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Density-functional theory of the crystallization of hard polymeric chains

Nazar Sushko,^{a),b)} Paul van der Schoot,^{a)} and M. A. J. Michels^{a)}
Dutch Polymer Institute, P. O. Box 902, 5600 AX Eindhoven, The Netherlands

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We study how connectivity influences the crystallization of fully flexible model polymers by applying a recently advanced amalgamation of the Green-function description of polymers, and the density-functional theory of simple liquids. Our calculations show that the model polymers only crystallize if the effective Kuhn length of the chains is sufficiently large compared with the range of the hard-core interaction between the segments. Also shown is the importance of bond-length fluctuations for the stability of the crystal phase. © 2001 American Institute of Physics.
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I. INTRODUCTION

The crystallization of polymers is still poorly understood, despite intense research spanning many decades. A likely reason for this may be the importance of kinetic effects, which seem to predominate the crystallization of polymers.¹ It is not surprising, then, that a great effort has been put in studying this particular aspect of the problem, and less so the thermodynamic driving force leading the polymeric melt to the crystalline state. This is unfortunate, however, since a meaningful kinetic theory is difficult to set up without a reliable statistical-thermodynamic description of the problem at hand. Indeed, as has become clear from recent discussions,² the presence of metastable states may play an important role in selecting kinetic pathways. The aim of this paper is first and foremost to create an understanding of how chain connectivity affects the stability of the crystal phase. As we shall see below, unconnected monomers appear to be easier to crystalline than freely hinged model polymers. This implies that angular correlations could play a more prominent role in promoting polymer crystallization than is often thought. The effects of angular correlation will be studied in a forthcoming publication.

Before going into the details of our calculations, let us briefly summarize the state of the art. There are essentially three modes of attack in dealing with the thermodynamics of the freezing transition in polymeric systems. These are the lattice-based models, the Landau-de Gennes types of approach and density-functional theories. Of these, the most well known are the lattice-based theories pioneered by Flory.³ He developed a simple mean-field theory to deal with the effect of interchain interactions, in combination with a (simplified) isomeric state model for the description of the loss of configurational free energy upon the freezing of the polymers. Flory found that, upon cooling, the stiffness of the chains increases, which, due to a concomitant increase in volume exclusion, in turn induces the transition to the crys-

talline state. Within the Flory theory the phase transition is entropically driven, and attractive interactions only perturb the location of the transition.⁴ Another important conclusion to be drawn from the Flory theory is (at least in solution) that stiffer chains crystallize more readily than flexible ones, in accord with recent computer simulations⁵ but also with experimental fact.⁶

The advantage of the Flory theory is its simplicity. The theory remains conceptually important in that it has drawn attention to the relevance of both packing effects and chain configurations. At the same time the Flory theory has a serious drawback, namely that when the fraction of lattice sites occupied by the polymers is set equal to unity, it cannot predict a density jump at the crystallization transition. Another problem is that it is not self-consistent in the sense that order is introduced on the lattice by hand.

Another interesting approach is due to Olmsted and co-workers.² Using the Landau-de Gennes theory of phase transitions, they proposed a simple phenomenological theory to explain the spinodal kinetics sometimes found in small-angle x-ray scattering experiments after a quench to the crystalline state. They proposed a coupling between the density and the conformational state of the chains, leading to a metastable liquid-liquid spinodal within the equilibrium liquid-to-crystalline solid coexistence region. Although useful, the theory provides no microscopic picture of the crystallization process. Indeed, information about the polymeric nature of the material is only put in via a phenomenological equation of state.²

Perhaps the most promising way to accurately describe both the thermodynamics of polymer crystallization and the structure of the crystal phase is given by the powerful tool known as density-functional theory (DFT), pioneered by Ramakrishnan and Yussouff⁷ for monatomic liquids. McCoy *et al.*⁴ applied the polyatomic density-functional theory developed by Chandler, McCoy, and Singer^{8,9} to chemically realistic polymeric systems. For the description of the melt phase they used a polymer reference interaction site model or PRISM,¹⁰⁻¹² whilst the crystal phase was described in a local-density type of approximation.^{13,14} The agreement of the theory with experimental data on the densities at which the polymers polyethylene and polytetrafluoroethylene crys-

^{a)}Also at: Polymer Physics Group, Department of Applied Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

^{b)}Electronic mail: n.b.sushko@phys.tue.nl

tallize was quite remarkable. Somewhat less good was the predicted phase gap, which was overestimated by a factor of about 3, as well the temperature dependence of the density. Also, the rather large discrepancy between the theoretical and experimental lattice parameters should cause some concern. We speculate that it could well be the lack of coupling between the positional and orientational degrees of freedom and the phantom nature of the bonds that is at the root of the problem.¹⁵

Our aim is not directly to improve on the work of McCoy and co-workers,⁴ although our approach does go beyond PRISM as it treats the melt and crystal phase on an equal footing. Rather, our aim is first to try to attack the problem in a limit that is consistent with the model assumptions of that work, and study the bare effects of connectivity. This has not been done before at the level of a density-functional theory. Although the model polymers we employ are unrealistic at small length scales, and we do take a step back from experiment, our approach intends to act as a stepping stone to come to a more realistic description of actual polymeric systems. Ultimately, we intend to extend our theory to include bond correlations, which within a PRISM-type theory is much more cumbersome.¹⁵

The remainder of this paper is organized as follows. In Sec. II we first briefly describe the model polymers considered. The formalism which we use for our calculations is explained in Sec. III. Section IV discusses the description of the polymeric melt and Sec. V that of the crystal phase. The calculation method is explained in Sec. VI. The results of our numerical calculations are represented in Sec. VII, and conclusions are presented in Sec. VIII. Some of the details of our derivations are explained in the Appendixes A and B.

