treat free energies of interaction in a schematic way, considering for each pair of units only the dependence on a handful of geometric parameters, as sketched in Fig. 1. Our effective potentials are constructed with attention to a few key physical facts and ideas: each unit excludes a roughly spherical volume of radius $a = 8.5$ nm; attractive interactions extend over distances small compared to a and vary weakly with rotation of a unit about its axis [23]; and potentials of mean force stabilize bindings pole-to-pole and equator-to-equator, as indicated by high-resolution microscopy [1].

In detail, our model consists of N non-overlapping spheres of radius a , each representing a single rosettasome unit. The attraction u_{pair} between units i and j possesses polar and equatorial contributions, both depending on the inter-unit separation vector $\mathbf{r}_{ij}$ and unit orientation vectors $\hat{\mathbf{n}}_i$ and $\hat{\mathbf{n}}_j$:

$$u_{\text{pair}}(\mathbf{r}_{ij}, \hat{\mathbf{n}}_i, \hat{\mathbf{n}}_j) = -\epsilon_{\text{eq}} v_{\text{eq}}(\mathbf{r}_{ij}, \hat{\mathbf{n}}_i, \hat{\mathbf{n}}_j) - \epsilon_{\text{pol}} v_{\text{pol}}(\mathbf{r}_{ij}, \hat{\mathbf{n}}_i, \hat{\mathbf{n}}_j). \quad (1)$$

The strengths ϵ_{pol} and ϵ_{eq} of these two interactions, relative to that of typical thermal excitations $k_{\text{B}}T$, constitute the most important control parameters of our study. In simulations that permit units to change conformation, these parameters become in effect fluctuating variables.

The short range of rosettasomes' interactions relative to their size motivates our simplified choice of the potential's distance dependence: the model functions v_{pol} and v_{eq} vanish for separations greater than $2a + a/4$, yielding an attraction range $a/4 \approx 2$ nm consistent with Debye

screening at experimental ionic strengths. Below this cutoff distance these functions vary only with particle orientations, and do so according to the equations

$$v_{\text{eq}} = \widehat{C}_1(\phi_{ij}; \sigma_{\text{align}}) C_0(\theta_i; \sigma_{\text{eq}}) C_0(\theta_j; \sigma_{\text{eq}}); \quad (2)$$

$$v_{\text{pol}} = \widehat{C}_1(\phi_{ij}; \sigma_{\text{align}}) \widehat{C}_1(\theta_i; \sigma_{\text{pol}}) \widehat{C}_1(\theta_j; \sigma_{\text{pol}}). \quad (3)$$

Equations (2) and (3) describe in mathematical terms the patchiness sketched in Fig. 1. The effective size of polar and equatorial patches is determined by inverse specificities σ_{align} , σ_{eq} and σ_{pol} ; these parameterize a function $C_\alpha(\psi; \sigma) \equiv e^{-(\cos \psi - \alpha)^2 / \sigma^2}$ that rewards the alignment of angles ψ and $\cos^{-1} \alpha$ within a tolerance σ . The function $\widehat{C}_\alpha(\psi; \sigma) \equiv C_\alpha(\psi; \sigma) + C_{-\alpha}(\psi; \sigma)$ is made symmetric to preserve the up-down equivalence of rosettosome units suggested by crystal structures of homologous proteins. We set $\sigma_{\text{align}} = \sigma_{\text{eq}} = 0.3$ and $\sigma_{\text{p}} = 0.12$ (see Supporting Information for a discussion of model parameters).

We report below on long trajectories of this model system, corresponding to roughly tens of milliseconds of evolution for an experimental system. Dynamics were propagated using a virtual-move Monte Carlo procedure [11] designed to mimic the aggregation kinetics of strongly associating nanoparticles [24]. We initiated each simulation by selecting particle orientations and positions at random (while respecting steric constraints) within a cubic box of length L . Periodic boundary conditions were imposed in imitation of bulk surroundings.

