Microscopically Resolved Simulations Prove the Existence of Soft Cluster Crystals

Dominic A. Lenz,[1] Ronald Blaak,[1] Christos N. Likos,[1] and Bianca M. Mladek[2]
[1]*Faculty of Physics, University of Vienna, Boltzmanngasse 5, A-1090 Vienna, Austria*
[2]*Department of Structural and Computational Biology, Max F. Perutz Laboratories GmbH, University of Vienna, Campus Vienna Biocenter 5, A-1030 Vienna, Austria*

(Received 26 July 2012; published 27 November 2012)

We perform extensive monomer-resolved computer simulations of suitably designed amphiphilic dendritic macromolecules over a broad range of densities, proving the existence and stability of cluster crystals formed in these systems, as predicted previously on the basis of effective pair potentials [B. M. Mladek *et al.*, Phys. Rev. Lett. **96**, 045701 (2006)]. Key properties of these crystals, such as the adjustment of their site occupancy with density and the possibility to heal defects by dendrimer migration, are confirmed on the monomer-resolved picture. At the same time, important differences from the predictions of the pair potential picture, stemming from steric crowding, arise as well, and they place an upper limit in the density for which such crystals can exist.

DOI: 10.1103/PhysRevLett.109.228301　PACS numbers: 82.70.−y, 64.70.D−, 82.30.Nr, 83.10.Tv

Soft cluster crystals (also termed bubble solids), i.e., solids where each lattice site is occupied by several, interpenetrating particles, arise in systems governed by generic, purely repulsive interactions which remain finite even if particles fully overlap [1–3]. The completely different character of these novel cluster crystals, as opposed to hard cluster phases [4,5], is testified by the fundamentally distinct nature of the interactions between their constituent particles. The clusters are not stabilized by a combination of short-range attractions and long-range repulsions, which result in well-defined aggregates in the liquid that disappear at high densities [4,5]. Rather, clustering is here a self-enhancing, cooperative phenomenon, where full overlaps with few particles are favored over costly partial overlaps with many neighbors. Thus, clusters remain stable due to their mutual repulsions with the surrounding ones [6]. Cluster crystals are thus high-density phases, in which fuzzy agglomerates, already formed in the liquid, freeze into well-defined and spatially ordered groups at higher concentrations [3]. Predicted for certain macromolecular [7–9] or atomic [10–13] systems, such clusters form exotic crystals that show mass transport [14,15], unusual reaction to compression [3,6,16] and shear [17], and rich phase behavior with a cascade of isostructural transitions [18,19]. Furthermore, they possess a unique rheological behavior, showing thixotropy and flow quantization [17].

All hitherto performed studies of the properties of soft cluster solids have been based on the assumption of ultrasoft, pairwise additive, density-independent interparticle interactions. According to theory, the necessary requirement for a system to display clustering behavior is that its pair interaction shows negative Fourier components [2,20]. The pair potential picture is realistic when understood as an effective representation of certain types of polymeric macromolecules in not too concentrated solutions [21–23]. However, the relevance of such an approach for experiments is here put into question, since the formation of clusters is a high-density phenomenon. Under such conditions, many-body effects, conformational deformations, and crowding are expected to play a crucial role, which could either hinder or favor cluster formation. For ring polymers, the zero-density pair interaction has negative Fourier components; however, due to the shrinkage of the rings at finite densities, the clustering ability is lost [8]. In this Letter, we show on a microscopic basis that soft cluster crystals can indeed be stabilized in a broad density regime for suitably designed macromolecular systems, motivating the experimental realization of such systems.

