Nucleation in \( n \)-alkanes: A density-functional approach

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A density-functional theory for a polyatomic system is applied to gas–liquid nucleation in \( n \)-butane and \( n \)-heptane, employing an interaction site model and the rotational isomeric state approximation. Effects of chain length and flexibility on equilibrium properties and nucleation are discussed. It is shown that the \( n \)-alkane systems cannot be well approximated by a system with the spherically symmetric Lennard-Jones potential, giving a nucleation rate scaled by the classical rate smaller by six orders of magnitude. © 1998 American Institute of Physics. [S0021-9606(98)50542-9]

I. INTRODUCTION

The density-functional approach to nucleation\(^1\) has given considerable physical insight into the ways in which classical nucleation theory breaks down for the small clusters that determine the rate of condensation from the vapor under realistic conditions of temperature and pressure. In particular, these calculations have shown the opposite (and, therefore, partially canceling) effects of droplet curvature and of the presence of a spinodal (both neglected in classical nucleation theory). These result in a systematically incorrect temperature dependence in classical theory, which gives too high a rate at high temperatures and too low a rate at low temperatures. The density-functional theory, on the other hand, incorporates both effects and shows a more realistic temperature dependence.

Direct comparison with experiment is hampered by the fact that the simple atoms and molecules interacting through spherically symmetric potentials, assumed in theoretical calculations, are generally not accessible to the new generation of experiments that measure not just critical supersaturations but actual rates of nucleation. Most experimental systems involve additional complications such as hydrogen bonding (water), dipolar interactions (acetonitrile), amphiphilic character (the alcohols), or elongated and flexible chains (the \( n \)-alkanes). In order to confront theory and experiment in a more direct way, it is necessary to extend the density-functional approach to these other more complex systems.

In this paper, we examine explicitly the role of chain length and flexibility in a model for the \( n \)-alkanes. Nonane (\( C_{9}H_{20} \)) is perhaps the best-studied nucleating material experimentally; although we study only butane (\( C_{4}H_{10} \)) and heptane (\( C_{7}H_{16} \)), the conclusions we draw can be extended to other hydrocarbons as well as potentially to other chain molecules. Our results show that chain length has a significant effect on the phase diagram, surface tension, and nucleation rates, so such molecules cannot be successfully modeled using effective spherically symmetric potentials. More detailed comparison with measured nucleation rates in the series of \( n \)-alkanes is difficult, however, because of the additional complicating factor that interaction parameters themselves change with chain length.

Section II gives the potential model employed in our calculations, including both the weighting of the different rotational isomeric states and the site–site interaction parameters. Section III then describes our extension of density-functional theory to a flexible polyatomic system, which is treated as a mixture of isomers (their dynamical interconversions is not relevant to the equilibrium properties calculated here). Section IV presents the resulting phase diagrams and surface free energies needed for the classical nucleation calculation, and Sec. V gives the results of the density-functional (nonclassical) nucleation theory. Section VI briefly summarizes some conclusions.

II. MOLECULAR MODEL

We approximate an \( n \)-alkane molecule as a linked chain of interaction sites where each site is located at the carbon nucleus. The CH\(_3\) group and the CH\(_2\) group are assumed to be identical. The interaction sites in different molecules are taken to interact via a Lennard-Jones potential with parameters of Ryckaert and Bellemans\(^2\) (\( \sigma = 3.923 \text{ Å} \) and \( \epsilon/k = 72 \text{ K} \)), and the intramolecular potential is determined by the configuration of the molecules, as will be discussed below.

The bond lengths and the angles between contiguous bonds are fixed at 1.53 Å and 109.5°.\(^6\) (The use of the more accurate bond angle 112° changes the results shown in this paper very little.) We also need to determine the dihedral angles, and employ the rotational isomeric state (RIS) model of Flory\(^3\) in which the bond rotation angles (dihedral angles) are assumed to take only discrete values corresponding to the minima on the torsional potential energy surface. Those minima are at 0° and near \( \pm 120° \), 0° corresponding to \textit{trans} and \( \pm 120° \) to \textit{gauche}\.\(^\pm\). \textit{Gauche} and \( \textit{gauche}^-\) are related by a mirror reflection, but are not superimposable.