We have explored the assembly dynamics of units with fixed conformation as a function of ϵ_{eq} and ϵ_{pol} . For many sets of values for these parameters, we ran trajectories of $N = 800$ units in a box of length $60a$. Units therefore occupied 1.5% of the box volume, corresponding to a protein concentration of 10.9 mg/ml, typical of experimental samples (1–20 mg/ml). Results of these numerous trajectories are summarized by the kinetic phase diagram in Fig. 2, which reports on both the occurrence of assembly (judged by the presence of clusters comprising 20 or more units [25]) and on resulting geometries.

We define an order parameter

$$S \equiv \frac{1}{6}(6 - n_{\text{eq}}) - \frac{1}{2}(2 - n_{\text{pol}}) \quad (4)$$

to quantify the morphology of each aggregate. For a given cluster above the cutoff size of 20 units, n_{eq} estimates the number of equatorial neighbors per particle (computed by summing v_{eq} over all interacting pairs and dividing by the number of particles); n_{pol} is calculated in an analogous manner. S takes the value +1 for an infinitely long filament, $S = -1$ for an infinitely extended close-packed sheet, and intermediate values for structures of finite size and for geometric character intermediate between sheets and strings. Any aggregate having $S > 1/4$ is identified as a ‘string’, while any aggregate for which $S < -1/4$ is classed as a ‘sheet’. We consider aggregates satisfying $-1/4 \leq S \leq 1/4$ to be of ambiguous character.

Kinetic accessibility is a crucial issue in the assembly of sheet-like structures. Although sheets are thermodynamically stable under many of the conditions we have considered, the range of ϵ_{eq} in which planar aggregates grow in an ordered fashion is small (see Supporting Information). The region $\epsilon_{\text{eq}} \geq 7k_{\text{B}}T$ is dominated by kinetic frustration, while the region

$\epsilon_{\text{eq}} = 6k_{\text{B}}T$, from $\epsilon_{\text{pol}} = 0$ to $\epsilon_{\text{pol}} = 4k_{\text{B}}T$ is supercooled: sheets are thermodynamically stable but nucleate too slowly to appear in the simulation times considered.

The kinetic phase diagram and illustrated configurations indicate a propensity for hybrid assembly when both equatorial and polar attractions are appreciable. Under no conditions do structures of distinct geometry coexist at the same thermodynamic state. Instead, we observe a continuous variation with model parameters from sheet- to string-like assembly. At some values of $(\epsilon_{\text{eq}}, \epsilon_{\text{pol}})$, the two modes of assembly clearly hinder one another, either by sequestering material or by leading the ordered growth of nascent clusters astray. At other parameter values these modes cooperate, generating well-ordered hybrid structures that interpolate smoothly between layered sheets and bundled strings.

This smooth evolution is expressly *not* what is observed in experiments. Instead, laboratory measurements suggest a very sharp crossover from sheets to strings with changing environmental conditions. The absence of an intermediate regime of hybrid assembly is highlighted by the observation of behavior akin to phase coexistence. TEM images in Figure 3 demonstrate the simultaneous occurrence of sheets and strings. The discrepancy with simulation results is striking. Accord between experiments and our patchy nanoparticle model is unlikely to be achieved by revising our choices of interaction strengths and specificities: we have performed many additional simulations in which we varied component concentrations, system sizes, binding tolerances and energy scales, and failed to observe sheet-string coexistence in all cases.

Why does the model we have presented fail to produce coexisting superstructure types? We cannot rule out the possibility that fine details of intermolecular forces are key to capturing this emergent behavior. We argue, however, that the qualitative contrast between binary assembly reminiscent of a phase transition and hybrid aggregation that varies smoothly with model parameters points to the neglect of a more fundamental feature. We propose that this missing ingredient is the conformational flexibility of each rosettasome unit.