Amphiphilic dendrimers constitute such a system predicted to show clustering [7,9]. Here, we consider amphiphilic dendrimers of second generation with two central monomers. The dendrimers' 14 monomers are divided into two classes: The eight outermost monomers form a solvophilic shell which surrounds the solphophobic core build from the interior generations' monomers. At sufficiently close separations, all monomers strongly repel each other via Morse potentials, while bonds between monomers are modeled by finitely extensible nonlinear elastic springs [24]. In previous studies, the zero-density effective pair interaction between various realizations of such dendrimers has been determined [7], showing the desired negative Fourier components [25]. Indeed, we then found the onset of clustering in the fluid phase of microscopically resolved amphiphilic dendrimers [9]. Here we demonstrate the stability of the cluster solid phase (see the scheme in Fig. S1 of the Supplemental Material). Let $\rho = N/V$ be the density of a system of N dendrimers in the volume V and R_g be the $\rho = 0$ radius of gyration of such a dendrimer. An estimate, $\tilde{\rho}_f$, of the freezing density ρ_f can be obtained on the basis of the infinite dilution pair potential $\Phi_{\mathrm{eff}}(r)$ [20]. Furthermore, theory predicts the number of dendrimers per cluster, i.e., the occupancy $\tilde{N}_{\mathrm{occ}}$, to be proportional to the density: $\tilde{N}_{\rm occ} \propto \rho$ [2,3]. Consequently, the lattice constant $\tilde{a} \propto (\tilde{N}_{\rm occ}/\rho)^{1/3}$ is predicted to be density-independent. For the dendrimers considered here, lattice site occupancies of $\tilde{N}_{\rm occ} = 3.5$ (bcc) and $\tilde{N}_{\rm occ} = 3.2$ (fcc) are predicted at the freezing density $\tilde{\rho}_f R_g^3 = 0.281$. The lattice constants are predicted as $\tilde{a} = 2.9R_g$ (bcc) and $\tilde{a} = 3.6R_g$ (fcc), leading in both cases to nearest-neighbor distances $\tilde{d} = 2.5R_g$.

These theoretical predictions are put to the test by performing *NVT* Monte Carlo simulations. First, we delimit the range of values of $N_{\rm occ}$ that can stabilize crystals: Although in the effective description $N_{\rm occ}$ can be arbitrarily large, in the monomer-resolved description local steric crowding is anticipated to put an upper limit to this quantity. To this end, we simulate disordered systems of dendrimers in a density regime around $\tilde{\rho}_f$. We study the cluster size probability distribution $P(N_{\rm occ})$, employing a cluster algorithm developed previously [9]. Representative results are shown in Fig. 1 for three different densities. Figure 1(a) shows $P(N_{\rm occ})$ of a system at low density, $\rho R_g^3 = 0.046$, i.e., well below $\tilde{\rho}_f$. Some small clusters are present, but single dendrimers dominate: This system is a fluid of single dendrimers. Increasing the density to $\rho R_g^3 = 0.138$ [Fig. 1(b)] while still staying below $\tilde{\rho}_f$, we find that a distinctive distribution of larger clusters has also developed. The sizes of these clusters are not uniformly distributed; rather a single cluster size, $N_{\rm occ}^{\rm pref}$, is favored, in full agreement with theoretical predictions [20]. Here, the system forms a cluster fluid, as already studied in detail in previous work, albeit for a different dendrimer model only showing clustering at higher occupancies than the present model [9,26]. Finally, the density was increased above $\tilde{\rho}_f$ to the value $\rho R_g^3 = 0.323$ [Fig. 1(c)]. Now, single dendrimers have almost completely vanished from the solution and have been replaced by clusters of a preferred occupation of $N_{\rm occ}^{\rm pref} = 4$–$5$. Visual inspection reveals that this system has spontaneously developed local crystalline order, albeit forming a distorted crystal. This finding is corroborated by an analysis of the radial distribution function of the clusters' centers of mass, which has developed a pronounced first peak centered at a value close to the predicted $\tilde{a}$ and clearly separated from the second peak. System sizes, however, do not allow for a positive determination of a particular structure. Similar results were found for several other densities above $\tilde{\rho}_f$, proving that the cluster liquid is unstable in this density regime.

