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Citation for published version (APA):

Sushko, N., Schoot, van der, P. P. A. M., & Michels, M. A. J. (2003). On the role of connectivity in the relative stability of crystal types for model polymeric solids. *Journal of Chemical Physics*, 118(13), 6098-6101. <https://doi.org/10.1063/1.1557433>

DOI:

[10.1063/1.1557433](https://doi.org/10.1063/1.1557433)

Document status and date:

Published: 01/01/2003

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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- The final published version features the final layout of the paper including the volume, issue and page numbers.

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On the role of connectivity in the relative stability of crystal types for model polymeric solids

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(Received 28 October 2002; accepted 10 January 2003)

We study the relative stability of two different lattice types for model polymeric solids, using a recently developed density functional theory for freely-hinged, polymeric chains of hard globular segments. The most stable crystal-lattice type appears to be determined by the mean length and the stretching stiffness of the bonds as well as by the size of the segments. We discuss the possible implications of this for the crystallization of chemically realistic polymers. © 2003 American Institute of Physics. [DOI: 10.1063/1.1557433]

According to current paradigm, the face-centered cubic (fcc) lattice is the preferred lattice type for the hard-sphere crystal. Theoretically, however, there still is some ambiguity as regards the optimal crystal symmetry for this type of system. In a remarkable paper, Alexander and McTague¹ argued on quite general grounds within a Landau type of approach that, irrespective of the type of interactions, spherical particles favor the body-centered cubic (bcc) lattice, not the fcc lattice. Recently, Groh and Mulder² showed with the help of (a highly approximate) density functional theory (DFT), that the relative stabilities of the bcc and fcc lattices are a function of the strength of the solid-phase order parameter, the latter type becoming more favorable when the order parameter is high. More sophisticated DFTs seem to point at the fcc crystal being the lowest free energy structure, but the differences in free energy of the fcc lattice and, e.g., the hexagonally close-packed (hcp) lattice are minute. (In some DFTs the bcc structure is found to be mechanically stable for some densities.³ However, it is thermodynamically metastable or absolutely unstable with respect to the fluid in case for all hard-sphere DFTs as far as we are aware.⁴) The crystallization of hard spheres has also been studied intensively by means of computer simulations.^{5–9} These studies also indicate that it is hard to determine which lattice the most stable, although the most recent results demonstrate that the fcc structure is indeed favored for systems of hard spheres.^{8,9} In experiment, hard-spherelike colloids seem to crystallize in a fcc crystal, as in fact do charged ones except at high ionic strength.^{10,11} (At low ionic strength a bcc structure seems to be preferred for the latter.)

Hard spheres are often considered convenient models for atoms or small molecules and by the same token chains of hard spheres are often treated as paradigmatic for actual polymer molecules.^{12,13} It seems useful, therefore, to investigate the impact of bonded interactions between hard spheres on their (preferred) crystal type. Of course, real polymeric crystals are very complex, and do not even necessarily represent the state of thermodynamic equilibrium. Almost

each polymer has its specific crystal structure,¹⁴ which depends on the external conditions such as the applied pressure, the type of the chemical bonds and other characteristics related to the chemical details of these materials. Naively, one would perhaps expect the influence of the bonds on the stability of the polymeric crystal to be minor compared with that of the packing constraints imposed by the geometry of the molecules. By applying density functional theory we show here that the stiffness of the bonded interactions is in fact important to the formation of the polymeric solid, and can destabilize one crystal type in favor of another. A similar situation is found in computer simulation studies involving particles that interact via a (nonbonded) Yukawa potential, where an increase of the range of the potential was found to suppress the fcc lattice in favor of the bcc lattice.¹⁵

Density functional theoretical methods have been extensively used in the study of crystallization of simple liquids.⁴ For instance, Igloi *et al.*¹⁶ used this method to study the relative stability of fcc and hcp lattices, first for hard-sphere systems (applying the Fourier approximation for the local segment density in the crystal) and later for simple liquid metals (using a direct correlation function of the liquid that was calculated *ab initio*, using quantum-mechanical methods).¹⁷ Their calculations predict correctly the preferred lattice type for Al and Mg at given external conditions of normal pressure and temperature. Other DFT studies were done for hard-sphere systems by Yussouff¹⁸ (within the Fourier approximation), and by Baus and Colot¹⁹ and by Laird *et al.*²⁰ (who used the Gaussian approximation for the local density distribution). They found the difference between the grand potentials for the fcc and hcp crystal structures at the same density near the freezing point to be very small (less than 0.05 in units of thermal energy per particle). By applying similar theoretical tools we find here that for polymeric chains of hard globular segments, this difference between the grand potentials can be increased by up to 0.07 in units of thermal energy *per segment*. Considering that the chains consists of many segments, such a stability gap must be viewed as huge.

