Effect of branches on the structure of narrowly confined alkane fluids: n-hexadecane and 2,6,11,15-tetramethylhexadecane

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Using realistic molecular models and accurately calculating the state condition of the fluids of linear and branched alkanes confined between two strongly adsorbing solid surfaces, we obtained strikingly different structure for the two confined fluids. The structure of the n-hexadecane is solid-like with the molecules clearly forming a layered structure. Within each molecular layer, the molecules are packed predominantly parallel to each other. The structures of adjacent layers are correlated such that the main chain axes of the molecules pack into a local hexagonal array. In contrast, the structure of the branched alkane (2,6,11,15-tetramethylhexadecane) fluid remains liquid-like. Although exhibiting density oscillations normal to the confining surfaces, the structure of the confined fluid of the branched alkane is disordered and the molecules are not confined to a particular layer. The amplitude of the density oscillations is much smaller than for the n-hexadecane. The in-plane positional correlation shows isotropic structure characteristic of liquid, and the orientation of the molecules shows very little correlation. © 2001 American Institute of Physics.

I. INTRODUCTION

It is generally recognized that the presence of branches reduces the tendency for alkane fluids to freeze. For example, linear n-tridecane has a melting temperature of 267.9 K, whereas 7-methyltridecane (a C_{14}H_{30} with a single side methyl group) has a melting temperature of 236.0 K; linear n-eicosane has a melting temperature of 309.8 K, whereas 3-methyleicosane has a melting temperature of 286.5 K and 10-methyleicosane has a melting temperature of 269.2 K. A similar trend has been found for a large number of other alkanes. This effect can have significant impact on the suitability of a given alkane for use as a lubricant base stock. In evaluating the properties of a lubricant, the viscosity of linear alkanes has generally been found to have the least temperature dependence, translating to large viscosity index values. However, their high freezing points mean that they can freeze within the operating range of temperature for an automobile (including cold starts). Hence, this eliminates many linear alkanes for consideration in lubrication applications. The branched alkanes, especially those with many short side groups, have much better performance against freezing at low temperature, although their viscosity-temperature performance may be slightly worse than that of the linear alkanes. Such resistance against freezing would especially be important for friction reduction under extreme conditions when two solid surfaces are at near contact. In magnetic hard disk drives, for example, the read/write slider can occasionally approach the surface of the disk very closely during high-speed operation; the disk is protected by a thin lubricant film, so a good understanding of lubricant behavior under extremely narrow confinement is crucial for developing this type of high-capacity, high-speed data storage system.

Many experiments with the surface force apparatus (SFA) have been carried out to study the effect of molecular shape and architecture on the properties of ultrathin films of confined fluid. In particular, molecules with simple architectures, such as octamethylcyclotetrasiloxane (OMCTS, approximately a spherical molecule) and normal alkanes (linear molecules), have been observed to show solid-like behavior with dramatic increase in viscosity by many orders of magnitude and increased structural order when confined between mica surfaces. The confined OMCTS has been observed in some experiments to sustain a finite yield stress. The solvation force measurement for linear alkanes showed highly oscillatory behavior, while that for the highly branched alkane, squalane (2,6,10,15,19,23-hexamethylocicosane) shows a slow variation with a single attractive minimum at a separation of 18 Å. With further decrease of the confining distance, the solvation force shows a steep monotonic increase (starting at about 16 Å).
solvent force is closely related to the structure of the confined fluids and its oscillatory behavior for linear alkanes suggests a strongly layered structure. The slowly varying behavior of the solvent force for squalane is consistent with a disordered liquid-like structure for this branched alkane system. The steep monotonic rise of the repulsive solvent force with decreasing surface separation shows why the branched alkanes, such as squalane, are good inhibitors against solid–solid adhesion and provide protection against damage. However, on the molecular level, the phenomena are still not fully understood, in particular the dramatic increase in the viscosity for OMCTS and linear alkanes.\(^\text{9,12}\)