For \( n \)-butane, there are two kinds of distinct isomers, \textit{trans} and \textit{gauche}, because configurations of mirror images are equivalent for the planar or spherical interfaces that interest us here. The potential-energy difference between the \textit{trans} and the \textit{gauche} isomer is taken to be 700 cal/mol.\(^4\)

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The configuration of \( n \)-heptane is determined by four torsional angles, giving 25 nonequivalent configurational isomers. The total intramolecular potential energy for a molecule is the sum of contributions from each torsional angle, assuming that the bond rotations are independent of each other. The same value for the \textit{trans}-\textit{gauche} potential energy difference as that for \( n \)-butane is used, so the total potential energy for each isomer relative to that for the all-\textit{trans} isomer is the number of \textit{gauche} angles times 700 cal/mol. In addition to the torsional potential, distant interaction sites in the same molecule may interact in a similar way to those in different molecules.\(^{3}\) The attractive interaction between distant sites is relatively unimportant because the effect is similar among different isomers, but those isomers with adjacent \textit{gauche} angles have large repulsive energies because the distance between the sites four bonds apart \((2.5 \text{ Å for } \text{gauche}^{\text{trans}}-\text{gauche}^{\text{trans}} \text{ and } 3.5 \text{ Å for } \text{gauche}^{\text{trans}}-\text{gauche}^{\text{trans}})\) are much smaller than the Lennard-Jones parameter \( \sigma = 3.923 \text{ Å} \). Since the isomers for \( n \)-heptane with adjacent \textit{gauche} angles form less than 7\% of the total population at 300 K when the repulsive energy is taken into account, they were ignored to reduce the amount of computation. As a result, only seven isomers for \( n \)-heptane are included in the calculations.

### III. DENSITY-FUNCTIONAL THEORY FOR A POLYATOMIC SYSTEM

We begin by discussing a simpler case in which the free energy is a functional of the total site densities summed over all isomers, and then look at a more general case which reduces to the first case with certain approximations. We derive expressions for the equilibrium site densities and the free energies, following the density-functional theory for a polyatomic system of Chandler, McCoy, and Singer.\(^{5}\) Weighted density approximations have been used for polyatomic systems by Cherepanova and Stekolnikov\(^{6}\) and Woodward,\(^{7}\) and here a similar approach is applied to the \( n \)-alkane systems employing the RIS.

We write the Hamiltonian of the system as

\[
H_{N} = \sum_{i=1}^{N} \sum_{a=1}^{n} \frac{p_{ia}^2}{2m_{a}} + V_{N}
\]

with

\[
V_{N} = \sum_{i=1}^{N} W(\{r_{ia}\}) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \sum_{a=1}^{n} \sum_{b=1}^{n} \phi(\mathbf{r}_{ia} - \mathbf{r}_{jb}) + \sum_{i=1}^{N} \sum_{a=1}^{n} V_{\text{ext}}^{a}(\mathbf{r}_{ia}),
\]

where \( N \) is the number of molecules, \( n \) is the number of interaction sites in a molecule, \( i \) and \( j \) are the indices for molecules, \( a \) and \( b \) are for interaction sites, \( m_{a} \) is the momentum, and \( \mathbf{r}_{ia} \) is the mass associated with site \( a \). \( W(\{r_{ia}\}) \) is the intramolecular bonding potential for the molecule \( i \), \( \phi(\mathbf{r}_{ia} - \mathbf{r}_{jb}) \) is the pair potential between intermolecular sites, and \( V_{\text{ext}}^{a}(\mathbf{r}_{ia}) \) is the external potential acting on site \( a \). The bonding potential \( W(\{r_{ia}\}) \) is not necessarily pairwise decomposable. Its Boltzmann factor \( e^{-\beta W} \) is zero when the configuration \( \{\mathbf{r}_{ia}\} \) results in a breakage of any bond, and can be expressed in terms of the Dirac delta function in the limit of rigid molecules.