Previous work has established as many as three different conformations for the *S. Shibatae* rosettasome [17,18]. Motivated by these studies and by our findings above, we have augmented our model of patchy nanoparticles by allowing each particle the freedom to change between two different conformations. One of these conformations is biased towards forming sheet-like geometries. When particles adopt this state, we refer to them as *planons*. Particles assuming the alternate conformation, which we dub *stringons*, have a preference for filamentous self-assembly. We will see that the ability of particles to fluctuate between these identities indeed greatly sharpens the transition between assembled structures and can effect coexistence of sheets and filaments.

These preferences conferred by internal degrees of freedom appear in our model through variations in binding energies. In all the calculations we will describe, the equatorial coupling strength ϵ_{eq} between two adjacent planons is set to $6.5 k_{\text{B}}T$, sufficient to ensure that a collection of particles constrained to their planon states can form large-scale ordered sheets. To ensure the possibility of filamentous growth we choose the strength ϵ_{pol} of polar interactions between two adjacent stringons to be $16 k_{\text{B}}T$ (these choices are discussed in detail in Supporting Information). We also assign *minor* couplings of varying strengths: these consist of polar interactions between planons; equatorial interactions between stringons; and inter-species interactions. These are summarised in Table 1.

In the course of model assembly dynamics we permit monomer conformations to fluctuate at random, subject to biases from interaction energies and from an intrinsic free energy difference between planon and stringon states. Each unit possesses an internal energy u_{internal} , which we

set to $-k_B T \ln \delta$ for stringons and 0 for planons. The parameter δ thus represents the ratio of stringons to planons in a sample of noninteracting rosettasome units. Just as internal states bias propensity for structure formation, however, so aggregation can bias conformational populations significantly away from ideal statistics.

Algorithmically, we attempted a change of each unit's conformation on average once every $M_{\text{change}} = 1000$ Monte Carlo sweeps, irrespective of that unit's position, orientation, or environment. By accepting such changes with probability

$$p_{\text{change}} = \min[1, \exp(-\beta \Delta E - \beta \Delta u_{\text{internal}})], \quad (5)$$

we established a basic rate $\omega_{\text{change}} = \omega_0(1+\delta)/M_{\text{change}} \approx 10^5 \text{ s}^{-1}$ for conformational fluctuations of isolated units that is consistent with estimates for similar large-scale rearrangements in related proteins [19] [26]. Here ω_0^{-1} is the duration of a single MC sweep (involving on average one proposed move per particle). Based on the diffusivity expected from Stokes Law for a sphere of radius 8.5 nm in liquid water, we estimate that $\omega_0 \approx 10^8 \text{ s}^{-1}$. In Eq. (5), ΔE and $\Delta u_{\text{internal}}$ are respectively the changes in interaction energy and internal energy resulting from a proposed conformation change. While the *attempt* rate for a unit's conformation change does not depend on that unit's environment, the *acceptance* rate for the change takes account of the energy of interaction between the unit and its neighbors, and so biases the conformation of an interacting unit with respect to that of its isolated counterpart.

We computed assembly trajectories for $N = 1500$ conformationally flexible particles in a box of length $64a$. By examining several values of δ and of the minor couplings, we varied the strength of interactions between planons and stringons, as well as the degree of distinction between them. Units' initial identities were randomly assigned as stringons with probability $\delta/(1 + \delta)$, or alternatively as planons with probability $1/(1 + \delta)$.