In a previous study,\(^\text{14}\) we demonstrated that strong, attractive wall–fluid interactions, such as those from mica surfaces used in the SFA experiment, can induce n-dodecane (with linear architecture) to form strong layering as well as in-plane orientational packing order at ambient temperature and pressure. Accompanying the structural order is a corresponding increase in density of the confined fluid. Such structural order had not been observed in previous simulation studies of linear alkanes. This raises the question whether a realistic treatment of the mica surface could also result in ordered structure for confined branched alkane fluids, such as squalane and other alkanes with similar molecular architecture. Most previous simulation studies on branched alkanes in confined geometry have been carried out for relatively short chain alkanes with a single side branch.\(^\text{15,16}\)

Relatively few studies\(^\text{17}\) were performed for alkanes with more complex molecular architecture, such as squalane. Most have attributed the results obtained in simulation to the effect due to the geometric confinement. In this work, we study the effect of realistic, strong wall–fluid interaction on the structure of fluids of two different molecular architectures. We examine the confined fluid structure for a linear and a branched alkane with the same backbone length: n-hexadecane, which has a linear molecular architecture; and the branched alkane, 2,6,11,15-tetramethylhexadecane, which has four symmetrically placed methyl side groups (similar to squalane).

A recent molecular simulation study showed significant difference in the density profiles in the direction normal to the confining surfaces between n-hexadecane and squalane.\(^\text{17}\) However, the structures for both the linear and the branched alkanes were liquid-like. A liquid-like structure with only layering would not be able to explain the dramatic viscosity increase observed experimentally. Increasingly, it has been recognized that structural order is required in both the direction normal to the wall surfaces and in the plane parallel to the wall surfaces for the confined fluids to show the many orders of magnitude slowing down in the dynamics, leading to the large increase in viscosity.\(^\text{18}\) However, detailed study of in-plane order of linear and branched alkanes in narrow confinement has until now been lacking. Most studies thus far have focused on the density oscillation of the confined fluids in the direction normal to the confining walls. Such density oscillation, however, occurs commonly for confined films even in the liquid state. Therefore, density oscillation alone cannot explain the solid-like behavior observed in experiments. For solid-like behavior to occur, three-dimensional order, including layering, in-plane order, and interlayer packing correlation, needs to be present in the confined film so that correlation in the motion of the molecules may significantly slow down the dynamical relaxation process. For a complete understanding of the behavior of narrowly confined fluids, it is necessary to examine the three-dimensional structure of confined fluid, including the normal and in-plane order, and interplane packing correlation. Such an understanding will provide a structural basis for the dynamical behaviors of the ultrathin confined fluid films.

In this work, we compare the structural properties of a linear alkane, n-hexadecane with those of a branched alkane with the same backbone length, 2,6,11,15-tetramethylhexadecane, under a confinement spacing corresponding to about six molecular layers between mica-like surfaces. We find that the fluid of n-hexadecane undergoes a dramatic structural transition to a well-ordered, solid-like structure, whereas the fluid of the branched alkane (2,6,11,15-tetramethylhexadecane) remains in a disordered liquid-like structure. We then analyze the structure of the confined ultrathin films to illustrate the predominant features of the confined film structures that are analogous to the three-dimensional bulk liquid or solid. In the process, we demonstrate the effect of the molecular architecture.