The grand canonical partition function \( \Xi \) of the system in a classical approximation is

\[
\Xi = \sum_{N=0}^{\infty} \frac{e^{\beta \mu N}}{N!} \nu^{N} (\Pi_{a} \Lambda_{a})^{\nu} \times \int \cdots \int [\Pi I_{a} d\mathbf{r}_{ia}] \exp(-\beta V_{N}),
\]

where \( \mu \) is the chemical potential, \( \nu \) is the symmetry number of the molecule which is equal to two for a chain molecule, and \( \Lambda_{a} \) is the thermal de Broglie wavelength for site \( a \). The grand potential \( \Omega \) is given by

\[
\Omega = -kT \ln \Xi,
\]

and is a natural functional of the external potential or \( u_{a}(\mathbf{r}) \), defined by

\[
u_{a}(\mathbf{r}) = \mu_{a} - V_{\text{ext}}^{a}(\mathbf{r}),
\]

where the chemical potential for site \( a \), \( \mu_{a} \), satisfies \( \Sigma_{a} \mu_{a} = \mu \). From the above definitions, the equilibrium site density \( \rho_{a}(\mathbf{r}) \) can be expressed as a functional derivative of the grand potential with respect to \( u_{a}(\mathbf{r}) \)

\[
\rho_{a}(\mathbf{r}) = -\frac{\delta \Omega}{\delta u_{a}(\mathbf{r})}.
\]

The site density and the ideal free energies can be obtained by considering an ideal system where only intramolecular interactions are retained and intermolecular interactions are removed. The ideal grand potential is a functional of \( u_{a}^{(0)}(\mathbf{r}) \)

\[
u_{a}^{(0)}(\mathbf{r}) = \mu_{a} - V_{\text{eff}}^{a}(\mathbf{r}),
\]

where \( V_{\text{eff}}^{a}(\mathbf{r}) \) is an as yet unknown effective external potential applied to the system to give the same density \( \rho_{a}(\mathbf{r}) \) as the real fluid with intermolecular interactions, and to be determined below using an equilibrium condition. The grand potential is

\[
\Omega_{id} = -\frac{kT}{\nu \Pi_{a} \Lambda_{a}} \int \cdots \int \Pi_{a} d\mathbf{r}_{ia} \times \exp(-\beta W(\{\mathbf{r}_{ia}\})) \exp \left[ \beta \sum_{a} u_{a}^{(0)}(\mathbf{r}_{ia}) \right],
\]

using Eq. (4) and \( e^{\beta} = \Sigma_{a} e^{\beta \Lambda_{a}}/N! \). The equilibrium site density can then be obtained from Eq. (6) as

\[
\rho_{a}(\mathbf{r}) = \frac{1}{e^{\beta} f_{a}(\mathbf{r})} \int \cdots \int \left[ \Pi_{a \neq a} d\mathbf{r}_{ia} f_{a}^{*}(\mathbf{r}_{ia}) \right] s^{(n)}(\{\mathbf{r}_{ia}\}) \]

where

\[
f_{a}(\mathbf{r}) = e^{\beta u_{a}^{(0)}(\mathbf{r})},
\]

\[
\lambda^{3} = \frac{kT}{\nu \Pi_{a} \Lambda_{a}},
\]

and
The value of $\lambda^3$ does not have to be calculated because it effectively adds a constant to the chemical potential, and is determined by the bulk density boundary conditions. $s^{(n)}(\{r_a\})$ thus defined is the normalized intramolecular correlation function for an ideal gas under no external field. For small molecules with small numbers of isomers $s^{(n)}(\{r_a\})$ can be calculated efficiently by considering all conformations, as in the Appendix. The density for a system of larger molecules may be calculated by single-chain Monte Carlo simulations under the effective external potential.8

This effective potential still needs to be determined. In order to do that let us define a Legendre transform of the grand potential $\Omega$ as

$$ F[\rho_a(r)] = \Omega[\rho_a(r)] + \sum_a \int dr \rho_a(r) u_a(r). \quad (13) $$

$F$ is then the Helmholtz free energy when there is no external field, and is a natural functional of the site densities $\rho_a(r)$. The functional derivative of the free energy $F$ is

$$ \frac{\delta F}{\delta \rho_a(r)} = u_a(r), \quad (14) $$

as can be obtained from Eqs. (6) and (13), and this relation is equivalent to the equilibrium condition $\delta \Omega/\delta \rho_a(r) = 0$. Let us write the free energy $F$ as the sum of an ideal part and an excess part

$$ F[\rho_a(r)] = F_{id}[\rho_a(r)] + F_{exc}[\rho_a(r)], \quad (15) $$

where $F_{id}$ is given by the exact relation

$$ F_{id}[\rho_a(r)] = \Omega_{id}[\rho_a(r)] + \sum_a \int dr \rho_a(r) u_a^{(0)}(r), \quad (16) $$