Spontaneous crystallization, however, does not provide information about which crystalline structure is the one of lowest free energy; crystallites formed could exhibit the structure with the lowest barrier separating it from the fluid state [27,28]. We therefore artificially prepared perfect bcc and fcc cluster crystals at various densities ρ, by placing $N_{\rm occ} \gtrsim N_{\rm occ}^{\rm pref}(\rho)$ dendrimers per perfect lattice site, and then delimited their range of mechanical stability by performing *NVT* and *NPT* Monte Carlo simulations. Nonstable crystals melted within a few simulation sweeps into diffusive fluids, as manifested by a steady increase of the dendrimers' mean-square displacement and an accompanying loss of the ordered structure. The mechanically stable systems, however, remained in the crystalline, clustered arrangement throughout the whole simulation runs. Figure 2(a) shows a typical simulation snapshot of a cluster crystal in the full-monomer representation of the dendrimers, where the clustering can be seen from the crowding of core monomers [black and blue (light gray)], which are surrounded by a cloud of shell monomers [red (dark gray); also cf. Fig. S1]. The clustering and the self-assembly of the clusters onto the lattice sites of a (fcc) crystal become even more evident when plotting just the dendrimers' centers of mass [Fig. 2(b)], denoted there by small spheres. The irregular shapes of the various clusters are a manifestation of the instantaneous fluctuations of

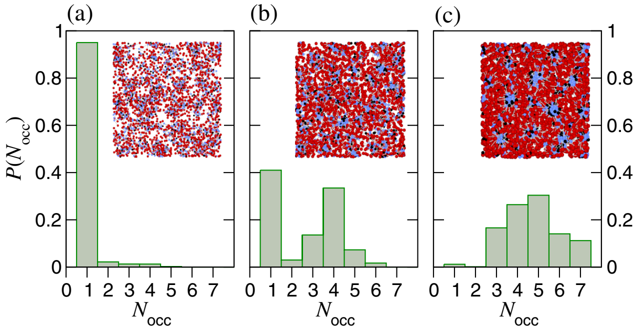

FIG. 1 (color online). The probability distribution $P(N_{\rm occ})$ to find cluster size $N_{\rm occ}$ in (a) the fluid state at $\rho R_g^3 = 0.046$; (b) the cluster fluid state at $\rho R_g^3 = 0.138$; and (c) the solid state at $\rho R_g^3 = 0.323$. The insets show simulation snapshots, where clustering can be seen from the crowding of the dendrimers' core monomers [black and blue (light gray)]. Shell monomers are shown in red (dark gray). Monomers are not drawn to scale.

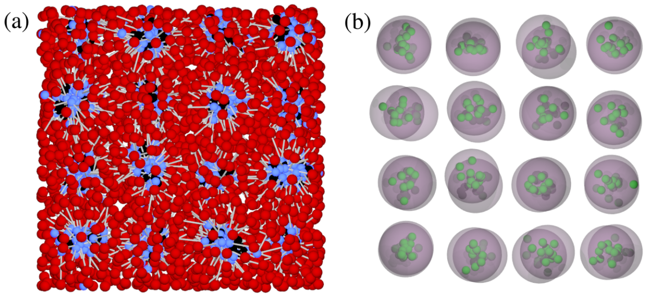

FIG. 2 (color online). Simulation snapshot of a fcc dendrimer cluster crystal of occupancy $N_{\rm occ} = 10$ at $\rho R_g^3 = 0.438$. (a) A full-monomer representation of the crystal. Clustering can be seen from the crowding of core monomers [black and blue (light gray)]. (b) The dendrimers' centers of mass (small spheres) are found to 99% in the big, gray spheres around the cluster's centers of mass.

each dendrimer around its lattice site and show that the centers of mass of the individual dendrimers are not tightly bound to lie on top of each other. These findings are in full agreement with the theoretical picture, which predicts these oscillations to give rise to intracluster breathing modes that manifest themselves as optical branches in the phonon spectrum of the crystal [18]. We quantify these fluctuations by plotting gray spheres, centered around the clusters' centers of mass, which contain the latter to a probability of 99%. Spheres from different lattice sites do not overlap, confirming the prediction that the clusters are well localized around their lattice sites [20].

