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1 Introduction

Traditional analytic criteria for solidification, such as those based on classical nucleation theory, typically work very poorly both for liquids with strong glassforming tendency and for polymeric liquids. This failure creates a need for alternative criteria predicting these systems' solidification transitions. Several have been proposed, such as the splitting of the first peak in the pair correlation function g(r), the height of this peak g_{max} and its ratio to the value g_{\min} of g(r) at its first minimum, and other criteria based on g(r) or on local, cluster-level structure.¹⁻⁶ Criteria based on the average coordination number $\langle Z \rangle$, such as the famous result that systems of spherical particles jam at isostaticity [$\langle Z \rangle = 2d$, where *d* is spatial dimension],^{7,8} are appealing candidate solidification predictors because they are so simple.

Recent work^{9–12} has suggested an interesting connection between isostaticity and solidification of polymeric liquids: that solidification occurs when the average number of noncovalent contacts per monomer $\langle Z_{\rm nc} \rangle$ exceeds its isostatic value $\langle Z_{\rm nc}^{\rm iso} \rangle$. These studies focused on liquids of fully flexible^{9–12} or infinitely stiff¹² chains, for which the definition of $\langle Z_{\rm nc}^{\rm iso} \rangle$ is straightforward. However, finite chain stiffness is well known to strongly and nontrivially affect polymer solidification in both thermal^{13–15} and athermal^{16,17} systems. Here we examine the connection of isostaticity to polymer solidification using molecular dynamics simulations of a simple crystallizable bead-spring model¹⁸ with continuously variable chain stiffness. By considering chains

Isostaticity and the solidification of semiflexible polymer melts

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Using molecular dynamics simulations of a tangent-soft-sphere bead-spring polymer model, we examine the degree to which semiflexible polymer melts solidify at isostaticity. Flexible and stiff chains crystallize when they are isostatic as defined by appropriate degree-of-freedom-counting arguments. Semiflexible chains also solidify when isostatic if a generalized isostaticity criterion that accounts for the slow freezing out of configurational freedom as chain stiffness increases is employed. The configurational freedom associated with bond angles (θ) can be associated with the characteristic ratio $C_{\infty} = (1 + \langle \cos(\theta) \rangle)/(1 - \langle \cos(\theta) \rangle)$. We find that the dependence of the average coordination number at solidification $[Z(T_s)]$ on chains' characteristic ratio C_{∞} has the same functional form $[Z \simeq a - b \ln(C_{\infty})]$ as the dependence of the average coordination number at jamming $[Z(\phi_J)]$ on C_{∞} in athermal systems, suggesting that jamming-related phenomena play a significant role in thermal polymer solidification.

> ranging from flexible to rodlike and employing a suitably generalized isostaticity criterion, we show that these model polymeric liquids are very generally isostatic at their solidification temperatures.

> Consider d = 3 chains of length N with monomer positions \vec{r}_i , covalent bond lengths $\ell_i = |\vec{r}_{i+1} - \vec{r}_i|$, and bond angles $\theta_i = \cos^{-1}[\vec{\ell}_{i-1} \cdot \vec{\ell}_i/(\ell_{i-1}\ell_i)]$. Maxwell's isostaticity criterion⁷ can be written as $\langle Z^{\text{iso}} \rangle = 2N^{-1}(Nd - n_{\text{constr}})$, where n_{constr} is the number of holonomic constraints per chain. Fixed-length $(\ell = \ell_0)$ covalent bonds and fixed bond angles $(\theta = \theta_0)$ respectively supply N - 1 and N - 2 constraints per chain.^{19,20} Thus fully-flexible chains with fixed-length covalent bonds have¹²

$$\langle Z_{\rm nc}^{\rm iso} \rangle = \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm flex} = \frac{2[3N - (N-1)]}{N} = 4 + \frac{2}{N},$$
 (1)

while infinitely stiff chains that also[†] have fixed bond angles have¹²

$$\langle Z_{\rm nc}^{\rm iso} \rangle = \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm stiff} = \frac{2[3N - (N-1) - (N-2)]}{N} = 2 + \frac{6}{N}.$$
 (2)