and $F_{exc}$ is to be calculated approximately. Taking a functional derivative with respect to $\rho_a(r)$ on both sides of Eq. (15), $u_a^{(0)}(r)$ is obtained as

$$ u_a^{(0)}(r) = u_a(r) - U_a(r) \quad (17) $$

where

$$ U_a(r) = \frac{\delta F_{exc}}{\delta \rho_a(r)} \quad (18) $$

In summary, the equilibrium site densities are given by Eqs. (9), (10), and (17), and the grand potential is

$$ \Omega[\rho_a(r), f_a(r)] = kT \sum_a \int dr \rho_a(r) \ln f_a(r) $$

$$ - \frac{kT}{\lambda^3} \int \cdots \int [\prod_a d \mathbf{r}_a f_a(\mathbf{r}_a)] s^{(n)}(\{\mathbf{r}_a\}) $$

$$ + F_{exc}[\rho_a(r)] - \sum_a \int dr \rho_a(r) u_a(r), \quad (19) $$

from Eq. (13). The site density in Eq. (9) is obtained once again using the above expression for $\Omega$ and $\delta \Omega/\delta \rho_a$.
\[ \beta U_a(r) = \frac{v_a}{v_m} \Psi[\vec{\eta}(r)] + v_a \int dr' \frac{\partial \Psi[\vec{\eta}(r')]}{\partial \vec{\eta}(r')} \rho_a(r') w(|r-r'|) + \beta \sum_b \int dr' \phi_{ab}(|r-r'|) \rho_b(r'). \] (26)

Next we consider a more general case in which the external potential acting on the interaction sites depends on the configuration of the molecule. This is equivalent to the case of an equilibrium mixture of isomers when the RIS is used. Because \( u_a(r_a) \) is not a function only of \( r_a \), we may introduce \( u_{al}(r_a) \) where \( l \) is the index for isomer. The grand canonical partition function is then

\[ \Xi = \sum_{N=0}^{\infty} \frac{1}{N! \lambda^N} \int \cdots \int [\Pi \Pi d\mathbf{r}_{ia} \] 
\[ \times \sum_l P_{l} g_{l}(\{\mathbf{r}_{ia}\}) \exp \left[ \beta \sum_a u_{al}(\mathbf{r}_{ia}) \right] \] 
\[ \times \exp \left[ -\beta \sum_{i \neq j,a,b} \phi(\mathbf{r}_{ia}-\mathbf{r}_{jb}) \right], \] (27)

where Eq. (A2) is used. We define the site density for isomer \( l \) as

\[ \rho_{al}(\mathbf{r}) = -\frac{\delta \Omega}{\delta u_{al}(\mathbf{r})}, \] (28)

and the density and the grand potential can be obtained in the same way as before, giving

\[ \rho_{al}(\mathbf{r}) = \frac{1}{\lambda^3} f_{al}(\mathbf{r}) \int \cdots \int \left[ \prod_{a'=a} \mathbf{d}\mathbf{r}_{a'} f_{a'l}(\mathbf{r}_{a'}) \right] P_{l}^{(n)}(\{\mathbf{r}_{a'}\}) \] (29)

and

\[ \Omega[\rho_{al}(\mathbf{r}),f_{al}(\mathbf{r})] = kT \sum_{a,l} \int d\mathbf{r} \rho_{al}(\mathbf{r}) \ln f_{al}(\mathbf{r}) \] 
\[ - \frac{kT}{\lambda^3} \sum_{a,l} \int \cdots \int \left[ \prod_{a} \mathbf{d}\mathbf{r}_{a} f_{al}(\mathbf{r}_{a}) \right] \] 
\[ \times P_{l}^{(n)}(\{\mathbf{r}_{a}\}) + F_{\text{exc}}[\rho_{al}(\mathbf{r})] = - \sum_{a,l} \int d\mathbf{r} \rho_{al}(\mathbf{r}) u_{al}(\mathbf{r}) \] (30)

where

\[ f_{al}(\mathbf{r}) = e^{\beta u_{al}(\mathbf{r}) - \Delta F_{\text{exc}}[\rho_{al}(\mathbf{r})].} \] (31)