The results of the simulations delimiting the range of mechanical stability are summarized in Fig. 3, revealing that a large, insular part of density-occupancy space allows for the formation of mechanically stable cluster solids. The minimum density to provide mechanical stability of the cluster crystals is found to be $\rho R_g^3 \cong 0.225$, independently of the occupation number. While the determination of the precise location of the freezing density ρ_f is not the subject of this Letter, these results demonstrate that $\rho_f \simeq \tilde{\rho}_f$.

As can be seen in Fig. 3, the minimum occupation number leading to mechanically stable solids increases linearly with density for both bcc and fcc. Systems with the lowest stable occupation $N_{\rm occ} \simeq 4$ showed single events of lattice site hopping and subsequent healing of the resulting defect. However, due to the limited time scales accessible in our simulations and the crowded systems studied, complex structural rearrangements and hopping events leading to long-time diffusion [14,15] have not been observed frequently. Crystals of high occupations $N_{\rm occ} \simeq 14$ further remained mechanically stable upon artificially introducing lattice defects like single clusters of lower occupancy, or even lattice vacancies or interstitials. Also mixed occupations, where not every lattice site was occupied by the same number of dendrimers, remained stable, provided the average value of $N_{\rm occ}$ was chosen from the island of stability (see Fig. 3), in full agreement with the theoretical prediction of cluster polydispersity in the crystal [14,20].

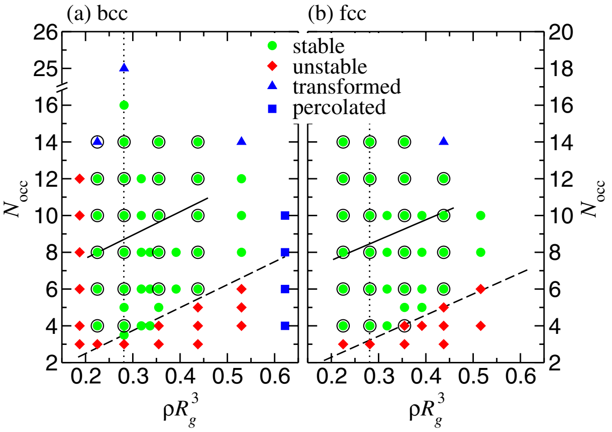

FIG. 3 (color online). The mechanical stability of dendrimer cluster crystals for (a) bcc and (b) fcc as a function of density ρR_g^3 and occupation number $N_{\rm occ}$. State points for which crystals remained stable are denoted by circles (closed circle); those where crystals melted as diamonds (closed diamond). The predicted freezing density $\tilde{\rho}_f$ is shown as a vertical, dotted line at $\rho R_g^3 = 0.281$. For high occupations and densities, systems transformed (closed triangle) or formed percolated networks (closed square) (see the text). Systems for which the free energy was measured are circled in black. The dashed line plots the theoretical prediction $\tilde{N}_{\rm occ}(\rho)$, while the equilibrium occupation $N_{\rm occ}^{\rm eq}(\rho)$ (see the text) is plotted as a solid line.

Crystals with even higher occupations, i.e., $N_{\rm occ} \gtrsim 16$, were not found to be stable: They transformed to distorted crystal structures of lower occupations by splitting clusters and halving the lattice constant, thereby taking these crystals back to the island of stability (Fig. 3, triangles). This shows the propensity of overoccupied crystals to adjust their occupancy towards an optimal value, a feature which will be confirmed quantitatively by free energy calculations in what follows. At high densities and rather low occupations, the lattice spacing accordingly shrinks and enters the length regime of the bonds between the dendrimers' monomers. Here, the crystalline arrangement of well-defined clusters also cannot be sustained: Dendrimers stretch and are shared between two clusters, leading to disordered percolated networks of dendrimers (Fig. 3, squares). This phenomenon reflects that at such high densities the effective pair potential picture, which predicts an unlimited growth of cluster occupancy with density, $N_{\rm occ} \propto \rho$, breaks down qualitatively, since steric crowding between the monomers prevents further cluster growth upon sufficient compression.