For semiflexible chains, a more general isostaticity criterion intermediate between eqn (1) and (2) may apply.²¹ If isostaticity controls solidification but angular degrees of freedom are gradually frozen out as chain stiffness increases, the average number of noncovalent contacts per monomer at the solidification temperature $T_{\rm s}$, $\langle Z_{\rm nc}(T_{\rm s}) \rangle$, should vary smoothly from $\langle Z_{\rm nc}^{\rm iso} \rangle_{\rm flex}$ to $\langle Z_{\rm nc}^{\rm c} \rangle_{\rm stiff}$. Below, we use molecular dynamics simulations to show that this indeed occurs in model systems, and



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 $[\]dagger$ The relation of eqn (1) and (2) to the standard isostaticity criteria derived from the Phillips–Thorpe treatment of network glass-formers^{19,20} and employed in ref. 11 and 12 is detailed in the Appendix.

derive a generalized isostaticity criterion describing the phenomenon.

2 Model and methods

Our simulations employ the soft-pearl-necklace polymer model described at length in ref. 15 and 18. It is comparable to the Kremer–Grest bead-spring model,²² but possesses crystalline ground states. All monomers have mass m and interact via the truncated and shifted Lennard-Jones potential

$$U_{\rm LJ}(r) = \varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r_{\rm c}}\right)^{12} - 2\left(\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r_{\rm c}}\right)^6\right) \right],\tag{3}$$

where ε is the intermonomer binding energy and $r_{\rm c} = 2^{7/6} \sigma$ is the cutoff radius. Bonds between adjacent beads along the chain backbone are modeled using the harmonic potential

$$U_{\rm c}(\ell) = \frac{k_{\rm c}}{2}(\ell - \sigma)^2, \qquad (4)$$

where ℓ is bond length and k_c is the bond stiffness. The large value of k_c employed here $(600\epsilon/\sigma^2)$ produces bonds of nearly fixed ℓ ; $U_c(\ell)$ effectively acts as a holonomic constraint fixing $\ell = \ell_0 = \sigma$ and preventing chain crossing.¹⁸ Bending stiffness is included using the standard potential²³

$$U_{\rm b}(\theta) = k_{\rm bend}(1 - \cos(\theta)), \qquad (5)$$

which favors straight trimers (sets the equilibrium bond angle $\theta_0 = 0$). Fully flexible chains have $k_{\text{bend}} = 0$, and rigid-rod-like chains are obtained in the limit $k_{\text{bend}} \rightarrow \infty$. Here we study systems with $0 \le k_{\text{bend}} \le 30\varepsilon$. As detailed in ref. 15, the model's solid morphologies – formed by cooling from the isotropic liquid state – range from random-walk close-packed crystals to glasses to nematic close-packed crystals over this range of k_{bend} . Since its solidification dynamics²⁴ also vary strongly with k_{bend} , the model is suitable for studying connections between solidification and isostaticity in a very general way.

All systems are composed of $N_{\rm ch} = 500$ chains of N monomers. Here, for simplicity, we focus mainly on unentangled systems with N = 25. Periodic boundaries are applied along all three directions of cubic simulation cells. Systems are first thoroughly equilibrated²³ at temperatures well above their $k_{\rm bend}$ -dependent solidification temperatures,¹⁵ then slowly cooled at zero pressure to T = 0 at a rate $|\dot{T}| = 10^{-6}/\tau$. This $|\dot{T}|$ is sufficiently low to be in a limit where finite-cooling-rate effects on melt structure are small.²⁴ Pressure is controlled using a Nose–Hoover barostat. The MD timestep used here is $\delta t = \tau/200$, where τ is the Lennard-Jones time unit $\sqrt{m\sigma^2/\epsilon}$. All simulations are performed using LAMMPS.²⁵