To extend the previous method for calculating the excess free energy \( F_{\text{exc}} \) to mixtures, we need the excess free energy per molecule of isomer \( I \), \( \Psi_I(\{\eta_I\}) \) as a function of the volume fractions \( \{\eta_I\} \). If \( \Psi_I(\{\eta_I\}) \) is approximated as \( \Psi(\eta) \) above in Eq. (20), where \( \eta = \Sigma I \eta_I \), and the site and molecular volumes are set equal to the averages \( v_a \) and \( v_m \), \( f_{al}(\mathbf{r}) \) becomes equal to \( f_a(\mathbf{r}) \) in Eq. (10), and \( \rho_a(\mathbf{r}) \) in Eq. (9) can be written as

\[ \rho_a(\mathbf{r}) = \sum_{l} \rho_{al}(\mathbf{r}). \] (32)

Therefore, the above more general formalism reduces to the previous case where the free energies are functionals of the total site densities \( \rho_a(\mathbf{r}) \) only, instead of the site densities for all isomers \( \rho_{al}(\mathbf{r}) \). In a homogeneous system, where \( \rho_{al}(\mathbf{r}) = \rho_I \) and \( \rho_a(\mathbf{r}) = \rho \), the above approximation gives the ratio \( \rho_I / \rho = P_I \), independent of the density. The same is not true for an inhomogeneous system, however.

We use the above approximate methods in the calculations below. It would be impractical to treat the free energies as functionals of \( \rho_{al}(\mathbf{r}) \) when there are large numbers of isomers. We also found that results for one kind of isomer (all-trans) do not differ very much from those for a mixture, and it seems that different isomers are similar enough to be treated in an averaged fashion.

**IV. EQUILIBRIUM PROPERTIES**

The bulk properties are calculated by setting the site densities equal to the bulk molecular density, \( \rho_a(\mathbf{r}) = \rho \), and the external potential to zero. From Eqs. (9) and (19)

\[ \mu = kT \ln(\lambda^3 \rho) + \sum_a \int U_a \] (33)

and

\[ -\beta P = \beta \Omega[\rho]/V = \rho \ln(\lambda^3 \rho) - 1 \] 
\[ + \rho \Psi(\eta) - \frac{1}{2} \alpha \rho^2 - \beta \mu \rho, \] (34)

where \( \rho \) is the pressure, \( V \) is the volume, \( \eta = v_m \rho \), and \( \alpha = -\beta n^2 \int d\mathbf{r} \phi_{ab}(\mathbf{r}) \). As can be seen from the above equations, the bulk properties depend on the flexibility of a chain molecule only through the excess free energy \( \Psi(\eta) \), but not through the intramolecular correlation function \( s^{(n)}(\{\mathbf{r}_a\}) \).

A phase diagram can be obtained by equating the chemical potential (and the pressure) of the liquid and the gas phases

\[ \mu_\ell(\rho_\ell, T) = \mu_g(\rho_g, T) \] (35)

and

\[ P_\ell(\rho_\ell, T) = P_g(\rho_g, T), \] (36)

where the subscript \( l \) stands for liquid and \( g \) for gas. The phase diagrams for \( n \)-butane, \( n \)-heptane, and a Lennard-Jones system are shown in Fig. 1. The Carnahan–Starling excess free energy \( \Psi \) is used for the reference hard-sphere system for a Lennard-Jones system, and the resulting equation of state follows the principle of corresponding states. The phase diagram for \( n \)-butane is almost the same as that for the Lennard-Jones system, while the longer chain molecule \( n \)-heptane shows more deviations from the Lennard-Jones system than \( n \)-butane. The critical temperatures obtained are \( T_c = 448 \text{ K} \) for \( n \)-butane and \( T_c = 786 \text{ K} \) for \( n \)-heptane. These are high compared to the experimental val-
ues (425 K for \( n \)-butane and 540 K for \( n \)-heptane\(^{13} \)), especially for \( n \)-heptane, because of the mean-field approximation and the crude potential parameters. The potential parameters were adjusted to fit the thermodynamic data for \( n \)-butane at a particular temperature,\(^2 \) so it is not surprising that the parameters give results very different from the experiments for \( n \)-heptane. \( T_c \) could be fitted to the experimental values by changing the parameters, but this change does not affect the corresponding states in reduced variables very much, as long as the change in \( \sigma \) is small enough to leave the change in \( \Psi(\eta) \) small. [\( \Psi(\eta) \) is determined by the excluded volumes, which in turn depends on \( \sigma \).] Therefore, the results as presented in this paper depend mainly on the molecular model itself, but not very much on the choice of the parameters.