We focus first on the case of vanishing minor couplings. Here, stringons and planons are orientationally ambivalent toward one another, interacting only through sterics but intimately linked through interconversion. In Figure 4 we show a time-ordered series of snapshots taken from a single trajectory featuring this extreme example of conformational change. Allowing unit identities to fluctuate can indeed yield at late times a coexistence of structures possessing sheet- and string-like symmetry. Interestingly, in order to observe such coexistence we must bias the internal energy of units strongly in favor of planons; here $\delta = 0.05$, corresponding to an internal bias of $3k_B T$. The necessity for this imbalance originates in an unambiguous physical mechanism: As one-dimensional structures, strings lack a nucleation barrier and thus form much more rapidly than sheets, which must await the appearance of a critical nucleus. This observation recalls the rule of Stranski and Totomanow [20], who proposed that the crystal phase that forms most readily is the one confronted by the smallest free energy barrier to its nucleation. We have quantified the free energy barrier to sheet nucleation at various planon concentrations using umbrella sampling simulations (see Supporting Information). At the highest density, corresponding to the initial state of an assembly trajectory, this barrier is little larger than energies typical of thermal fluctuations, so that sheet initiation is only weakly impeded. However, string formation quickly sequesters units, in effect diluting the pool of monomers available for sheet formation. Our umbrella sampling results show that removing 60% of the available units raises $\Delta G^\ddagger$ by several $k_B T$, slowing nucleation more than 100-fold. This dynamic elevation of the nucleation barrier necessitates a large bias in internal energy in favor of planons (small δ) in order to obtain coexistence. These considerations underscore the fundamentally nonequilibrium nature of assembly within our model: when fully relaxed (at inaccessible long times), this system would possess almost no strings or stringons.

Equipping units with nonzero minor couplings introduces inter-species attractions, which, as one might expect, facilitate the formation of structures of a composite character, namely stacked sheets and bundled filaments. The minor couplings also control inter-species energetic interactions, which influence the ease of unit interconversion. We find that the kinetic bias toward string formation identified previously is qualitatively unchanged, but interactions between species modify quantitatively the rate at which structures of the two species proliferate (see Supporting Information). In Figure 5 we show qualitatively the effect of minor couplings by presenting snapshots from long trajectories generated using nine different sets of parameters (representing a variety of thermodynamic states in the real system). These states differ in the internal energies of conformational states (set by δ), and in their minor energetic couplings.

Cooperative binding as a mechanism for precipitous response is a textbook notion of biochemistry: interactions with one ligand heighten affinity for additional binding events, establishing positive feedback and enabling sharp switching behavior. Our results illustrate the dramatic *kinetic* implications of this kind of cooperativity. The molecular dynamics of self-assembly enriches traditional cooperativity scenarios in several interesting ways. The growth of extended structures, for example, introduces spatially heterogeneous effects of binding and leads to the emergence of ‘microphases’ of distinct response types. In addition, kinetic barriers to the formation of distinct structures can dramatically alter the threshold conditions at which switching occurs, imbuing the resulting behavior with a fundamentally nonequilibrium character. Further, cooperative binding can drive the formation of composite assemblies through fusion of well-defined superstructures (see Supporting Information).

In the context of rosettasome self-assembly our results support a picture in which internal conformational fluctuations bias superstructure nucleation, thereby inducing the simultaneous growth of structures with distinct symmetries. Rosettasome allostery is a known phenomenon, while superstructure coexistence is a striking feature of recent experiments involving the wild-type protein and its genetically-engineered variants. While the function of many proteins depends on self-organization at the nanometer scale, the emergence of long-range order with a *variable* outcome is exceptional. Such a capability might be of considerable use to a hyperthermophilic organism seeking to respond to extremes of heat by promoting, for instance, the rapid assembly of membrane-stabilizing scaffolding (biases for particular rosettasome conformations might be mediated by changes in their protein composition, known to vary in response to environmental cues [21]). From the perspective of nanoscience, mimicking such cooperativity offers a plausible route to adaptive assembly, whereby subtle changes in environment can engender a dramatic change in the assembly products of a system.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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23. Rosettasomes are 9-fold symmetric, but are observed to pack in hexagonal lattices incommensurate with such symmetry. We assume therefore that equatorial interactions vary weakly with longitude.
24. We drew translation magnitudes from a uniform distribution with maximum 0.5a, and drew rotation angles from a uniform distribution with maximum 22.5°. We scaled collective translation acceptance rates by the reciprocal of an approximate hydrodynamic radius of the moving cluster [11], and scaled acceptance rates for rotations by the cube of the same factor.
25. The ‘no assembly’ cutoff of size 20 means that we ignore assembly in regions of the phase diagram where short filaments form, but this neglect does not change in an important way the trends we identify.
26. The results we present are qualitatively unchanged by varying M_{change} from 1 to 1000. This robustness suggests that assembly behavior is not strongly sensitive to changes in the rate of conformational fluctuations, provided it outpaces the rate of basic structure formation.