3 Results

Ref. 15 presented a detailed analysis of these systems' solidification behavior for $k_{\text{bend}} \leq 12.5\varepsilon$, but did not consider staticity. Fig. 1 presents staticity-related results. Panel (a) shows how $\langle Z_{\text{nc}}(T) \rangle$ increases during cooling for four representative chain stiffnesses: flexible ($k_{\text{bend}} = 0$), semiflexible ($k_{\text{bend}} = 4\varepsilon$), semistiff ($k_{\text{bend}} = 10\varepsilon$), and stiff ($k_{\text{bend}} = 30\varepsilon$). Here

$$\langle Z_{\rm nc} \rangle = \frac{2}{N_{\rm ch}N} \sum_{i=1}^{N_{\rm ch}N} \sum_{j=i+1}^{N_{\rm ch}N} \Theta(\sigma - r_{ij}) f_{ij}, \tag{6}$$

where $\Theta(x)$ is the Heaviside step function; $f_{ii} = 0$ if monomers *i* and *j* are covalently bonded and 1 otherwise. Thus $\langle Z_{nc} \rangle$ only counts repulsively interacting particles (those with $r_{ii} \equiv |\vec{r}_i - \vec{r}_i| < 1$) as being in contact, as is appropriate for thermal systems.²¹ Flexible chains crystallize into a random-walk-closepacked (RWCP) structure wherein monomers close-pack but chains retain random-walk-like structure and are isotropically oriented.¹⁵ Semiflexible chains form glasses; $k_{\text{bend}} = 4\varepsilon$ systems have been shown to be typical fragile glassformers.²⁴ Semistiff chains form moderately defective nematic close-packed (NCP) crystals,15 while stiff chains form nearly perfect NCP crystals. Solidification temperatures T_s increase by more than a factor of three – from $k_{\rm B}T_{\rm s}/\varepsilon = 0.53$ for flexible chains to $k_{\rm B}T_{\rm s}/\varepsilon = 1.75$ for stiff chains - as stiffness increases (Table 1). The densities of these systems at T_s also drop sharply with increasing k_{bend} over the same range; Table 1 reports the packing fractions $\phi_s = \phi(T_s)$, where $\phi = \pi \rho/6$ is the usual packing fraction for spherical particles [and $\rho = N_{\rm ch} N/V$ is the monomer number density]. Thus these systems collectively exhibit a wide range of solidification behaviors.

Crystallizing systems exhibit sharp, first-order-transitionlike jumps in $\langle Z_{\rm nc}(T) \rangle$ at $T = T_{\rm s}$. Glassforming systems exhibit smoothly increasing $\langle Z_{\rm nc}(T) \rangle$ as T decreases, with only slight cusps [discontinuities in $\partial^2 \langle Z_{\rm nc}(T) \rangle / \partial T^2$] at $T = T_{\rm s}$.‡ Below $T_{\rm s}$, $\langle Z_{\rm nc}(T) \rangle$ continues to increase as cooling proceeds, not because of any major structural rearrangements, but simply because systems continue to densify. It is clear that both flexible-chain systems and stiff-chain systems are approximately isostatic at $T = T_{\rm s}$, *i.e.* they respectively have $\langle Z_{\rm nc}(T_{\rm s}) \rangle \simeq \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm flex}$ and $\langle Z_{\rm nc}(T_{\rm s}) \rangle \simeq \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm stiff}$. It is also clear that intermediatestiffness systems display intermediate solidification behavior that exhibits a smooth crossover between the flexible-chain and stiffchain limits.

Ref. 10 and 11 reported $\langle Z_{\rm nc}(T_{\rm s}) \rangle \simeq \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm flex}$ in singleflexible-chain systems. Ref. 11 and 12 argued that $\langle Z_{\rm nc}(T_{\rm s}) \rangle$ should be $\langle Z_{\rm nc}^{\rm iso} \rangle_{\rm flex}$ in bulk glassforming polymeric liquids when chains are fully flexible, and $\langle Z_{\rm nc}^{\rm iso} \rangle_{\rm stiff}$ when chains are infinitely stiff (have holonomic $\theta = \theta_0$ constraints). Panel (b) shows $\langle Z_{\rm nc}(T_{\rm s}) \rangle$ for all systems as a function of $k_{\rm bend}$. $\langle Z_{\rm nc}(T_{\rm s}) \rangle$ is roughly constant for $k_{\rm bend} \lesssim \varepsilon$, then drops sharply with increasing $k_{\rm bend}$ until the stiff-chain $\langle Z_{\rm nc}(T_{\rm s}) \rangle \simeq \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm stiff}$ limit is approached as $k_{\rm bend}$ exceeds ~10 ε . The data in panels (a) and (b) clearly show that $\langle Z_{\rm nc}(T_{\rm s}) \rangle \simeq \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm flex}$ also holds true for crystal-forming flexible-chain liquids, and that $\langle Z_{\rm nc}(T_{\rm s}) \rangle \simeq \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm stiff}$ holds for crystal-forming stiff-chain liquids. They also strongly suggest that semiflexible chains'