II. MODEL

Since our aim is to study the role of connectivity in polymer crystallization, we focus on simple, coarse-grained polymer models, in particular the Gaussian-chain model, the freely hinged-chain model and an intermediate model that interpolates (in a way) between these two. The model chains are thought to consist of N identical segments, which in the Gaussian model are connected by Hookean springs with a root-mean-square extension a , in the freely hinged model by rigid links of fixed length l , and in the intermediate model by links of root-mean-square length b . The step length of the intermediate model b itself depends on a mean bond length l and root-mean-square deviation ξ via $b = \sqrt{l^2 + \xi^2}$. For $\xi \ll l$ this intermediate model turns into freely hinged chain model, and for $\xi \gg l$ into the standard Gaussian chain model with ξ playing the role of a . All models behave like random-flight chains in the long-chain limit, so for convenience we put $l_K \equiv a \equiv l \equiv b$, with l_K the Kuhn length of the chains. Note that this provides a reasonable description of the chains in the melt, for intrachain correlations are screened and the chains behave ideally. As we shall see later, in Sec. VII, varying the stiffness of the bond of the intermediate model allows us to study the effects of lattice frustration.

The pair interactions between the segments are modeled by a simple hard-core repulsive potential of range σ , inde-

FIG. 1. Schematic diagram of the influence of the segment fusion parameter $\Gamma \equiv l_K / \sigma$ on the model polymer. When $\Gamma > 1$ there is no overlap of neighboring segments within the chain (a), for $\Gamma < 1$ the segments “fuse” (b).

pendent of the segment ranking numbers, and independent of the chain configurations. The range of the potential need not be the actual diameter of the hard-sphere segments, because connectivity (in a way) renormalizes the pair interaction.¹⁶ To be able to study the influence of this renormalization, we introduce a *segment fusion parameter* defined as

$$\Gamma \equiv l_K / \sigma. \quad (1)$$

As it is unclear how connectivity renormalizes the local interaction, we keep Γ as a free parameter. Figure 1 makes clear why Γ may indeed be called fusion parameter; if $\Gamma > 1$ the hard cores of the neighboring segments along a chain do not overlap, whereas if $\Gamma < 1$ they do.

The polymeric model system is fully described by the fusion parameter Γ , the number of segments per chain N , and the effective packing fraction of the segments $\phi = \pi \rho \sigma^3 / 6$, where ρ denotes the number density of the segments. In the melt, the segments are (in the mean) homogeneously distributed, and the bonds connecting the segments randomly oriented. Because the interaction potential is isotropic and of the pair type, and because the links freely hinged, orientational bond-order correlations cannot build up. As a consequence, although in the crystal phase the segments do crystallize, i.e., order positionally, there cannot be any associated long-range bond ordering within our model description. In other words, the chains in the crystal phase behave like random flights on a lattice. Although physically inaccurate, it is consistent within our treatment, and allows us to focus on the effects of connectivity alone.

In the following we first explain the general formalism with which we attack the problem in hand, and next describe how we apply this theory to describe the melt and crystal phases. Our treatment of the melt turns out to be equivalent to the so-called polymer reference interaction site model or PRISM theory, while that of the crystal is a DFT-type theory with corrections for bond connectivity. Those readers not interested in the technical details we refer directly to the results of our calculations presented in Sec. VII.

III. FORMALISM

In the mean-field approximation, the partition function $\mathcal{Z}$ of a collection of M polymeric chains of N segments in a volume V is given by the product of the single-chain partition functions Z_N

$$\mathcal{Z} = \frac{1}{M!} Z_N^M. \quad (2)$$

The single-chain partition function can be written as the spatial integral over the positions of the ends of a single chain

$$Z_N = \int d\mathbf{r} \int d\mathbf{r}' Z(\mathbf{r}', \mathbf{r}; N), \quad (3)$$

with $Z(\mathbf{r}', \mathbf{r}; N)$ the (conditional) partition function of a chain of N segments of which the ends are fixed at the positions $\mathbf{r}$ and $\mathbf{r}'$. The latter quantity is often referred as the Green function of the polymer,¹⁷ and satisfies the following recursive equation:

$$Z(\mathbf{r}', \mathbf{r}; N+1) = \exp[-U_{\text{scf}}(\mathbf{r})(\mathbf{r})] \hat{g} Z(\mathbf{r}', \mathbf{r}; N). \quad (4)$$

Here, $U_{\text{scf}}(\mathbf{r})$ denotes the self-consistent, molecular field a chain experiences from the presence of the other chains, and $\hat{g}$ the so-called step operator.¹⁸

If $f(\mathbf{r})$ is an arbitrary integrable function, the step operator is defined as

$$\hat{g}f(\mathbf{r}) \equiv \int d\mathbf{r}'' g(\mathbf{r}, \mathbf{r}'') f(\mathbf{r}''), \quad (5)$$

with the kernel $g(\mathbf{r}, \mathbf{r}')$ the *a priori* probability that a bond that starts at $\mathbf{r}''$, ends at $\mathbf{r}$. For the standard Gaussian chain in three spatial dimensions,¹⁸

$$g(\mathbf{r}, \mathbf{r}') = g_G(\mathbf{r} - \mathbf{r}') \\ = (2\pi l_K^2/3)^{-3/2} \exp[-3(\mathbf{r} - \mathbf{r}')^2/2l_K^2], \quad (6)$$

whilst for the freely hinged chain¹⁸

$$g(\mathbf{r}, \mathbf{r}') = g_{fh}(\mathbf{r} - \mathbf{r}') = \frac{1}{4\pi l_K^2} \delta(|\mathbf{r} - \mathbf{r}'| - l_K). \quad (7)$$

For the intermediate model we take the convolution $g_i(\mathbf{r}) \equiv g_G \circ g_{fh}(\mathbf{r}) \equiv \int d\mathbf{r}'' g_{fh}(\mathbf{r} - \mathbf{r}'') g_G(\mathbf{r}'')$ or the kernel of a freely hinged model with a bond length l and that of a Gaussian model with root-mean-square bond length ξ , giving

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

Note that for all models $g(\mathbf{r}, \mathbf{r}')$ is normalized, i.e., $\hat{g}1 \equiv 1$, and that the “initial” condition associated with the operator equation (4) is $Z(\mathbf{r}', \mathbf{r}; 1) \equiv \delta(\mathbf{r}' - \mathbf{r})$.