### II. MODELS AND METHODS

We briefly describe here the models and methods that we used for the simulation; more details can be found in published literature. The n-hexadecane is described by the united atom model of Siepmann et al.\(^\text{19}\) The branched alkane, 2,6,11,15-tetramethylhexadecane, is a molecule with a structure similar to that of squalane. It has a 16-carbon backbone and four symmetrically placed side-methyl groups. We thus chose the model used by Mondello et al.\(^\text{20}\) for squalane to describe it. The solid walls are composed of simple Lennard-Jones atoms with energy and size parameters reproducing the surface energy of a real mica surface. The wall atoms are placed on an fcc lattice with the (100) surface being the wall surface. The size parameter \(\sigma_w = 3.5\ \text{Å}\), is chosen approximately equal to the size of potassium atoms on mica surface (note that for an fcc crystal, the nearest-neighbor distance, \(d\), is related to the Lennard-Jones parameter by \(d \approx 1.09\sigma_w\).\(^\text{21}\) Our estimate suggests that for a Lennard-Jones energy parameter \(\varepsilon_w = 7.815\ \text{kJ/mol}\) for the wall atoms, the surface energy density is about 220 mJ/m\(^2\), consistent with surface energy density of \(\sim 200–400\ \text{mJ/m}^2\) for a real mica surface.\(^\text{12}\) The wall–fluid interaction was obtained by using the Lorentz–Berthelot combining rules, which gives a wall–fluid atom interaction energy parameter \(\varepsilon_{wf} \approx 4.47\varepsilon_{CH_2} \approx 1.747\ \text{kJ/mol}\), and a size parameter \(\sigma_{wf} = 3.715\ \text{Å}\), the values used in this work. Each solid wall consists of three layers of explicit atoms. The effects of the walls beyond three layers were modeled using the Steele potential\(^\text{22}\) for five additional layers.

To accurately treat the long-range contribution to the interaction and to the pressure tensor, we used a very large cutoff distance, 19.65 Å (5\(\sigma\), where \(\sigma = 3.93\ \text{Å}\) is the Lennard-Jones diameter of a united atom of the alkane molecules). Such a long cutoff distance makes the long-range correction essentially negligible.\(^\text{23}\) The pressure tensor of the
system is calculated using the method of Todd et al.,\textsuperscript{24} which has been shown to be exact for fluids under narrow confinement. It is verified in our simulation that the normal pressure in the interior of the confined film is equal to the external normal load, as determined from summing over all the forces of interaction between the wall atoms and the fluid molecules. Periodic boundary conditions are used in the two lateral directions, and the box length in these two directions is fixed during the simulation. This is justified based on the fact that the lateral dimensions in experiment are on the order of micrometers and are at least several hundred times larger than the length of the simulation box.

The confined system consists of 128 alkane molecules and 972 wall atoms for both the n-hexadecane and the 2,6,11,15-tetramethylhexadecane. The equations of motion were integrated using a multiple time-step method.\textsuperscript{25,26} The simulations were performed by thermostating the walls at \( T = 300 \text{ K} \) for 2,6,11,15-tetramethylhexadecane and at \( T = 323 \text{ K} \) for n-hexadecane. The reason for performing the calculation for n-hexadecane at a higher temperature is that we wanted to choose a temperature which is substantially above the melting temperature (291.2 K) of the system and previously published bulk results are available for this system at this temperature. Simulations were performed at the lower temperature of \( T = 300 \text{ K} \) and qualitatively similar results to those at \( T = 323 \text{ K} \) were obtained.

In our simulation, the final wall spacing was adjusted to yield normal pressure of approximately one atmosphere. Although this was not achieved exactly, the method yields accurate equilibrium spacing since the spacing is quite insensitive to the variation in normal pressure (e.g., the isothermal compressibility\textsuperscript{27} of liquid linear alkanes at ambient temperature is on the order of 0.001 MPa\textsuperscript{−1}; a change in normal pressure of 10 MPa would result in deviations in wall spacing about 1%, or less than 0.5 Å) for a six molecular layer film.

### III. BULK PROPERTIES

We first carried out calculations for bulk 2,6,11,15-tetramethylhexadecane at constant volume and temperature \( T = 300 \text{ K} \) using 100 molecules. Our results show that at atmospheric pressure, the density is 0.825 g/cm\(^3\). Compared to the experimental density\textsuperscript{1} of 0.7815 g/cm\(^3\), the model overestimates the density by about 5.5%. This result is consistent with published results for the model. The experimental melting temperature of 2,6,11,15-tetramethylhexadecane is, to the best of our knowledge, not yet determined. Based on the experimental melting temperature of 291.2 K for n-hexadecane, it is expected that the melting temperature of tetramethylhexadecane is lower than 291.2 K. Visualization of the structure obtained from simulation shows that it is a disordered liquid at 300 K and ambient pressure. It is noted that although the model for 2,6,11,15-tetramethylhexadecane used in this study does not precisely reproduce the bulk density, our main interest is the relative change of the density upon confinement and the general features of the corresponding structure.