[‡] As in ref. 15, values of T_s were determined by locating the jump in packing fraction $\phi(T)$ for crystallizing systems, or the intersection of low-*T* and high-*T* linear fits to $\phi(T)$ for glassforming systems. In all cases, the trends in $\langle Z_{nc}(T) \rangle$ reported herein closely mirror trends in $\phi(T)$.



Fig. 1 Measures of noncovalent repulsive contact in slowly cooled, semiflexible, unentangled (N = 25) polymer melts. Panel (a) shows $\langle Z_{nc}(T) \rangle$: blue, green, orange and red curves show data for selected k_{bend} , while the correspondingly colored vertical dotted lines indicate the respective $T_s(k_{bend})$ [Table 1]. Panel (b) shows the k_{bend} -dependence of $\langle Z_{nc}(T_s) \rangle$ for all systems. In panel (c), points show the same $\langle Z_{nc}(T_s) \rangle$ as in panel (b), but plotted vs. $C_{\infty}(T_s)$. The red solid line shows a fit to our generalized isostaticity criterion (eqn (9)), and the angled dashed lines show the maximal statistical uncertainties on this fit, including uncertainties on both the slope *b* and the intercept [$\langle Z_{nc}^{iso} \rangle_{flex} - \langle Z_{nc}^{iso} \rangle_{stiff}$]/*b*. In all panels, the upper and lower horizontal gray dashed lines respectively indicate $\langle Z_{nc}^{iso} \rangle_{flex} = 4.08$ and $\langle Z_{nc}^{iso} \rangle_{stiff} = 2.24$. See the Appendix for a discussion of how these results depend on chain length.

solidification behavior should be describable by a suitably generalized criterion for $\langle Z_{nc}(T_s) \rangle$.

One commonly used measure of chain stiffness that is easily connected to the configurational freedom associated with bond

Table 1 Solidification temperatures, densities, and solid morphologies for selected chain stiffnesses (for N = 25). Values of T_s and ϕ_s for $k_{bend} \le 12.5\varepsilon$ and morphology descriptions were reported in ref. 15

$k_{ m bend}/\varepsilon$	$k_{ m B}T_{ m s}/\varepsilon$	$\phi_{ m s}$	Morphology
0	0.53	0.684	RWCP
2	0.49	0.673	Glass/RWCP
4	0.61	0.646	Glass
6	0.91	0.606	Nematic glass
8	1.13	0.581	Multidomain NCP
10	1.26	0.580	Defected NCP
15	1.32	0.582	NCP
20	1.57	0.558	NCP
25	1.66	0.556	NCP
30	1.75	0.552	NCP

angles is the characteristic ratio $C_{\infty} = (1 + \langle \cos(\theta) \rangle)/(1 - \langle \cos(\theta) \rangle)$.§ $C_{\infty} = 1$ for ideally flexible chains with no excluded volume, ~ 1.7 for $k_{\text{bend}} = 0$ chains,^{23,27} and ∞ for $k_{\text{bend}} = \infty$ rod-like chains. Thus the variation of C_{∞} can be taken as a rough proxy for the slow freezing out of the bond-angular degrees of freedom as chain stiffness increases and/or temperature decreases. While many-body effects can considerably alter C_{∞} in bulk systems (e.g. dense liquids at $T = T_{\text{s}}$ or athermal systems at $\phi = \phi_{\text{J}}^{17,27}$), it is still reasonable to posit that a generalized isostaticity criterion based on C_{∞} exists. We postulate is that the effective number of holonomic constraints per chain at solidification is