In units of thermal energy, the free energy of our system of chains is given by

$$F = -\ln \mathcal{Z}, \quad (9)$$

which at this point is still an implicit function of the as yet unknown molecular field U_{scf} . The molecular field may be fixed by following a procedure pioneered by Lifshitz.¹⁹ First, we subtract from Eq. (9) the internal energy of the system, to give the contribution of the configurational free energy, F_{conf} , to the free energy

$$F_{\text{conf}} = F - \int d\mathbf{r} U_{\text{scf}}(\mathbf{r}) \rho(\mathbf{r}). \quad (10)$$

Here, $\rho(\mathbf{r})$ denotes the number density of segments, itself a functional of the conditional partition function

$$\rho(\mathbf{r}) \equiv NMZ_N^{-1} \int d\mathbf{r}' \int d\mathbf{r}'' \sum_{s=1}^N Z(\mathbf{r}', \mathbf{r}; s) Z(\mathbf{r}, \mathbf{r}''; N). \quad (11)$$

The next step is to surmise that actual free energy F must be the sum of Eq. (10) and an excess free energy F_{exc} describing the interactions between the segments and a possible coupling to an external field

$$F = F_{\text{conf}} + F_{\text{exc}}. \quad (12)$$

For any choice of F_{exc} , we can establish the conditions for phase coexistence by subsequently equating the chemical potentials $\mu = \delta F / \delta \rho(\mathbf{r})$ and the pressures $P = -F + \mu \int d\mathbf{r} \rho(\mathbf{r})$ of both phases. This, however, is not straightforward, for we would have to solve Eqs. (3)–(12) self-consistently. A much more efficient way to achieve the same, is to make the connection with liquid-state (integral equation) theory. As will become clear below, we then do not need to specify F_{exc} of the melt state. The free energy of the crystal state relative to that of the melt can be calculated perturbationally from that of the melt using the theory described above.

IV. DESCRIPTION OF THE MELT

To make the connection with liquid-state theory, we seek to derive an Ornstein–Zernike-type equation between the total correlation function of two segments on different chains $h(\mathbf{r}, \mathbf{r}')$, and the associated two-particle direct correlation function $C^{(2)}(\mathbf{r}, \mathbf{r}') \equiv -\delta^2 F_{\text{exc}} / \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')$. This is possible by calculating the response of the density field to an externally applied potential, and linking the response function to the static structure factor with the help of the well-known Yvon equation.¹⁵ We find that the so-called polymeric reference interaction site model or PRISM equation is consistent with the formalism described in the previous Sec. III. See Ref. 15 or the Appendix A for details. This equation reads in Fourier space

$$\hat{h}(\mathbf{q}) = \hat{\omega}^2(\mathbf{q}) \hat{C}^{(2)}(\mathbf{q}) + \rho_L \hat{\omega}(\mathbf{q}) \hat{C}^{(2)}(\mathbf{q}) \hat{h}(\mathbf{q}), \quad (13)$$

where the hats indicate Fourier-transformed quantities, $\mathbf{q}$ the wave vector and ρ_L the average melt density. The intramolecular correlations between segments on a single chain are described by the form factor $\hat{\omega}$, which depends on the model used. For the models under consideration²⁰

$$\hat{\omega}(q) = \frac{1 - \hat{g}^2 - \frac{2}{N} \hat{g} + \frac{2}{N} \hat{g}^{N+1}}{(1 - \hat{g})^2}, \quad (14)$$

where $q \equiv |\mathbf{q}|$ and $\hat{g}_G(q) \equiv \exp(-q^2 l_K^2/6)$ for the Gaussian model, $\hat{g}_{fh}(q) \equiv q^{-1} l_K^{-1} \sin ql_K$, for the freely hinged chain, and $\hat{g}_i(q) \equiv q^{-1} l^{-1} \sin ql \exp(-q^2 \xi^2/6)$ for the intermediate model. The last expression follows from the standard properties of the Fourier transform of the convolution of two functions.

Equation (13) has to be implemented by a suitable closure. We use the well-known Percus–Yevick or PY closure, which was quite successfully applied by various authors to describe the structure of polymeric melts.^{4,10} The PY closure is defined by

$$\begin{aligned} h(|\mathbf{r}| < \sigma) &= -1 \\ C^{(2)}(|\mathbf{r}| > \sigma) &= 0 \end{aligned} \quad (15)$$

and describes hard-core interactions between the segments. With this closure, the PRISM integral equation (13) can be solved self-consistently. We applied the algorithm put forward by Honnell *et al.*,²¹ by assuming the direct correlation function to be a cubic polynomial, and solving numerically the system of nonlinear algebraic equations for the expansion coefficients. For this system of nonlinear equations we used standard modification of the Powell hybrid method from the NAG[®] library (Mark 18, C05NBF). With the coefficients so obtained we calculated the direct correlation function.

V. DESCRIPTION OF THE CRYSTAL

To describe the crystal phase, we use an extension of the standard density-functional theory (DFT), set up within the local-density approximation (LDA) developed by Ramakrishnan and Yussouff,⁷ and by Haymet and Oxtoby,²² for monatomic liquids in the context of the freezing of hard spheres.^{23,24} The DFT can be derived from the theory of Sec. III. We refer to the Refs. 7, 23–25 for details regarding the estimate of the excess free energy. The modification of the usual ideal free energy functional, needed to deal with the connectivity of the polymers, is outlined in the Appendix B. Within our treatment, only those chain-connectivity corrections are included that are of leading order in the density modulation.

The expansion of the free energy gives us for the grand potential of the crystal relative to that of the melt

$$\Delta\tilde{\Omega} = \Delta F - \int d\mathbf{r} [\mu_S \rho_S - \mu_L \rho_L], \quad (16)$$

where ΔF is the difference in the Helmholtz free energies of the crystal and melt phases, μ_S the chemical potential of the crystal and μ_L the chemical potential of the reference state (the melt); ρ_S is the mean density of the crystal phase and ρ_L as before that of the melt. ΔF can be written as $\Delta F = \Delta F_{\text{conf}} + \Delta F_{\text{exc}}$. As it turns out, at length scales relevant to the crystallization of the beads, ΔF_{conf} can be written as the sum of an ideal entropy of unconnected beads, and corrections coming from the connectivity of the beads.