In previous studies we considered the thermodynamic

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stability as well as the mechanical properties of model polymeric solids by means of a polymer DFT, obtained from a self-consistent field-type argument.^{21,22} In our present investigation we use the same model polymer. The model polymer under consideration consists of beads interacting through a hard-core repulsive potential, and connected by freely-hinged bonds with an adjustable bond stiffness. The bonds are of a phantom nature, i.e., can pass through each other. In our theory we define $g(\mathbf{r}, \mathbf{r}')$ as the normalized *a priori* probability that a bond that starts at position $\mathbf{r}'$ ends at $\mathbf{r}$. The following choice of bond probability interpolates between the standard Gaussian and Kuhn models,²¹

$$g(\mathbf{r}, \mathbf{r}') = \frac{\sqrt{6}}{8\pi^{3/2}\xi|\mathbf{r}-\mathbf{r}'|l} \left(\exp - \frac{3(|\mathbf{r}-\mathbf{r}'|-l)^2}{2\xi^2} - \exp - \frac{3(|\mathbf{r}-\mathbf{r}'|+l)^2}{2\xi^2} \right), \quad (1)$$

where l denotes the mean length of a bond, and ξ is the root-mean-square deviation about this mean length. The effective Kuhn length l_K of the model depends on l and ξ , and equals $\sqrt{l^2 + \xi^2}$. For $\xi \ll l$ our model turns into a freely-hinged chain with fixed bond length $l_K = l$. The other limiting case is for $\xi \gg l$, when our model behaves as the Gaussian-chain model with a root-mean-square bond extension $l_K = \xi$.

We denote the range of the (effective) hard-core interactions between the beads by σ . To describe how the chain connectivity renormalizes these interactions, we introduced in our previous work the so-called fusion parameter $\Gamma \equiv l_K/\sigma$.^{21,22} For $\Gamma \ll 1$ neighboring beads along a chain overlap, while for $\Gamma \gg 1$ they do not. Our aim now is to study how the parameters Γ and ξ influence the stability of either hcp or fcc structures, and in particular which lattice is preferable for our athermal polymeric system. We note that for our model polymers the fcc crystal is the only stable cubic lattice type, and then only if $\Gamma \gtrsim 3$ (see Ref. 21 for a discussion). The hcp crystal structure does not belong to the group of cubic lattices.

In our calculations we approximate the density distribution in the crystal phase by a sum of narrow Gaussians²¹

$$\rho(\mathbf{r}) = (\pi\epsilon^2)^{-3/2} \sum_{\{\mathbf{R}_n\}} \exp[-(\mathbf{R}_n - \mathbf{r})^2/\epsilon^2] \quad (2)$$

with the width ϵ of the local density profile presumed to be much smaller than the distance between the lattice points, whose positions are given by the vectors $\mathbf{R}_n$. $\{\mathbf{R}_n\}$ is the set of all real-space crystal-lattice vectors. The equilibrium width of the density distributions ϵ we fix by a free-energy minimization. The unit cell of the fcc lattice is defined by the set of vectors,

$$\begin{aligned} \mathbf{a}_1 &= (a/2)(\mathbf{j} + \mathbf{k}), \\ \mathbf{a}_2 &= (a/2)(\mathbf{i} + \mathbf{k}), \\ \mathbf{a}_3 &= (a/2)(\mathbf{i} + \mathbf{j}), \end{aligned} \quad (3)$$

with $\mathbf{i}, \mathbf{j}, \mathbf{k}$ the basis vectors in the Cartesian system of coordinates, and a the nearest-neighbor separation. The following vectors describe the hcp structure,

$$\begin{aligned} \mathbf{a}_1 &= a\mathbf{i}, \\ \mathbf{a}_2 &= -(a/2)\mathbf{i} + (\sqrt{3}a/2)\mathbf{j}, \\ \mathbf{a}_3 &= c\mathbf{k}, \end{aligned} \quad (4)$$

where $c/2$ denotes the separation of neighboring hexagonal planes.