Having established the existence of a broad region of their mechanical stability, it is pertinent to assess the crystals' thermodynamic stability and their optimal occupation at given density. To this end, we calculated the excess free energy per particle $\beta f_{\rm ex} = \beta F_{\rm ex}/N$ for the mechanically stable crystals with the help of thermodynamic integration as outlined in Refs. [6,16]. Here, the reference state is chosen as noninteracting dendrimers confined to the desired crystal structure by potential wells. Being the same for all crystal structures, the reference free energy $\beta F_{\rm id}/N$ may be disregarded. Measuring $\beta f_{\rm ex}$ for several values of $N_{\rm occ}$ at given crystal structure and fixed density, we determine the equilibrium occupancy $N_{\rm occ}^{\rm eq}$ as the one that minimizes the free energy; see Fig. 4(a) [19]. In qualitative agreement with theoretical predictions, $N_{\rm occ}^{\rm eq}$ increases linearly with density [Fig. 4(b)]. However, there exist quantitative deviations between the two, manifesting the role of the many-body interactions. Whereas the pair-potential description predicts $N_{\rm occ} \propto \rho$, here there is a nonzero offset d: $N_{\rm occ} = c\rho + d$. At freezing, the optimal occupation number from the monomer-resolved simulations turns out to be higher than theoretically predicted. This indicates that the many-body interactions, whose importance grows with