$$n_{\rm constr}^{\rm eff}[C_{\infty}(T_{\rm s})] = (N-1) + (N-2)g[C_{\infty}(T_{\rm s})], \qquad (7)$$

where $g(C_{\infty})$ smoothly increases from 0 to 1 as C_{∞} varies from 1 to ∞ . Then a potential generalized isostaticity criterion is

$$\langle Z_{\rm nc}^{\rm iso} \rangle_{\rm gen} = 2N^{-1} (Nd - n_{\rm constr}^{\rm eff} [C_{\infty}(T_{\rm s})]). \tag{8}$$

with $n_{\text{constr}}^{\text{eff}}$ given by eqn (7). This formula automatically satisfies $\langle Z_{\text{nc}}^{\text{iso}} \rangle_{\text{gen}} = \langle Z_{\text{nc}}^{\text{iso}} \rangle_{\text{flex}}$ when $C_{\infty} = 1$ and $\langle Z_{\text{nc}}^{\text{iso}} \rangle_{\text{gen}} = \langle Z_{\text{nc}}^{\text{iso}} \rangle_{\text{flex}}$ when $C_{\infty} = \infty$, and thus is consistent with eqn (1) and (2). Since it is not clear how to calculate $g(C_{\infty})$ "*ab initio*", we will attempt to determine a functional form for $g(C_{\infty})$ by examining our simulation-generated dataset.

Fig. 1(c) shows $\langle Z_{nc}(T_s) \rangle$ for all systems as a function of $C_{\infty}(T_s)$. Systems with $k_{\text{bend}}/\varepsilon \lesssim 1.5$ [$C_{\infty}(T_s) \lesssim 7$] are apparently in the flexible-chain limit where $g(C_{\infty}) \simeq 0$ and $\langle Z_{nc}(T_s) \rangle \simeq \langle Z_{nc}^{\text{iso}} \rangle_{\text{flex}}$. For larger k_{bend} and $C_{\infty}(T_s)$, the decrease of $\langle Z_{nc}(T_s) \rangle$ with increasing chain stiffness is approximately logarithmic in $C_{\infty}(T_s)$. Stiff chains with $C_{\infty}(T_s) \simeq 50$ have $\langle Z_{nc}(T_s) \rangle \simeq \langle Z_{nc}^{\text{iso}} \rangle_{\text{stiff}}$. The data suggest $g(C_{\infty}) \sim \ln[C_{\infty}]$ for $7 \lesssim C_{\infty} \lesssim 50$, and that a generalized isostaticity criterion of form

$$\langle Z_{\rm nc}^{\rm iso} \rangle_{\rm gen} = \min \left[\langle Z_{\rm nc}^{\rm iso} \rangle_{\rm flex}, \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm stiff} - b \ln \left(\frac{C_{\infty}}{C_{\infty}^{\rm max}} \right) \right]$$
(9)

[§] The characteristic ratios obtained from this formula for C_{∞} are, of course, chain-length-dependent. Finite-*N* effects include those associated with hindered dihedral rotations (*e.g.* pentane interference²⁶), as well as other factors that affect solidification.^{13–15,17} They will also in general differ from those obtained using the formula $(C_{\infty} = \langle R_{ee}^2 \rangle / [(N-1)\ell_0^2])$ typically used to measure C_{∞} in scattering experiments.¹⁴ See the Appendix for a further discussion.

describes the solidification of semiflexible polymers over the full range of C_{∞} considered here; as shown in panel (c), the fit of eqn (9) to the data for $k_{\text{bend}}/\varepsilon \ge 2$ is very good. Note that this range of C_{∞} is comparable to the range exhibited by natural polymers, from very flexible ones such as polyethylene to stiff ones such as actin.^{13,14} Very stiff chains with $C_{\infty} \ge C_{\infty}^{\text{max}} \simeq 10^2$ lie in a different regime where chains behave as though they were single rigid-rod-like particles^{28,29} rather than polymers, and are not considered here.