Within the ground-state approximation, the grand-potential difference $\Delta\Omega[\rho(\mathbf{r})]$ of the crystal and a molten reference state reads²¹

$$\begin{aligned} \frac{1}{k_B T} \frac{\Delta\Omega}{\rho_L V} &\equiv \Delta\omega[p(r)] = \frac{1}{\rho_L V} \int d\mathbf{r} \rho(\mathbf{r}) \ln \rho(\mathbf{r})/\rho_L \\ &\quad - \frac{1}{\rho_L^2 V} \int d\mathbf{r}' g(|\mathbf{r}-\mathbf{r}'|) [\rho(\mathbf{r}) - \rho_S] \\ &\quad \times [\rho(\mathbf{r}') - \rho_S] - \frac{1}{\rho_L V} \sum_{p=2}^{\infty} \frac{1}{p!} \int \cdots \int C^{(p)} \\ &\quad \times (\mathbf{r}_1, \dots, \mathbf{r}_p) \prod_{i=1}^p d\mathbf{r}_i (\rho(\mathbf{r}_i) - \rho_L) \\ &\quad - \frac{1}{k_B T} (\mu_S - \mu_L) \frac{1}{\rho_L V} \int d\mathbf{r} \rho(\mathbf{r}) \\ &\quad - \frac{1}{\rho_L V} \int d\mathbf{r} (\rho(\mathbf{r}) - \rho_L), \end{aligned} \quad (5)$$

where for the density distribution $\rho(\mathbf{r})$ we insert the Gaussian profiles of Eq. (2). In Eq. (5), V is the volume of the system, μ_S is the chemical potential of the solid, and μ_L is that of the liquid reference phase, and ρ_S and ρ_L are the segment densities of, respectively, the solid and liquid state. $C^{(p)}(\mathbf{r}_1, \dots, \mathbf{r}_p)$ is the p -particle direct correlation function of the liquid reference state, T is the temperature, and k_B is Boltzmann's constant. We calculate $C^{(p)}(\mathbf{r}_1, \dots, \mathbf{r}_p)$ from a generalized Lifshitz theory, formally equivalent to the so-called polymeric reference interaction site model (PRISM).²³ To solve the PRISM equations we impose the usual Percus–Yevick (PY) closure, mimicking a hard-core interaction between the beads.

In the free-energy functional the information about the connectivity of the beads within a polymer enters via the second term in the right-hand side of Eq. (5), which contains the step probability g , but also via the direct correlation functions in the third term. The term containing g is accurate only at length scales small compared to the size of the chains.^{21,22} As a result, the monomeric units do order positionally onto either the fcc or hcp lattice, but long-range *bond order* does not build up. (See again Refs. 21 and 22 for a discussion.)

For obvious reasons the calculations are more conveniently done in Fourier space, so we use the Fourier representation of the density distribution given in Eq. (2),

$$\rho(\mathbf{r}) = \rho_L \left[1 + \eta + \sum_{\{\mathbf{q}\}} \zeta(\mathbf{q}) \exp i\mathbf{q} \cdot \mathbf{r} \right] \quad (6)$$

FIG. 1. The liquid density at the freezing point as a function of the dimensionless parameter ξ/σ measuring the stretching stiffness of the bonds for the fcc and hcp lattices, given at a value of the fusion parameter $\Gamma=5$ and degree of polymerization $N=100$. The fusion parameter $\Gamma=l_K/\sigma$ is a measure for the bending stiffness of the chain. The hcp structure is preferable in the range $0 < \xi/\sigma \leq 0.6$. At large ξ , both fcc and hcp structures are equally probable.

with $\{\mathbf{q}\}$ the set of the reciprocal-lattice vectors of the fcc or hcp lattice, $\eta=(\rho_s-\rho_L)/\rho_L$ the fractional density change across the crystallization transition, and

$$\zeta(\mathbf{q}) = (1 + \eta) \exp - \mathbf{q}^2 \epsilon^2 / 4. \quad (7)$$

The expression for the dimensionless grand potential density $\Delta\omega$ reduces to

$$\begin{aligned} \Delta\omega = 1 - (1 + \eta) & \left(5/2 + \ln \rho_L + 3/2 \ln \pi \epsilon^2 - \frac{1}{k_B T} \right. \\ & \times (\mu_s - \mu_L) \Big) - \sum_{\{\mathbf{q}\}} \hat{g}(\mathbf{q}) \zeta^2(\mathbf{q}) - \frac{1}{2} \eta^2 \rho_L \hat{C}_L^{(2)}(0) \\ & - \frac{1}{2} \rho_L \sum_{\{\mathbf{q}\}} \zeta^2(\mathbf{q}) \hat{C}_L^{(2)}(|\mathbf{q}|) - \frac{1}{6} \eta^3 \rho_L^2 \hat{C}_L^{(3)}(0,0), \end{aligned} \quad (8)$$

where, following Laird and co-workers,²⁴ we include, apart from the usual two-body direct correlation function, only the zero- q three-body direct correlation function. This expression we minimize with respect to the liquid density ρ_L , the parameter η and the width of the density profile ϵ .