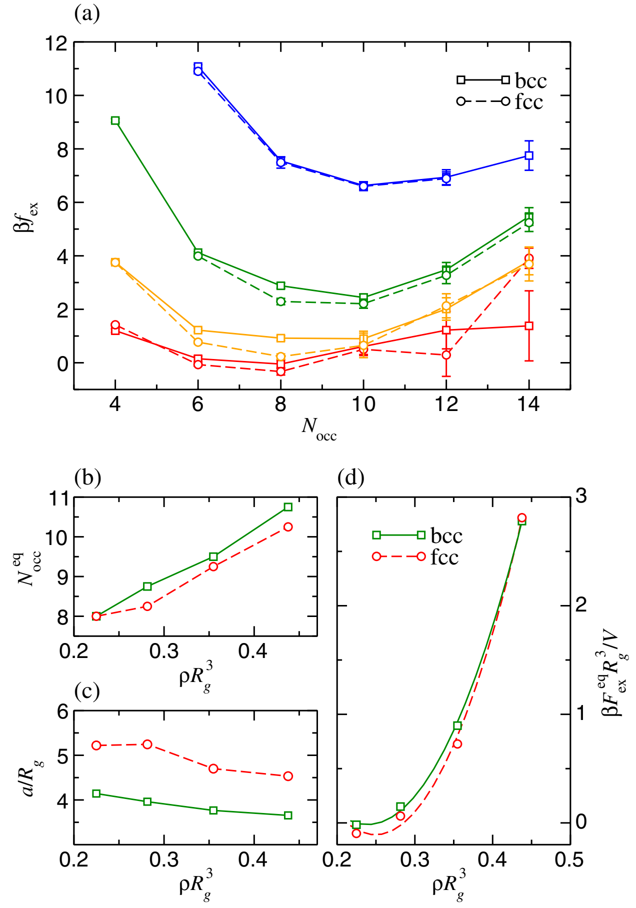

FIG. 4 (color online). All data are plotted for fcc (open circle) and bcc (open square) lattices. (a) The free energy per dendrimer, βf_{ex}, as a function of N_{occ} at different densities, from bottom to top: $\rho R_g^3 = 0.22$, 0.28, 0.36, and 0.44, showing for each density a different optimal occupancy $N_{\mathrm{occ}}^{\mathrm{eq}}$ that minimizes it. (b) The equilibrium occupancy $N_{\mathrm{occ}}^{\mathrm{eq}}$ as a function of density ρR_g^3. (c) The equilibrium lattice constant a/R_g shrinks with increasing density. (d) The equilibrium free energy per volume, $\beta F_{\mathrm{ex}} R_g^3/V$, as a function of the density ρ, evaluated at the equilibrium occupancy $N_{\mathrm{occ}}^{\mathrm{eq}}(\rho)$. Fcc is found to be the thermodynamically stable crystal.

occupancy, have the effect of strengthening the overall attractions between the soft particles at close approach. Since these properties are model-specific, we do not attempt a more detailed analysis here. However, we point out that the theoretical prediction of $\tilde{N}_{\mathrm{occ}}(\rho)$ is found to be an excellent estimate for the lower limit in occupancy of mechanically stable crystals (see Fig. 3). Indeed, these occupancies are sufficiently low for pair potentials to still be approximately valid, their degree of validity diminishing as N_{occ} grows. In Fig. 4(d), we show the free energy per volume of the equilibrium crystals as a function of density. We find that the fcc crystals have a slightly lower free energy than bcc for all densities considered.

In contrast to amphiphilic dendrimers, ring polymers cannot form cluster crystals due to their drastic shrinkage upon compression [8]. It is therefore pertinent to study the conformations of dendrimers in the clusters of the thermodynamically stable crystals. The radius of gyration of the dendrimers shows little variation with density, due to the necessary balance between the exterior and interior osmotic pressure of clusters and the constraints imposed by the regularly branched dendritic architecture. Nevertheless, the configurations of the dendrimers change considerably upon increasing density, a fact manifested by a density dependence of the most probable distance of shell monomers from their dendrimer's center of mass. While shell monomers can backfold to the dendrimer's core at low densities, the cluster formation at finite densities increasingly forces the shell monomers to move to the rim of the molecules [29].

Altogether, the cluster crystals discovered in our study are characterized by a hierarchy of self-organization at various interconnected levels. First, the individual dendrimers adjust their conformations to the thermodynamic conditions; second, the individual clusters adjust their population and are thus robust against cluster polydispersity and crystal defects; and finally at the macroscopic level, the flexibility of the cluster crystals is manifested through the mechanism of restructuring of nonoptimally occupied cluster crystals, the hopping of dendrimers among crystal sites, and the adjustment of the associated lattice constant. Discrepancies between the fully microscopic and the effective potential pictures exist due to the fact that the strong steric repulsions of the monomers prohibit the *ad libitum* growth of the clusters' population. Still, the salient features of soft cluster crystals have been confirmed. The range of stability of these structures is sufficiently broad to render them into materials of practical as well as fundamental importance.

In summary, we have shown at a microscopic level that cluster crystals exist in suitably synthesized soft matter systems. More detailed computational investigations in both the effective and the microscopical description will be needed to uncloak the whole beauty of these intriguing systems and understand, for example, the nucleation of soft cluster crystals or the transformations of dendrimer crystals at high occupations and densities; this will be the topic of future investigations. Our results convey the clear message that an experimental realization of cluster crystals employing simple and easy to synthesize dendritic macromolecules is possible. We thereby provide guidelines to achieve this goal, which will lead to the production of a new class of materials with most intriguing physical properties.

We thank Daan Frenkel (Cambridge) for helpful discussions. D. A. L. thanks the Wolfgang Pauli Institute. B. M. M. acknowledges the MFPL VIPS program (funded by BMWF and the City of Vienna) and EU funding (Grants No. FP7-PEOPLE CIG-2011 and No. 303860). Partial support by the ITN-COMPLOIDS (Grant Agreement No. 234810) and computer time at the Vienna Scientific Cluster are gratefully acknowledged.