Using standard DFT for ΔF_{exc} , which is identical to that of hard-sphere systems, and using the results of the Appendix B, we find

$$\begin{aligned} \Delta\hat{\omega} &\equiv \frac{\Delta\tilde{\Omega}}{\rho_L V} = \frac{1}{\rho_L V} \int d\mathbf{r} \{ \rho(\mathbf{r}) \ln \rho(\mathbf{r}) / \rho_L - \Delta \} \\ &\quad - \frac{1}{2\rho_L V} \sum_{p=2}^{\infty} \frac{1}{p!} \int \cdots \int C^{(p)}(\mathbf{r}_1, \dots, \mathbf{r}_p) \\ &\quad \times \prod_{i=1}^p d\mathbf{r}_i (\rho(\mathbf{r}_i) - \rho_L) - (\mu_S - \mu_L) \\ &\quad \times \frac{1}{\rho_L V} \int d\mathbf{r} \rho(\mathbf{r}) - \frac{1}{\rho_L V} \int d\mathbf{r} (\rho(\mathbf{r}) - \rho_L), \end{aligned} \quad (17)$$

with $C^{(p)}(\mathbf{r}_1, \dots, \mathbf{r}_p) = -\delta^{(p)} F_{\text{exc}} / \prod_{i=1}^p \delta \rho(\mathbf{r}_i)$ the p -particle direct correlation function of the melt. One recognizes in the first term on the right the usual ideal entropy. The next term Δ enters due to the existence of the (phantom) bonds. We find to quadratic order in density modulations

$$\Delta = \frac{1}{\rho_L} \int d\mathbf{r}' g(\mathbf{r}, \mathbf{r}') [\rho(\mathbf{r}) - \rho_L] [\rho(\mathbf{r}') - \rho_L], \quad (18)$$

with g as before the kernel of the step operator. The other terms are connected with the excess free energy and mass conservation. We truncate the summation involving the direct correlation functions after the second term, because higher-order terms are presumably negligibly small. Indeed, they are known to be small for hard spheres.²²

VI. CALCULATION METHOD

For reasons of computational convenience we do not use the exact density distribution, obtained by minimizing the free energy, but rather approximate it by a sum of Gaussians,

$$\rho(\mathbf{r}) = (\pi\epsilon^2)^{-3/2} \sum_{\{\mathbf{R}_n\}} \exp[-(\mathbf{R}_n - \mathbf{r})^2/\epsilon^2], \quad (19)$$

where we assume the crystal to be face-centered cubic. (We found that of all cubic lattices only the FCC lattice supports a stable solid phase for our model polymers, in common with systems of hard spheres.²⁴) In Eq. (19), $\{\mathbf{R}_n\}$ denotes all the real-space crystal-lattice vectors, and ϵ is a measure of the width of the Gaussian density distribution around each lattice point. The latter we fix by a free-energy minimization. As usual, the density modulations are assumed to be non-overlapping.^{23,26–28} It turns out to be useful to express the density modulations in their Fourier components $\zeta(\mathbf{k}_n)$ ²³

$$\rho(r) = \rho_L \left[1 + \eta + \sum_{\{\mathbf{k}_n\}} \zeta(\mathbf{k}_n) \exp^{i\mathbf{k}_n \cdot \mathbf{r}} \right], \quad (20)$$

with $\{\mathbf{k}_n\}$ the set of reciprocal lattice vectors of the FCC crystal, and $\eta = (\rho_S - \rho_L)/\rho_L$ the relative density jump across the crystallization transition. In the Gaussian approximation to the density profile we have

$$\zeta(\mathbf{k}_n) = (1 + \eta) \exp -\mathbf{k}_n^2 \epsilon^2 / 4. \quad (21)$$

Equation (17) now simplifies to

FIG. 2. Packing fractions ϕ of the co-existing melt and crystal phases of the Gaussian model chains as a function of the fusion parameter $\Gamma = l_K/\sigma$. The chain length is $N=100$. Also shown are the results for hard spheres (the HS limit, $N=1$, indicated by the dotted lines).

$$\Delta\tilde{\omega} = 1 - (1 + \eta) \left[\frac{5}{2} + \ln \rho_L + \frac{3}{2} \ln \pi \epsilon^2 \right] - \eta^2$$

$$\begin{aligned} & - \sum_{\{\mathbf{q}_n\}} \hat{g}(\mathbf{q}_n) \zeta^2(\mathbf{q}_n) - (1 + \eta)(\mu_S - \mu_L) \\ & - \frac{1}{2} \eta^2 \rho_L \hat{C}_L^{(2)}(0) \\ & - \frac{1}{2} \rho_L \sum_{\{\mathbf{q}_n\}} \zeta^2(\mathbf{q}_n) \hat{C}_L^{(2)}(|\mathbf{q}_n|) - \frac{1}{6} \eta^3 \rho_L^2 \hat{C}_L^{(3)}(0,0). \end{aligned} \quad (22)$$

The summation in Eq. (22) is over all reciprocal lattice vectors $\mathbf{q}_n$.

In Eq. (22) we neglected four-body and higher-order correlation functions, and approximated the three-body one by its value at zero wave vector. It exactly obeys²³

$$\hat{C}_L^{(3)}(q,0) = \left. \frac{\partial \hat{C}_L^{(2)}(q)}{\partial \rho} \right|_{\rho=\rho_L}. \quad (23)$$

Only the zero- $\mathbf{q}$ part of $\hat{C}_L^{(3)}$ is included in Eq. (22), because Haymet²² has shown that, at least for hard spheres, the non-zero $\mathbf{q}$ contributions of $\hat{C}_L^{(3)}$ tend to cancel each other.