The properties of the n-hexadecane using the model of Siepmann et al.\textsuperscript{19} have been published before.\textsuperscript{28} At the temperatures 300 and 323 K, the experimental densities are 0.770 and 0.753 g/cm\(^3\), respectively.\textsuperscript{1} At these densities, simulations using the model of Siepmann et al. yield the pressure values of \(-10.4 \text{ MPa} \) at \( T = 300 \text{ K} \) and \(-9.2 \text{ MPa} \) at \( T = 323 \text{ K} \), respectively. The model has been found to predict diffusion coefficients for alkanes higher than experiment, probably because of the reduced hindrance by the united atoms where the hydrogen atoms have been collapsed onto the carbon atoms. This suggests that the melting temperature of the model n-hexadecane is likely to be lower than in the experiment.

### IV. PROPERTIES OF THE CONFINED FLUIDS

The state conditions of the confined and bulk fluids are tabulated in Table I. It is seen that because of the strongly attractive wall–fluid interaction, the densities of the confined fluids are higher than those of the corresponding bulk fluids at the same temperature and pressure. This is most dramatic for the linear molecule n-hexadecane. The density is higher than that of the bulk fluid by about 13% (based on the comparison with experimental density at ambient pressure and \( T = 323 \text{ K} \)). At \( T = 323 \text{ K} \), the experimental freezing density for the bulk liquid n-hexadecane\textsuperscript{29} is 0.828 g/cm\(^3\). The density of 0.854 g/cm\(^3\) obtained from simulation for the confined n-hexadecane is about 3.1% higher than the bulk freezing.

### Table I. The state conditions of the confined fluids.\textsuperscript{4}

<table>
<thead>
<tr>
<th>Type of fluid</th>
<th>( T ) (K)</th>
<th>( N_f )</th>
<th>( N_w )</th>
<th>( H(\AA) )</th>
<th>( P_\parallel ) (MPa)</th>
<th>( P_\perp ) (MPa)</th>
<th>( \rho_{\text{eff}} ) (g/cm(^3))</th>
<th>( \rho_{\text{bulk}} ) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexadecane</td>
<td>323</td>
<td>128</td>
<td>972</td>
<td>38.40</td>
<td>5.9(1.3)</td>
<td>(-43.7(3.6))</td>
<td>0.854</td>
<td>0.753</td>
</tr>
<tr>
<td>2,6,11,15-Tetramethylhexadecane</td>
<td>300</td>
<td>128</td>
<td>972</td>
<td>42.17</td>
<td>17.4(1.0)</td>
<td>1.4(3.9)</td>
<td>0.866</td>
<td>0.825</td>
</tr>
</tbody>
</table>

\( T, N_f, N_w, H, P_\parallel, P_\perp, \rho_{\text{eff}}, \) and \( \rho_{\text{bulk}} \) are the temperature, the numbers of fluid and wall molecules, the equilibrium system width, normal and parallel component of the pressure tensor, the effective density of the confined films, and the calculated bulk density at atmospheric pressure for the model, respectively. The effective density is estimated by using the middle point between the first peak of the fluid layers and the position of the layer of wall atoms adjacent to the fluid as the boundary in calculating the width of the fluid film. The numbers in the parentheses indicate the statistical uncertainty. The negative pressure value in the directions parallel to the surfaces suggests the systems could be slightly compressed in these directions, which would result in a slightly higher density.
density. Correspondingly, an ordered structure is observed as described in the following sections. For the 2,6,11,15-tetramethylhexadecane, the density for the confined fluid is higher than in bulk by a small amount of about 4.9%.