[1] W. Klein, H. Gould, R. A. Ramos, I. Clejan, and A. I. Mel'cuk, Physica (Amsterdam) **205A**, 738 (1994).

[2] C. N. Likos, A. Lang, M. Watzlawek, and H. Löwen, Phys. Rev. E **63**, 031206 (2001).

[3] B. M. Mladek, D. Gottwald, G. Kahl, M. Neumann, and C. N. Likos, Phys. Rev. Lett. **96**, 045701 (2006).

[4] F. Sciortino, S. Mossa, E. Zaccarelli, and P. Tartaglia, Phys. Rev. Lett. **93**, 055701 (2004).

[5] H. Sedgwick, K. Kroy, A. Salonen, M. B. Robertson, S. U. Egelhaaf, and W. C. K. Poon, Eur. Phys. J. E **16**, 77 (2005).

[6] B. M. Mladek, P. Charbonneau, C. N. Likos, D. Frenkel, and G. Kahl, J. Phys. Condens. Matter **20**, 494 245 (2008).

[7] B. M. Mladek, G. Kahl, and C. N. Likos, Phys. Rev. Lett. **100**, 028301 (2008).

[8] A. Narros, A. J. Moreno, and C. N. Likos, Soft Matter **6**, 2435 (2010).

[9] D. A. Lenz, B. M. Mladek, C. N. Likos, G. Kahl, and R. Blaak, J. Phys. Chem. B **115**, 7218 (2011).

[10] M. O. Goerbig, P. Lederer, and C. Morais Smith, Phys. Rev. B **68**, 241302 (2003).

[11] N. Cooper, Adv. Phys. **57**, 539 (2008).

[12] S. Saccani, S. Moroni, and M. Boninsegni, Phys. Rev. B **83**, 092506 (2011).

[13] S. Saccani, S. Moroni, and M. Boninsegni, Phys. Rev. Lett. **108**, 175301 (2012).

[14] A. J. Moreno and C. N. Likos, Phys. Rev. Lett. **99**, 107801 (2007).

[15] D. Coslovich, L. Strauss, and G. Kahl, Soft Matter **7**, 2127 (2011).

[16] B. M. Mladek, P. Charbonneau, and D. Frenkel, Phys. Rev. Lett. **99**, 235702 (2007).

[17] A. Nikoubashman, G. Kahl, and C. N. Likos, Soft Matter **8**, 4121 (2012).

[18] T. Neuhaus and C. N. Likos, J. Phys. Condens. Matter **23**, 234 112 (2011).

[19] K. Zhang, P. Charbonneau, and B. M. Mladek, Phys. Rev. Lett. **105**, 245701 (2010).

[20] C. N. Likos, B. M. Mladek, D. Gottwald, and G. Kahl, J. Chem. Phys. **126**, 224 502 (2007).

[21] J. Dautenhahn and C. K. Hall, Macromolecules **27**, 5399 (1994).

[22] A. A. Louis, P. G. Bolhuis, J. P. Hansen, and E. J. Meijer, Phys. Rev. Lett. **85**, 2522 (2000).

[23] B. Capone, J.-P. Hansen, and I. Coluzza, Soft Matter **6**, 6075 (2010).

[24] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.109.228301 for details on the dendrimer model chosen here.

[25] See Supplemental Material (Fig. S1) at http://link.aps.org/supplemental/10.1103/PhysRevLett.109.228301 for the general shape of the effective interactions of amphiphilic dendrimers.

[26] D. A. Lenz, B. M. Mladek, C. N. Likos, and R. Blaak (to be published).

[27] S. Alexander and J. McTague, Phys. Rev. Lett. **41**, 702 (1978).

[28] R. A. Van Santen, J. Phys. Chem. **88**, 5768 (1984).

[29] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.109.228301 for details on this behavior.