For a fixed value of the parameter Γ , the free energy Eq. (22) is a function of three quantities: The width ϵ of the density profile, and the mean densities ρ_S and ρ_L . Conditions for phase coexistence are found by setting $\mu_L = \mu_S$ in Eq. (22), minimizing $\Delta\tilde{\omega}$ with respect ϵ and η , and finding the value of ρ_L for which $\Delta\tilde{\omega}=0$. This way we ensure a balancing of the pressures of both phases, $P_L = P_S$, because in equilibrium $\Delta\Omega = -V(P_L - P_S)$. We found the minimum of the function $\Delta\tilde{\omega}$ using a standard quasi-Newton algorithm from the NAG[®] library (Mark 18, E04JYF). We used 5832 reciprocal lattice vectors and varied ρ_L with a step length of 10^{-5} units. We verified that this is quite sufficient to get a stable result for the minimum of $\Delta\tilde{\omega}$.

VII. RESULTS AND DISCUSSION

We now present the results of our calculations. Figure 2 shows the calculated phase diagram of the hard Gaussian chains for the $N=100$. Indicated is the (dimensionless) packing fraction $\phi = \pi \rho \sigma^3/6$ at the melt-crystal phase coexistence as a function of the fusion parameter Γ . For comparison

FIG. 3. Packing fraction ϕ of the co-existing melt and crystal phases of Gaussian model chains as a function of the chain lengths N . The fusion parameter was fixed at a value of $\Gamma=3.5$.

we have also indicated the results for hard spheres ($N=1$). The figure clearly shows that in the limit $\Gamma \rightarrow \infty$ the chains crystallize at the same density as hard spheres do. From Eq. (22) we understand that the reason for this is that all polymeric corrections become negligibly small in this regime, because these contain a function which decays fast with increasing values of Γ . Indeed, neighboring beads along a chain are then so far removed from each other on the crystal lattice that they no longer feel the influence of the connectivity. Packing effects dominate in this regime.

Lowering Γ we observe that the solidification density goes up. In other words, it becomes more difficult for the chains to crystallize. In fact, for $\Gamma \lesssim 3.25$ a crystal phase is no longer found for densities below close packing. The difficulty of crystallizing Gaussian chains in the low- Γ range was in fact already observed by McCoy and co-workers, and was attributed to the enormous amount of entropy stored in the melt.⁴ Contrary to a previous conclusion by one of us,¹⁵ the results of Fig. 2 seem to bear out this conclusion.

Shown in Fig. 3 is the dependence on the length of the polymers of the densities at phase coexistence, again for the Gaussian model at fixed $\Gamma=3.5$. Apparently, ϕ_L and ϕ_S quickly saturate with increasing degree of polymerization. Apparently, shorter chains are easier to crystallize, in accord with experimental observation.⁶ A possible cause of this is that in our model calculations the configurational fluctuations and therefore also the entropy of the chains in the melt increase with increasing N .

Figure 4 shows the dependence of the Lindemann ratio L on the fusion parameter Γ . This ratio is defined as the root-mean-square deviation of the position of a particle from its lattice site divided by the nearest-neighbor distance. It is usually thought that if the Lindemann ratio of a crystal phase drops below 0.1, this crystal melts.²⁹ The value of Lindemann ratio saturates for large Γ at $L \approx 0.063$, what roughly corresponds to the hard-sphere result.²³ For small Γ the densities at co-existence are higher, so one would expect

FIG. 4. Lindemann ratio of the model polymer as a function of the segment fusion $\Gamma \equiv l_K / \sigma$. The chain length is $N = 100$.

L to go down as there is less room for the beads to fluctuate around their lattice sites.

Results for the Gaussian and freely hinged models are compared in Fig. 5. Both models show a saturation of the crystallization density for large Γ , albeit that the results for the freely hinged model do exhibit a seemingly irregular oscillatory behavior that we attribute to the effects of lattice frustration (explained in more details below).³⁰ We found the crossover to hard-spherelike behavior for the freely hinged model to occur at much larger Γ than for the Gaussian model. Note that both models predict the crystal phase to become absolutely unstable below a critical value of Γ , 3.25 for the Gaussian model and 2.45 for the freely hinged model. The oscillatory behavior of the freely-hinged model is zoomed on in the Fig. 6, showing that the oscillations are not as erratic as they appear in on Fig. 5. We have indications that this behavior is caused by the interference of the properties of the crystal lattice and those of the polymeric chains. Indeed, if we rely on the Verlet rule³¹ to estimate the solidi-

FIG. 5. Packing fraction ϕ at freezing as a function of the fusion parameter Γ . Compared are results obtained for the Gaussian model, and those for the freely hinged model. Also indicated are results for hard spheres (HS , $N = 1$).

FIG. 6. Packing fraction ϕ at freezing, as a function of the fusion parameter Γ for the freely hinged model with a higher resolution than given in the Fig. 5. Also indicated are results for hard spheres (HS , $N = 1$).

fication density, which uses only information on the structure of the melt, we retrieve the long-wavelength oscillations visible in the results of Fig. 6, (see also Fig. 9).

That lattice frustration effects become important for stiff bonds is shown in Fig. 7. The figure shows our results for the intermediate model for different values of the degree of bond stiffness ξ . The transition in behavior between the floppy Gaussian and the completely stiff freely hinged models is clearly seen. For small ξ the bonds are stiff, leading to an oscillatory dependence of the packing density at freezing on the fusion parameter Γ , similar to that found for the freely hinged model. If ξ is sufficiently large the dependence of the freezing density on the fusion parameter becomes smoother, and we retrieve a Gaussian-type behavior. The transition occurs roughly when $\xi \sim \epsilon$, i.e., when root-mean-square deviation ξ is comparable to the width of the density field around a lattice site.

That lattice frustration may cause the freezing density of freely hinged chains with a degree of bond stiffness $\xi < \epsilon$ to

FIG. 7. Packing fraction ϕ at freezing as a function of the fusion parameter Γ . Compared are results obtained for the intermediate model for the different value of the degree of the stiffness ξ . Also indicated are results for hard spheres (HS , $N = 1$).