The surface tension \( \gamma \) is calculated for a planar interface of liquid and vapor at coexistence using\(^{14} \)

\[
\gamma A = \Omega[\rho_a(r)] - \Omega[\rho],
\]

where \( A \) is the area of the interface. The surface tensions for \( n \)-butane, \( n \)-heptane, and a Lennard-Jones system are compared in Fig. 2. Lennard-Jones systems with different parameters give almost the same surface tensions in reduced units because the two length scales (\( \sigma \) and the hard-sphere diameter \( d \)) are almost identical. (0.97 < \( d/\sigma < 1 \)) At low temperatures \((T/T_c < 0.53)\) our calculations for the Lennard-Jones systems showed solidlike oscillations at the interfaces, probably because of the existence of the solid phase in the phase diagram near those temperatures. This agrees with the fact that the calculated triple point is 0.53 \( T_c \) when a similar weighted density approximation as ours is used.\(^9 \) No such behavior was found for \( n \)-butane or \( n \)-heptane in the temperature range studied here. The surface tensions of \( n \)-alkanes are lower than the corresponding Lennard-Jones systems, as in Fig. 2. The large difference of the surface tensions between \( n \)-butane and the Lennard-Jones system, despite the similarity in the phase diagrams, may come from the fact that the liquid–vapor interface of \( n \)-butane has a more complicated structure (see below). However, our results are not quantitative. Experimental surface tensions for
n-alkanes are higher than those calculated here, but that for n-butane is higher than n-heptane, just as in our results.

The orientation or conformation of a chain molecule may depend on local environments such as density. The population ratios of different rotational isomers in homogeneous systems have been fixed to the ideal gas values irrespective of the density, as discussed at the end of the previous section. However, the ratios of different conformers may change across the interface, as shown in Fig. 3. In Fig. 3, the site densities \( \rho_a(z) \), where the \( z \) axis is perpendicular to the planar interface, are shown together with the local population of that isomer, defined by a weighted average of the site densities \( P_a(z) = \Sigma_a u_a \rho_a(z) / \Sigma_a \rho_a(z) \). Because of the symmetry, it is sufficient to show densities of two sites for n-butane and four sites for n-heptane. One can see from the site density profiles \( \rho_a(z) \) that the densities of outer sites on the vapor side of the interface are slightly larger than the densities of inner sites. This is more pronounced in the longer molecule n-heptane. More of the outer sites on the vapor side of the interface are also those of more extended isomers, as can be seen from \( P_a(z) \) in Fig. 3(a). Both these facts make physical sense. By observing \( P_a(z) \) we see that the probability of finding a more extended isomer on the vapor side of the interface is higher; \( P_a(z) \) is shown for the most extended isomers in Fig. 3. Similar curves of distribution of conformers are obtained across the spherical interface of a critical nucleus when that nucleus is large. When a critical nucleus is small, its shape cannot be approximated as spherical, and more complicated structure and conformations will result.

V. NUCLEATION

A. Density-functional theory

In the density-functional theory (DFT) of nucleation, a critical nucleus is identified as a saddle point on the grand potential surface for an open system, satisfying

\[
\frac{\delta \Omega}{\delta \rho_a(\mathbf{r})} = \frac{\delta F}{\delta \rho_a(\mathbf{r})} - \mu_a = 0.
\]

(38)

This is equivalent to finding a minimum on the Helmholtz free energy surface for a system with the same boundary condition, or enclosed by a perfectly nonwetting–nondrying surface, at a fixed number of molecules.

\[
N = \int_V d\mathbf{r} \rho_a(\mathbf{r}).
\]

(39)

If the volume of the system and the number of molecules are given, the chemical potential, which plays the role of a Lagrange multiplier, is determined by the condition Eq. (39), and the density profiles are given by Eq. (9). The resulting equation is

\[
\rho_a(\mathbf{r}) = \frac{\exp[ - \beta U_a(\mathbf{r}) ]}{\int_V \exp[ - \beta U_a(\mathbf{r}) ]} s_n(\{ \mathbf{r}_a \})
\]

(40)

We found that \( \int_V d\mathbf{r} \rho_a(\mathbf{r}) \) are not exactly the same for different \( a \) for a finite system enclosed by a spherical shell, but the differences are so small (about 0.001% for a usual system radius of 14\( \sigma \)) that we arbitrary set \( N = \int_V d\mathbf{r} \rho_a(\mathbf{r}) \). The integration over \( \mathbf{r}_1 \) in the denominator of Eq. (40) is then restricted to the enclosed volume.