Snapshots showing configurations for the linear and the branched alkanes are presented in Figs. 1(a) and (b). The configurations were obtained from initially disordered fluid states after molecular dynamics runs of length, 8.67 ns for the linear alkane, and 9.66 ns for the branched alkane. As can be seen from the configuration, the linear alkane fluid has transformed into well-ordered structure. The branched alkane fluid, on the other hand, remained in a disordered liquid-like structure. Our calculations give an average end-to-end distance for n-hexadecane of about 4.69σ (18.43 Å) compared to the fully extended chain length of 4.93σ (19.37 Å). In comparison, for the branched alkane, the average end-to-end distance is about 3.62σ (14.23 Å), although its backbone length is the same as n-hexadecane. Thus, the n-hexadecane was essentially fully extended but the branched alkane much less so. The components of the end-to-end distance in the directions normal and parallel to the walls are another indication of molecular ordering. For n-hexadecane, the normal and in-plane components are 0.49σ (1.93 Å) and 4.66σ (18.31 Å), respectively, whereas for the branched alkane, the corresponding components are 1.64σ (6.45 Å) and 3.23σ (12.69 Å), respectively, reflecting the more liquid-like structure for the branched alkane and the solid-like structure of the n-hexadecane. These results also show that, in contrast to the linear alkane, the backbone of the branched alkane is not confined to a single molecular layer. In Fig. 1(a), it is noted that some molecules straddle more than one layer of the structure formed by other molecules. Such a feature is primarily determined by the density of the molecules and is in turn determined by the state condition of the confined film. This suggests that in general some conformational defect may exist in a predominantly ordered structure, especially when the chains are longer and conformational defect is more likely to occur.

Further quantitative structural analyses were carried out for the confined linear and branched alkane fluids. Figure 2(a) presents the density profile in the direction normal to the confining solid surfaces for the linear alkane, n-hexadecane, and Fig. 2(b) presents the normal density profile for the branched alkane, 2,6,11,15-tetramethylhexadecane. It is seen that the density profile for the linear alkane exhibits dramatic solid-like oscillation, with sharp density peaks and interpeak valleys close to zero. The magnitude of the internal density peak heights is 2.5 times the average density. On the other hand, for the branched alkane, the density profile exhibits much weaker oscillation. Except for the surface layer peak, the magnitude of the internal peak heights is less than 1.5 times the average density, much smaller than that of the linear alkane. The average interlayer distance for the branched alkane is also larger, about 1.2σ (4.72 Å) compared with 1.0σ (3.93 Å) for n-hexadecane, reflecting the more bulky nature of the branched alkane. For the branched alkane, it is also noted that there is a small secondary peak between the surface layer and the second layer main peaks which is a result of the presence of the methyl side groups. Such peaks are not seen between internal peaks because the diminished order in the internal molecular layers leads to broadening, which results in negligible secondary peaks.

We studied the in-plane order of the confined films by plotting the two-particle correlation function in each plane for layers one to six (each layer is defined as occupying the space between two neighboring minima in the density pro-

![FIG. 1. (a) The configuration for confined linear n-hexadecane at T = 323 K after a simulation run of 8.67 ns. (b) The configuration for the branched alkane, 2,6,11,15-tetramethylhexadecane at T = 300 K after a simulation run of 9.66 ns.](https://example.com/fig1.png)

![FIG. 2. (a) The density profile for the confined n-hexadecane fluid in the direction normal to the surfaces of the confining walls. The dashed line is drawn as a guide to the eyes. (b) The density profile for the fluid of confined branched alkane, 2,6,11,15-tetramethylhexadecane in the direction normal to the surfaces of the confining walls. The dashed line is drawn as a guide to the eyes. σ=3.93 Å is the size of a united atom.](https://example.com/fig2.png)
Since all layers exhibited essentially similar features, we present the results for one internal layer (~layer 3) only. Figure 3(a) shows a two-dimensional plot of the site–site pair correlation function versus in-plane relative position between two atomic sites in n-hexadecane. The series of pronounced peaks in the two orthogonal directions in Fig. 3(a) corresponds to the intramolecular correlation of the linear alkane along the chain. Such correlation is consistent with the configuration in Fig. 1(a), where the linear chains are essentially fully extended.