FIG. 8. Illustration of the lattice frustration effect. When the length of the polymeric bond l_K is less than the distance between two neighboring lattice points in a nearly close-packed crystal, what is always the case when $\Gamma = l_K/\sigma \lesssim d/\sigma \approx 1$, the system will find it very hard to crystallize because it would have to stretch the bonds. When $\Gamma \gtrsim 1$, a different type of lattice frustration takes over. If the bonds cannot (in the mean) find two sites conjugate to their length, i.e., two sites separated by a multiple bond length, the system has to either stretch or compress the bonds, or to adjust its density to change the lattice constant to the point where it does become possible to fit in the bonds. In the freely-hinged model, the bond length cannot be adjusted, only the density. The associated lattice-adjustment effect leads to the seemingly erratic dependence of the crystal density on the fusion parameter discussed in the main text.

vary abruptly with varying Γ may be understood as follows. The optimal lattice distance is obviously set by the density and by the hard-core diameter σ . When the length of a bond does not fit the distance between two lattice points and the bonds are very stiff, the system must crystallize at a higher or lower density, such that the bond length does indeed become conjugate to the lattice constant (Fig. 8). On the other hand, if ξ is large enough to allow for the bonds to stretch, a match accommodating the lattice may be found without abruptly changing the lattice parameter too much.

Finally, in the last Fig. 9 we demonstrate the usefulness of the phenomenological Verlet rule,³¹ applied to polymer crystallization. According to this rule, the freezing of simple liquids occurs for those conditions where the primary maxi-

FIG. 9. Packing fraction ϕ at freezing according to the Verlet rule as a function of the fusion parameter $\Gamma = l_K/\sigma$.

mum of the static structure factor of the fluid reaches the value of 2.85. Figure 9 shows that this remains approximately true for our model polymers, although the rule's accuracy does deteriorate with decreasing values of Γ (cf. Fig. 5). We have no explanation for this. As already indicated, the Verlet rule cannot reproduce the strongly oscillatory dependence of the freezing density on the fusion parameter exhibited by the freely hinged model, because it draws its information from the fluid structure, not the crystal structure.

VIII. CONCLUSION

In our density-functional theory we found model chains consisting of hard beads to be able to crystallize, but only if the effective Kuhn length exceeded the hard-core radius of the beads by a sufficient amount.

We attribute this to the circumstance that only then the loss of configurational entropy upon freezing is sufficiently low to be compensated by the increased packing entropy. The latter is the driving force for the formation of the crystal phase. When the monomeric units of the model polymers are small on the scale of the bonds, the behavior of the chains is hard-spherelike. Connectivity then plays a minor role in the crystallization of the polymeric chains. We observed that short chains crystallize more easily than long ones, because the loss of configurational entropy upon freezing is larger for long chains. This is not obvious, because in our model calculations the chains remain random walkers (albeit on a lattice), and the orientational freezing is only weak due to the lack of bond correlations.

We found lattice frustration to be important for models with sufficiently stiff bonds. This effect could play an important role in the crystallization of real polymers too, because $\xi \sim 0.01\sigma$ for realistic polymeric chain models often used in computer simulations.³² It may well be that lattice frustration effects are in part responsible for the host of crystal lattice types observed for real polymers.⁶

It seems likely that a more realistic polymeric model, one that, e.g., exhibits a finite bending energy, will stabilize the crystal phase over a larger range of bond lengths. This we investigate in future work, using the Green-function formalism rather than PRISM. The reason is that the former can be more straightforwardly extended to include bond correlations than the latter.¹⁵

APPENDIX A: PRISM AND THE GREEN-FUNCTION FORMALISM

Here we show the equivalence of the Green-function formalism and PRISM theory for isotropic polymeric models. For that purpose we switch on a position dependent external potential $\phi(\mathbf{r})$ acting on each segment. The excess free energy appearing in Eq. (12) can then be written as

$$F_{\text{exc}} = F_{\text{int}} + F_{\text{pot}}, \quad (\text{A1})$$

with $F_{\text{pot}} = \int d\mathbf{r} \rho(\mathbf{r}) \phi(\mathbf{r})$ the free energy associated with the coupling of the segments to the external potential and F_{int} the free energy associated with the interactions between the beads. Therefore, the full free energy becomes [cf. Eq. (12)]

$$F = F_{\text{conf}} + F_{\text{int}} + F_{\text{pot}}. \quad (\text{A2})$$

Minimizing Eq. (A2) we find, using Eq. (10) and the equality $\mu = \delta F / \delta \rho(\mathbf{r})$, that the self-consistent field obeys³³

$$U_{\text{scf}}(\mathbf{r}) = \phi(\mathbf{r}) + \frac{\delta F_{\text{int}}}{\delta \rho} - \mu, \quad (\text{A3})$$

where we note that U_{scf} will be treated as an external field, although obviously it is not.¹⁵ [Note also that F in Eq. (10) only becomes a functional of ρ after the minimization.] We functionally expand the second term on the right-hand side of Eq. (A3), assuming the external field to be sufficiently weak

$$\begin{aligned} \frac{\delta F_{\text{int}}}{\delta \rho} = & -C^{(1)}(\mathbf{r}) - \int d\mathbf{r}'' C^{(2)}(\mathbf{r}-\mathbf{r}'') \\ & \times \int d\mathbf{r}' \chi(\mathbf{r}''-\mathbf{r}') \phi(\mathbf{r}') + \dots, \end{aligned} \quad (\text{A4})$$

with $C^{(1)}(\mathbf{r}) \equiv C^{(1)}$ the zero-field one-particle direct correlation function (which is a constant for the homogeneous systems), $C^{(2)}(\mathbf{r}, \mathbf{r}')$ the zero-field two-particle direct correlation function, and $\chi(\mathbf{r}, \mathbf{r}') \equiv \delta \rho(\mathbf{r}) / \delta \phi(\mathbf{r}')$ the response function that we identify below with the structure factor. In Fourier space we thus find for weak fields

$$\begin{aligned} \hat{U}_{\text{scf}}(\mathbf{q}) = & \hat{\phi}(\mathbf{q}) - \mu \delta(\mathbf{q}) - C^{(1)} \delta(\mathbf{q}) - \hat{C}^{(2)}(\mathbf{q}) \hat{\chi}(\mathbf{q}) \hat{\phi}(\mathbf{q}) \\ & + \dots. \end{aligned} \quad (\text{A5})$$