The crossover from the flexible to the semiflexible regime (*i.e.* the crossover between the two functional forms for $\langle Z_{nc}^{iso} \rangle_{gen}$ given in eqn (9)) is a subtle issue. The data in Fig. 1 actually suggests that polymer melts are very slightly hypostatic at solidification, to a degree that is nearly independent of chain stiffness; specifically, $\langle Z_{nc}(T_s) \rangle \simeq \langle Z_{nc}^{iso} \rangle - 0.1$. This slight deviation may be related to solidification occurring when iso/hyper-static clusters percolate rather than when $\langle Z_{nc} \rangle = \langle Z_{nc}^{iso} \rangle_{gen}$ ³⁰ but analyses of such clusters in our systems were inconclusive. Alternatively, the deviation may be related to thermal effects including nonperturbative effects of attractive interactions and the shape of the repulsive part of the potential,31 or to many-body phenomena including dimer-interlocking.32 Such effects are usually subtle and would require intensive analyses that are beyond our present scope. Thus the generalized isostaticity criterion developed here (eqn (9)) can be considered a peer of those proposed in ref. 1-6 in the sense that while it is neither rigorous nor precise, it can serve as a useful guide.

4 Discussion and conclusions

The trends illustrated in Fig. 1 strongly suggest that isostaticity is a broadly important concept for improving our understanding of semiflexible polymer solidification. The $\ln(C_{\infty})$ dependence of $\langle Z_{\rm nc}(T_{\rm s})\rangle$ in our thermal systems is also observed in jamming of athermal semiflexible polymers, which have $\langle Z_{\rm nc}(\phi_{\rm I}) \rangle \simeq$ $a - b \ln(C_{\infty})$ in the range $10^1 \leq C_{\infty} \leq 10^{2.17}$ This similar functional dependence of monomer coordination at solidification upon C_{∞} is present despite the fact that ref. 17 employed a different angular potential $[U_b = (k_{bend}/2)(\theta - \theta_0)^2]$ and varied C_{∞} by varying θ_0 rather than by varying k_{bend} . The common behavior supports previous work (e.g. ref. 9, 11, 12 and 16) suggesting that jamming-related phenomena play a role in controlling polymer melt solidification despite the fact that polymer melts are highly thermal. For example, the well-known increase in $T_{\rm g}$ with increasing C_{∞} in microscopic synthetic polymers,^{13,14} the observed decrease in $\phi_{\rm J}$ with C_∞ in athermal polymers,^{16,17} and the data presented herein all form a consistent picture if one accepts the idea that all these trends are dominated by the gradual freezing out of configurational freedom as chain stiffness increases. In conclusion, the accumulated evidence now strongly suggests that C_{∞} is an axis on the polymeric counterpart of Liu and Nagel's jamming-glass phase diagram.³³

Conflicts of interest

There are no conflicts to declare.

Appendix

Relation to Phillips/Thorpe isostaticity criteria

Phillips and Thorpe^{19,20} derived the following criteria for the fraction *f* of phonons that are "soft" (have imaginary frequencies) in network glassformers as a function of the mean coordination numbers $\langle Z_{\rm co} \rangle$ and $\langle Z_{\rm nc} \rangle$ for covalent and noncovalent bonds:

$$f = 1 - \frac{1}{3} \left[\frac{\langle Z_{\rm co} \rangle}{2} + (2 \langle Z_{\rm co} \rangle - 3) + \frac{\langle Z_{\rm nc} \rangle}{2} \right].$$
(10)

Soft modes vanish and systems are isostatic when f = 0, *i.e.* when

$$\langle Z_{\rm nc} \rangle = \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm PT} = 2 \left[3 - (2 \langle Z_{\rm co} \rangle - 3) - \frac{\langle Z_{\rm co} \rangle}{2} \right].$$
 (11)

This criterion (with the linear-polymeric value $\langle Z_{\rm co} \rangle = 2[1 - N^{-1}]$) was used to obtain the isostaticity criterion $\langle Z_{\rm nc}^{\rm iso} \rangle = 2$ proposed for long chains in ref. 11 and 12. It is equivalent to our isostaticity criterion for rigid chains (eqn (2)) in the limit $N \to \infty$. However, the Phillips–Thorpe criteria assume that all angles corresponding to covalently bonded trimers are constrained.^{19,20} When such angles are unconstrained, the $(2\langle Z_{\rm co} \rangle - 3)$ terms appearing in eqn (10) and (11) must be removed, yielding the flexible-network isostaticity criterion

$$\langle Z_{\rm nc} \rangle = \langle Z_{\rm nc}^{\rm iso} \rangle_{\rm FN} = 2 \left[3 - \frac{\langle Z_{\rm co} \rangle}{2} \right].$$
 (12)

Eqn (12) yields $\langle Z_{nc}^{iso} \rangle = 4 + 2/N$ and is therefore equivalent to our isostaticity criterion for flexible chains (eqn (1)).