The minimization was done at the freezing point, using a standard quasi-Newton algorithm from the NAG[®] library (Mark 18, E04JYF). The conditions of mechanical and thermodynamical equilibrium were imposed by insisting on the equality of the pressures and chemical potentials in the liquid and solid phases (so $\Delta\omega = -\Delta P/k_B T \rho_L \equiv 0$ and $\mu_s - \mu_L \equiv 0$). We determine the minimum number of reciprocal-lattice vectors $\{\mathbf{q}\}$ needed to accurately describe the crystal phase for the fcc and hcp lattices empirically, and find it to be approximately 6000 for both lattice types. Only the ideal hcp lattice was considered, so we set $c/a = (8/3)^{1/2}$ in Eq. (4).

As our interests concern the influence of the bond stiffness on the relative stability of the fcc and hcp lattices, we

FIG. 2. The relative density difference of the melt at freezing into the fcc and hcp structures, $100(\rho_{fcc} - \rho_{hcp})/\rho_{fcc}$, for different values of the fusion parameter Γ and the degree of polymerization $N=100$. In the range $0 < \xi/\sigma \leq 0.6$ the preferred lattice type is dependent on the fusion parameter Γ . For large Γ and/or large ξ both fcc and hcp structures are equally stable.

calculate the freezing densities for fcc and hcp at different values of the parameter ξ . Figure 1 gives the liquid freezing density of chains of degree of polymerization 100 for both lattices as a function of the parameter ξ at $\Gamma=5$. The figure clearly demonstrates the hcp structure to be more stable than the fcc structure in the range $0 < \xi/\sigma \leq 0.6$, i.e., if the bonds are sufficiently stiff. Interestingly, the polymers then freeze at a lower density than hard monomers do. Apparently, in that case connectivity stabilizes the (hcp) crystal phase. Although the differences in the densities at the freezing for both lattices seem modest (less than 5%), they do exceed our numerical accuracy, which is about 0.5%. In the opposite limit of floppy bonds, with $\xi/l \gg 1$, the hcp and fcc structures are equally stable within the numerical accuracy of the calculations. In this limit the freezing of the polymer occurs at roughly the same density as that of hard monomers. For certainty, we also investigated a possible fcc-hcp transition deep in the crystal phase by directly comparing free energies, but did not find such a transition between the two lattice structures.

The relative stability of the hcp and fcc crystals not only depends on the stretching stiffness of the bonds ξ , but also on the value of the fusion parameter Γ , which (in a way) measures the bending stiffness of the chain. To illustrate this, the percentage difference of the liquid densities at freezing between the fcc and hcp lattices is given as a function of ξ/σ for different values of the fusion parameter Γ in Fig. 2. The values of Γ used here are chosen arbitrarily to represent the full range of the fusion parameter. For large Γ or large ξ , there is no significant difference between the two close-packed structures. The influence of the fusion parameter on the relative stability of two crystal types becomes evident from a comparison of the results for $\Gamma=3.25$ (when the fcc structure is more stable at $0.1 \leq \xi/\sigma \leq 0.6$) and the results for $\Gamma=5$ (when the hcp structure is favorable for $\xi/\sigma \leq 0.6$).

It is important to point out that the somewhat erratic dependence of the freezing density on the bond stiffness is not caused by numerical errors, but by so-called lattice frustration effects. These are especially prominent when the bonds are stiff, and are caused by a geometrical mismatch between the effective bond length and the distance between two neighboring lattice sites. We refer to Refs. 21 and 22 for a closer examination of this phenomenon for the fcc model polymeric solid. Note that the hcp lattice, being less symmetric than the fcc lattice, the effects of the lattice frustration for a given ξ or Γ are different and that (in effect) lattice frustration dictates which lattice is more stable than the other. So, the geometrical factors other than those due to the shape of the interacting moieties can play an important role in the stability of the polymer crystal. For realistic models of polymers such as polyethylene, the parameter ξ/σ is in order of 0.01,²¹ and at this regime the hcp structure seems to be more favorable.

In summary, we have investigated the relative stability of the fcc and hcp crystal types for idealized model polymers using polymeric density functional theory.²¹ We conclude from our studies that the most favorable lattice type of the two is determined by both the stiffness of the polymeric bonds and by the fusion parameter. Therefore, we propose that in addition to, say, enthalpic interactions, connectivity does play a significant role in the crystal structure of polymers, and that this is one possible explanation for the diversity of crystal lattices observed for polymers.

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