The Yvon identity, which establishes the connection between the response of the density of the isotropic fluid $\hat{\delta} \rho(\mathbf{q}) = \rho(\mathbf{q}) - \rho_L \delta(\mathbf{q})$ in Fourier space and the structure factor $S(q)$, is given by

$$\hat{\delta} \rho(\mathbf{q}) = \hat{\chi}(\mathbf{q}) \hat{\phi}(\mathbf{q}) = -\rho_L S(q) \hat{\phi}(\mathbf{q}), \quad (\text{A6})$$

with ρ_L the density in the absence of the field. If we switch off the interactions and neglect the forward scattering associated with the delta peaks around $\mathbf{q}=0$,¹⁰ the self-consistent field in this case is simply $\hat{U}_{\text{scf}}(\mathbf{q}) = \hat{\phi}(\mathbf{q})$. We then find for the structure factor $S(q) = \hat{\omega}(q)$, with $\hat{\omega}(q)$ the form factor of the single chain. In other words, for noninteracting chains $\hat{\delta} \rho(\mathbf{q}) = -\rho_L \omega(q) \hat{\phi}(\mathbf{q})$. From Eq. (A5) we immediately read off that to get the response of the interacting system, we merely need to replace $\hat{\phi}(\mathbf{q})$ by $\hat{\phi}(\mathbf{q})(1 - \hat{C}^{(2)}(\mathbf{q}) \hat{\chi}(\mathbf{q})) = \hat{\phi}(\mathbf{q})(1 + \rho_L \hat{C}^{(2)}(\mathbf{q}) S(q))$, so that

$$S(q) = \frac{\hat{\omega}(q)}{1 - \rho_L \hat{C}^{(2)}(q) \hat{\omega}(q)}, \quad (\text{A7})$$

which indeed is equivalent to the PRISM equation (13). Note the similarity of our arguments with that of the standard random-phase approximation.³³ A more elaborate derivation can be found in Ref. 15.

APPENDIX B: ENTROPY OF THE CRYSTAL PHASE

In this appendix we derive the change in the configurational entropy of the chains upon freezing, based on the theory of Sec. III. Since (within our model) freezing entails only processes at short wavelengths, it is justifiable to apply the so-called ground-state approximation.¹⁸ In this approximation the spectrum is assumed to be discrete, and nonde-

generate, so that one can order the eigenvalues $\Lambda_0 > \Lambda_1 > \Lambda_2 \dots$. Retained only is the first term of the formal expansion $Z(\mathbf{r}, \mathbf{r}') = \sum_{n=0}^{\infty} \Lambda_n \psi_n^+ \psi_n - \Lambda_0^N \psi_0^+ \psi_0$, with ψ_n^+ and ψ_n the eigenfunctions of the non-Hermitian operator equations $e^{-U_{\text{scf}} \hat{g}} \psi_n = \Lambda_n \psi_n$, $\hat{g} e^{-U_{\text{scf}} \psi_n^+} = \Lambda_n \psi_n^+$. It is easy to see that $\psi_n^+ = e^{U_{\text{scf}}(\mathbf{r})} \psi_n$.¹⁸ As was argued in Ref. 15, the use of the ground-state approximation is justifiable because the direct correlation function as well as the self-consistent field are short ranged. Note that $\int d\mathbf{r} \psi_m^+(\mathbf{r}) \psi_n(\mathbf{r}) = \delta_{n,m}$, i.e., the eigenfunctions are normalized.

Multiplying both sides of the eigenvalue equation for ψ_0 with ψ_0^+ , and integrating over space, we find for the largest eigenvalue

$$\Lambda_0 = \int d\mathbf{r} \psi_0 \hat{g} \psi_0, \quad (\text{B1})$$

because of the normalization of ψ_0 and ψ_0^+ . The free energy thus becomes

$$F = -\ln \int d\mathbf{r} d\mathbf{r}' Z(\mathbf{r}, \mathbf{r}'; N) \sim MN \ln \Lambda_0, \quad (\text{B2})$$

where $MN = \int d\mathbf{r} \rho(\mathbf{r})$.

The eigenfunction in the very short wavelength limit can be obtained by recursive iteration, assuming the operator $e^{-U_{\text{scf}}(\mathbf{r}) \hat{g}}$ to represent a contraction mapping.³⁴ Although easy to prove in the Banach space of normed scaling functions $f(\mathbf{r}/\sigma)$ in three spatial dimensions, at least for $l_K/\sigma > 1$, the general proof for arbitrary integrable functions $f(\mathbf{r})$ has so far evaded us.³⁵ We truncate the recursive iterations after two iterations, giving

$$\psi_0(\mathbf{r}) \cong \frac{e^{-U_{\text{scf}}(\mathbf{r})} \hat{g} e^{-U_{\text{scf}}(\mathbf{r})}}{\int d\mathbf{r} e^{-U_{\text{scf}}(\mathbf{r})} (\hat{g} e^{-U_{\text{scf}}(\mathbf{r})})^2}. \quad (\text{B3})$$

Note that this expression obeys the normalization condition of the eigenfunctions. At the level of the ground-state approximation, the following relation now holds between the eigenfunctions and the density:

$$\begin{aligned} \rho(\mathbf{r}) = & NM \psi_0^+ \psi_0 = MN e^{-U_{\text{scf}}(\mathbf{r})} \\ & \times (\hat{g} e^{-U_{\text{scf}}(\mathbf{r})})^2 / \int d\mathbf{r} e^{-U_{\text{scf}}(\mathbf{r})} (\hat{g} e^{-U_{\text{scf}}(\mathbf{r})})^2 \end{aligned} \quad (\text{B4})$$

Conversely,

$$\psi_0(\mathbf{r}) = (MN)^{-1/2} e^{-U_{\text{scf}}(\mathbf{r})/2} \rho^{1/2}(\mathbf{r}), \quad (\text{B5})$$

so that

$$U_{\text{scf}}(\mathbf{r}) = -\ln \rho(\mathbf{r}) + \ln \frac{NM (\hat{g} \rho(\mathbf{r}))^2}{\int d\mathbf{r} \rho(\mathbf{r}) (\hat{g} \rho)^2}. \quad (\text{B6})$$