Applicability of criteria based on persistence length. In Section 3, we presented results for $\langle Z_{\rm nc}(T_{\rm s}) \rangle$ as a function of $C_{\infty}(T_{\rm s}) \equiv (1 + \langle \cos(\theta)[T = T_{\rm s}] \rangle)/(1 - \langle \cos(\theta)[T = T_{\rm s}] \rangle)$. A more commonly used²⁶ metric of polymer chain stiffness is the persistence length $\ell_{\rm p}$. In simulations, $\ell_{\rm p}$ is usually measured in one of two ways. The explicitly *N*-dependent formula

$$\frac{\ell_{\rm p}}{\ell_0} = \frac{2\ell_0^{-2}}{N_{\rm ch}N} \sum_{k=0}^{N_{\rm ch}} \sum_{i=1}^{N-1} \sum_{j=0}^{N-1-i} \vec{b}_i^k \cdot \vec{b}_{i+j}^k,$$
(13)

where \vec{b}_i^k is the *i*th bond vector on chain *k*, is dominated by the finite-*j* cutoff for our large-*k*_{bend} systems, giving the unenlightening result $\lim_{k_{bend}\to\infty} (\ell_p/\ell_0) = N - 1$. Alternatively, the formula

$$\frac{\ell_{\rm p}}{\ell_0} = \sum_{j=0}^{\infty} \left\langle \cos(\theta) \right\rangle^j \tag{14}$$

is not explicitly *N*-dependent, but is subject to the same implicit *N*-dependencies mentioned in Section 3, and in any case has a one-to-one mapping to C_{∞} : $C_{\infty} \equiv 2(\ell_p/\ell_0 - 1)$. Here we have chosen to present results in terms of C_{∞} because C_{∞} is closely analogous to the "aspect ratio" α , which is a critical parameter influencing jamming of anisotropic particles.^{28,34,35}

Chain length dependence

Eqn (1) and (2) predict that $\langle Z_{nc}(T_s) \rangle$ will increase with decreasing chain length. Fig. 2 presents the same measures shown in Fig. 1(b and c), but contrasts N = 25 results to those for N = 13 and N = 50. To within our statistical uncertainties, the predictions of eqn (1) and (2) are borne out; the N = 13 systems have

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Fig. 2 Measures of noncovalent repulsive contacts in slowly cooled semiflexible polymer melts; chain length dependence. Panels (a and b) respectively show the same quantities plotted in Fig. 1(b and c), but compare results for systems with N = 13, 25, and 50. For N = 50, we present results only for $k_{\text{bend}} \leq 12.5\varepsilon$ because avoiding spurious finite-size effects for larger k_{bend} requires larger systems that are computationally prohibitive to simulate at our chosen cooling rate.

the highest $\langle Z_{\rm nc}(T_{\rm s}) \rangle$ for most of the studied $k_{\rm bend}$. As shown in panel (b), $C_{\infty}(T_{\rm s})$ is somewhat *N*-dependent; longer chains have slightly higher $T_{\rm s}(k_{\rm bend})^{17}$ and hence slightly lower $C_{\infty}(T_{\rm s})$ for our chosen $U_{\rm b}(\theta)$. However, this *N*-dependence does not appear to decrease the efficacy of our generalized isostaticity criterion (eqn (9)). Finally, note that our stiffer ($k_{\rm bend} \gtrsim 4\varepsilon$) N = 50 chains are sufficiently long to be slightly entangled;³⁶ larger *N* will produce increasingly strong \dot{T} -dependent effects and therefore are not considered here.

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