In order to determine the volume and the number of molecules that give a nucleation rate in a range we want, we first perform a calculation finding a saddle point at a certain supersaturation and temperature, using a technique similar to that in Ref. 14. This takes a relatively long time on the computer because many initial profiles must be tried, but once appropriate volume and number are obtained, the critical nuclei and nucleation rates at other supersaturations can be computed much more quickly using the minimization method, changing the previous profiles and number by a small amount.

B. Results and discussion

We compare our results with the classical nucleation theory, as in the previous theoretical and experimental studies. The nucleation rates calculated as above for n-butane are presented in Fig. 4 with the classical nucleation rates

\[
J_{\text{CL}} = J_0 e^{-\beta \Delta \Omega_{\text{CL}}}.
\]

(41)
where J_o is the nucleation rate against the number of molecules in a classical critical nucleus. Figure 6 by plotting uncertainties.

The nucleation rate J_DFT in Fig. 4 is calculated from

$$J_{DFT} = J_o e^{-\beta \Delta \Omega_{DFT}},$$

where J_o is the same preexponential factor in Eq. (43), \(DFT\) and \(\Delta \Omega_{DFT}\) is obtained by the density-functional theory. The results shown in Fig. 4 are similar to those from the previous studies in that the log J_DFT vs log J_CL curves are almost linear with slopes close to one, showing that the classical nucleation theory gives similar dependence of nucleation rate on the supersaturation at fixed temperature, and that it predicts nucleation rates several orders of magnitude too high or too low depending primarily on temperature.

Deviations from the classical nucleation theory can also be seen by plotting the excess number

$$\Delta n_{DFT} = \int dq [\rho_o(q) - \rho_e],$$

against the number of molecules in a classical critical nucleus

$$n_{CL} = \frac{32 \pi \gamma^3}{3 \rho_l (kT \ln S)^3},$$

as in Fig. 5. According to the nucleation theorem, \(\Delta n_{DFT}\) and \(n_{CL}\) would be the same if the curves of log J_DFT versus log J_CL had slopes of one. The calculated slopes of the curves in Fig. 5 are the same as those in Fig. 4, as expected.

Plots for n-heptane and a Lennard-Jones system show similar linear curves as in Fig. 4, but with different slopes and intercepts. The slope for the Lennard-Jones system is far away. At T/T_c = 0.55, J_CL/J_DFT for the Lennard-Jones system is six orders of magnitude smaller than the value for n-heptane. The agreement between the experimental results and those from density-functional theory for n-heptane in Fig. 6 is quite good, but the nucleation rate scaled by the classical rate differs from the experiment by almost ten orders of magnitude around T/T_c = 0.5 when n-heptane is modeled by a Lennard-Jones system. We may not expect quantitative agreement between the experimental results and ours because of the simple model and crude parameters for n-alkanes, in addition to the approximations made in the theory. However, it is remarkable that such a simple model for the n-alkane systems gives

ent isomers. Only high-temperature data are shown for the Lennard-Jones system for the reason discussed in Sec. IV. In Fig. 6, the n-heptane and n-heptane curves are close, but that for the Lennard-Jones system is far away. At T/T_c = 0.55, J_CL/J_DFT for the Lennard-Jones system is six orders of magnitude smaller than the value for n-heptane. The agreement between the experimental results and those from density-functional theory for n-heptane in Fig. 6 is quite good, but the nucleation rate scaled by the classical rate differs from the experiment by almost ten orders of magnitude around T/T_c = 0.5 when n-heptane is modeled by a Lennard-Jones system. We may not expect quantitative agreement between the experimental results and ours because of the simple model and crude parameters for n-alkanes, in addition to the approximations made in the theory. However, it is remarkable that such a simple model for the n-alkane systems gives
results comparable to experiment, whereas the Lennard-Jones system completely fails in predicting the nucleation rate for n-alkanes even though its equilibrium properties are closer to experiment.