The largest eigenvalue obeys

$$\Lambda_0 = \frac{1}{NM} \int d\mathbf{r} \rho(\mathbf{r}) \hat{g} \rho(\mathbf{r}'). \quad (\text{B7})$$

Using the Lifshitz procedure implied in Eq. (10) we obtain¹⁹

$$F_{\text{conf}} = MN \ln \Lambda_0$$

$$- \int d\mathbf{r} \rho(\mathbf{r}) \left(-\ln \rho(\mathbf{r}) + \ln \frac{NM(\hat{g}\rho)^2}{\int d\mathbf{r} \rho(\mathbf{r})(\hat{g}\rho)^2} \right). \quad (\text{B8})$$

Expansion of the density around the liquid state $\rho(\mathbf{r}) = \rho_L + \Delta\rho(\mathbf{r})$, we find

$$\Lambda_0 \approx (MN)^{-1} \int d\mathbf{r} \hat{g}(\rho_L^2 + \Delta\rho(\mathbf{r})\Delta\rho(\mathbf{r})) + \dots, \quad (\text{B9})$$

or equivalently,

$$\ln \Lambda_0 = \ln \rho_L + \frac{1}{\rho_L V} \int d\mathbf{r} \Delta\rho(\mathbf{r}) \hat{g} \Delta\rho(\mathbf{r}) + \dots. \quad (\text{B10})$$

Neglecting the terms of higher than second order in $\Delta\rho$, we get for the free energy of setting up density modulations in a homogeneous melt

$$\Delta F_{\text{conf}} = \int d\mathbf{r} \rho(\mathbf{r}) \ln \rho(\mathbf{r}) - \int d\mathbf{r} \rho_L \ln \rho_L - \frac{1}{\rho_L} \int d\mathbf{r} \Delta\rho(\mathbf{r}) \hat{g} \Delta\rho(\mathbf{r}) + O(\Delta\rho^3). \quad (\text{B11})$$

For a homogeneous liquid, this expression becomes equal to zero as it should. Equation (B11) is only valid at small length scales relative to the size of the chains.

¹A. Keller and G. Goldbeck-Wood, in *Comprehensive Polymer Science*, edited by S. L. Aggarwal and S. Russo, Suppl. Vol. II (Pergamon, Oxford, 1996).

²P. D. Olmsted, W. C. K. Poon, T. C. B. McLeish, A. J. Ryan, and N. J. Terrill, *Phys. Rev. Lett.* **81**, 373 (1998).

³P. J. Flory, *Proc. R. Soc. London, Ser. A* **234**, 60 (1956).

⁴J. D. McCoy, K. G. Honnell, K. S. Schweizer, and J. G. Curro, *J. Chem. Phys.* **95**, 9348 (1991).

⁵J. M. Polson and D. Frenkel, *J. Chem. Phys.* **109**, 318 (1998).

⁶U. W. Gedde, *Polymer Physics* (Chapman and Hall, London, 1992).

⁷T. V. Ramakrishnan and M. Yussouff, *Phys. Rev. B* **19**, 2775 (1979).

⁸D. Chandler and S. J. Singer, *J. Chem. Phys.* **85**, 5971 (1986); **85**, 5977 (1986).

⁹J. D. McCoy, S. J. Singer, and D. Chandler, *J. Chem. Phys.* **87**, 4853 (1987).

¹⁰K. S. Schweizer and J. G. Curro, *Phys. Rev. Lett.* **58**, 246 (1987).

¹¹J. G. Curro and K. Schweizer, *J. Chem. Phys.* **87**, 1842 (1987).

¹²D. Chandler, Y. Singh, and D. Richardson, *J. Chem. Phys.* **57**, 1930 (1972).

¹³D. E. Sullivan, *Phys. Rev. B* **20**, 3991 (1979).

¹⁴D. E. Sullivan, *J. Chem. Phys.* **74**, 2604 (1981).

¹⁵P. van der Schoot, *Macromolecules* **33**, 8497 (2000).

¹⁶K. G. Honnell and C. K. Hall, *J. Chem. Phys.* **90**, 1841 (1998).

¹⁷S. F. Edwards, *Proc. Phys. Soc. London* **85**, 613 (1965).

¹⁸A. Yu. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (AIP, New York, 1994).

¹⁹I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, *Rev. Mod. Phys.* **50**, 683 (1978).

²⁰K. S. Schweizer and J. G. Curro, *Adv. Polym. Sci.* **116**, 319 (1994).

²¹K. G. Honnell, J. G. Curro, and K. S. Schweizer, *Macromolecules* **23**, 14 (1990); **23**, 3496 (1990).

²²A. D. J. Haymet and D. W. Oxtoby, *J. Chem. Phys.* **74**, 2559 (1981).

²³B. B. Laird, J. D. McCoy, and A. D. J. Haymet, *J. Chem. Phys.* **87**, 5449 (1987).

²⁴M. Baus and J. L. Colot, *Mol. Phys.* **55**, 653 (1985).

²⁵L. Verlet, *Phys. Rev.* **163**, 201 (1968).

²⁶G. Jones and U. Mohanty, *Mol. Phys.* **54**, 1241 (1985).

²⁷P. Tarazona, *Phys. Rev. A* **31**, 2672 (1985); *Phys. Rev. A* **32**, 3148 (1985).

²⁸R. L. Jacobs, *J. Phys. C* **16**, 273 (1983).

²⁹J. P. Hansen and I. R. McDonalds, *Theory of Simple Liquids* (Academic, New York, 1986).

³⁰We have of course verified that numerical errors are not the cause of the oscillatory behavior found for the freely-hinged model, by varying the precision of integration, the number of the reciprocal lattice vectors and the discretization of the variable ρ_L .

³¹J. P. Hansen and L. Verlet, *Phys. Rev.* **184**, 151 (1969).

³²H. Takeuchi and R.-J. Roe, *J. Chem. Phys.* **94**, 7446 (1991).

³³P.-G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).

³⁴I. Stakgold, *Green's Functions and Boundary Value Problems* (Wiley, New York, 1998).

³⁵It turns out that for the Gaussian trial functions we use to describe the crystal phase, the recursive iteration converges very rapidly.