FIG. 1. Geometry for our model of associating rosettasomes. Angular variables are related to orientation vectors by $\hat{\mathbf{n}}_i \cdot \hat{\mathbf{n}}_j = \cos \phi_{ij}$ and $\hat{\mathbf{n}}_i \cdot \frac{\vec{r}_{ij}}{|\vec{r}_{ij}|} = \cos \theta_i$.

FIG. 2.

Kinetic phase diagram for units of fixed conformation. We identify regions in which assembled structures are string-like, e.g. (a), sheet-like, e.g. (d), or of ambiguous character, e.g. (c). Kinetically-frustrated structures, e.g. (b), are found with increasing abundance as we increase the potency of the equatorial coupling.

FIG. 3.

TEM images taken from a single sample of self-assembling rosettasomes demonstrate the coexistence of superstructures with distinctly different architectures: (a) a close-packed sheet (spanning the whole image but partially obscured by overlay material) and (b) bundled strings. For Materials and Methods, see Supporting Information.

FIG. 4.

Time sequence of the assembly of conformation-changing units. Here, units of different types interact only through interconversion and sterics ($\epsilon_{\text{eq}}^{(\text{min})} = 0 = \epsilon_{\text{pol}}^{(\text{min})}$). The internal energy bias parameter is $\delta = 0.05$, so that isolated planons (blue) are strongly favored thermodynamically over stringons (yellow). However, string formation is facile, leading to an increase in the number of stringon units with time. Parameters are such that we observe coexistence between large-scale assembled structures of the two distinct symmetries. Time is measured in millions of Monte Carlo moves per particle.

FIG. 5.

Long-time conformations for self-assembly of conformation-changing units at nine different thermodynamic states. Columns contain states at fixed values of δ ; rows contain states at fixed values of the minor couplings. (a) Non-attracting species ($\epsilon_{\text{eq}}^{(\text{min})}=0=\epsilon_{\text{pol}}^{(\text{min})}$); (b) conditions under which planons have a tendency to stack ($\epsilon_{\text{eq}}^{(\text{min})}=0, \epsilon_{\text{pol}}^{(\text{min})}=3k_{\text{B}}T$) and (c) strongly-attracting species ($\epsilon_{\text{eq}}^{(\text{min})}=4k_{\text{B}}T, \epsilon_{\text{pol}}^{(\text{min})}=5k_{\text{B}}T$). Assemblies with hybrid character appear as minor couplings are increased, but the fundamental kinetic bias in favor of string formation remains.

TABLE I

Stringon and planon interaction strengths. We consider fixed major couplings and different sets of minor couplings. The specific case $\epsilon_{\text{eq}}^{(\text{min})} = \epsilon_{\text{pol}}^{(\text{min})} = 0$ corresponds to planons and stringons interacting only through hard core constraints. We have considered minor equatorial attractions as strong as $\epsilon_{\text{eq}}^{(\text{min})} = 4k_B T$ and minor polar attractions as strong as $5k_B T$. In the limit $\epsilon_{\text{pol}}^{(\text{min})} = 16k_B T, \epsilon_{\text{eq}}^{(\text{min})} = 6.5k_B T$ the distinction between planons and stringons vanishes.

interacting species	ϵ_{eq}	ϵ_{pol}
planon-planon	$6.5 k_B T$	$\epsilon_{\text{pol}}^{(\text{min})}$
stringon-planon	$\epsilon_{\text{eq}}^{(\text{min})}$	$\epsilon_{\text{pol}}^{(\text{min})}$
stringon-stringon	$\epsilon_{\text{eq}}^{(\text{min})}$	$16 k_B T$