We have also compared n-alkane systems with the Lennard-Jones systems with potential parameters chosen to give the same critical points. This approach gives different equilibrium properties for the n-alkane and the Lennard-Jones systems at a given temperature, rendering a direct comparison difficult. Therefore, we tried to employ a semiempirical approach\(^{24}\) where the potential parameters (\(\sigma, \epsilon, \) and \(d\)) in the Lennard-Jones system were adjusted to fit the properties used in classical nucleation theory from the model n-alkane systems. [\(P_r, \rho_1, \) and \(\gamma\); see Eq. (42).] However, this approach was not successful because the Lennard-Jones systems show solidlike oscillations or peaks at the interfaces with those parameters, indicating that the Lennard-Jones systems are in a different region of the phase diagram from the n-alkanes.

VI. CONCLUSIONS

Our calculations show a clear effect of chain length on nucleation behavior; an n-alkane cannot be modeled as a spherical molecule. The role of flexibility is somewhat smaller than that of elongation in our calculation, though, as shown by the fact that the results for all-trans heptane do not differ significantly from those for a realistic distribution of rotational isomeric states. In our density-functional calculation, the end sites show the expected higher relative probability on the vapor side, although this effect may have been partially suppressed by the mean-field averaging implicit to any such calculation.

Detailed comparison with experiment (and, in particular, prediction of trends in nucleation behavior with chain length of the n-alkanes) is made difficult by the fact that the choice of a single set of parameters for interactions between units of a chain does not adequately describe the equilibrium properties of such a system. In other words, the effective forces between methyl and methylene groups are also changing as well as the number of such groups in a chain molecule. For the near future, therefore, detailed comparison with experiment will be heavily dependent on modeling of intermolecular potentials. Once such potentials are selected, it will also be of interest to carry out direct Monte Carlo simulations of nucleation barriers.\(^{25}\) Such simulations can then be compared with density-functional theory using a consistent and known set of interaction potentials.

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APPENDIX

The intramolecular correlation function \(s_i^{(n)}(\{r_a\})\) for an ideal gas in the rotational isomeric state model is a weighted sum of the intramolecular correlation functions for all rotational isomers \(I_i\), \(s_i^{(n)}(\{r_a\})\)

\[
s_i^{(n)}(\{r_a\}) = \sum_j P_j s_i^{(n)}(\{r_a\}),
\]

(A1)

where the weights \(P_j\) are

\[
P_j = \frac{\exp(-\beta V_j)}{\sum_j \exp(-\beta V_j)},
\]

(A2)

and \(V_j\) is the potential energy for isomer \(I_i\).

Since the bond lengths and the bond angles are fixed, \(s_i^{(n)}(\{r_a\})\) is a function of the dihedral angles \(\{\phi_{al}\}\) (\(a = 3, 4, \ldots, n - 1\)) formed by sites \(a - 2, a - 1, a,\) and \(a + 1\), and written as

\[
s_i^{(n)}(\{r_a\}) = \frac{1}{8\pi^2} \int_{-1}^{1} d\cos \theta \int_{0}^{2\pi} d\phi \int_{0}^{2\pi} d\phi' \times \sum_{a=3}^{n-1} \delta(\mathbf{r}_{12} - \mathbf{I}_{12}(\theta, \phi)) \delta(\mathbf{r}_{23} - \mathbf{I}_{23}(\theta, \phi, \phi')) \times \delta(\mathbf{r}_{aa+1} - \mathbf{I}_{aa+1}(\theta, \phi, \phi', \{\phi_{al}\})),
\]

(A3)

where \(\delta(\mathbf{r})\) is the Dirac delta function, and \(\mathbf{r}_{aa+1} = \mathbf{r}_{a+1} - \mathbf{r}_{a}\). \(\mathbf{I}_{aa+1}\) is determined by the angles \(\theta, \phi, \phi', \{\phi_{al}\}\), and can be easily calculated using the transformation matrix introduced by Flory.\(^{5}\) The equilibrium density in Eq. (9) is then simplified as

\[
\rho_a(\mathbf{r}) = \frac{1}{\lambda} f_a(\mathbf{r}) \frac{1}{8\pi^2} \int_{-1}^{1} d\cos \theta \int_{0}^{2\pi} d\phi \times \int_{0}^{2\pi} d\phi' \sum_{a' \neq a} P_j \sum_{a'} f_a(\mathbf{r}_{a'}, \{\theta, \phi, \phi', \{\phi_{al}\}\}).
\]

(A4)


23 Ref. 22 of Ref. 19.