Figure 3(b) shows the corresponding two-dimensional plot for the in-plane correlation for 2,6,11,15-tetramethylhexadecane. Each in-plane function is calculated by identifying the space between two neighboring minima in the density profile [Fig. 2(b)] as corresponding to a particular layer. The lack of in-plane order for the branched alkane is striking in contrast to that of the linear alkane shown in Fig. 3(a). It is seen that the first two peaks exhibit essentially a circular character, corresponding to random orientations for the first and the second neighbors along the backbone in the molecule. Although some anisotropy exists, no isolated peaks are seen, unlike the case for linear alkanes. The long-range correlation due to intramolecular order along the backbone has disappeared. This is related to the fact that for the branched alkane the in-plane orientations of the molecules are essentially random in the liquid-like state, and the molecules are more likely to have more gauche conformations along the backbone than for n-hexadecane molecules. The side groups also more likely contribute in random orientation to the two-dimensional in-plane correlation. The third peak exhibits ring-like character with much smaller amplitude, and the higher order peaks show only a slight hint of orientational anisotropy.

To aid identification of the peaks, we show in Fig. 4(a) the orientation averaged site–site pair correlation versus the in-plane distance ($r_1$). Various characteristic intramolecular and intermolecular distances can clearly be seen from the figure. The inset shows the in-plane intermolecular correlation function as a function of in-plane distance ($r_1$). (b) The in-plane molecular correlation function as a function of in-plane distance ($r_1$) for 2,6,11,15-tetramethylhexadecane. The inset shows the in-plane intermolecular correlation function as a function of the in-plane distance ($r_1$).
The first peak in Fig. 4(a) corresponds to the united atom directly bonded to the atom in consideration, the second peak corresponds to the second neighbor on the chain, and so on. In the inset of Fig. 4(a), we plot only the intermolecular correlation as a function of the in-plane distance. It shows that the first intermolecular peak occurs at about 1.3\( \sigma \) (5.11 Å), which corresponds roughly to the distance between two parallel linear alkane molecules in trans conformation lying flat in the plane (i.e., the zigzag bonds lying in the plane). It is interesting to note in Fig. 4(a) that the position of the fourth peak coincides with the first peak of the intermolecular correlation function and so is not directly visible in Fig. 4(a). A careful examination of the background, however, reveals a slowly varying wave corresponding to the intermolecular correlation. In Fig. 3(a), the broad crests run in parallel to the series of intramolecular peaks corresponding to the intermolecular peaks (with a distance between neighboring peaks of about 1.3\( \sigma \) (5.11 Å)).

The corresponding angular averaged two-particle correlation function versus the in-plane distance in layer 3 for 2,6,11,15-tetramethylhexadecane is plotted in Fig. 4(b). This can be compared with the corresponding function in Fig. 4(a). The peaks corresponding to the intramolecular atomic distances along the main chain backbone can be identified by comparing to the figure for linear n-hexadecane [Fig. 4(a)]. There are a few additional features in the function. It is first noted that before the first sharp peak and near the origin there is nonzero probability of finding another atom. This may appear surprising at first since the first sharp peak corresponds to the first bonded neighbor. However, it should be noted that the distance in Fig. 4(b) is an in-plane distance so that if the in-plane distance is zero it means that the branched atom is directly above or below the atom at the center when viewed in the direction normal to the plane. We have verified this by calculating the pair distribution function, \( g(r) \), with \( r \) the three-dimensional distance for which we obtained \( g(r) = 0 \) when \( r \) is smaller than the nearest-neighbor bond distance, consistent with expectation. For the same reason, there is nonzero probability in the valley between the first and the second sharp peaks. The small peak at about 0.8\( \sigma \) between the second and third sharp peaks (at 0.66\( \sigma \) and 1.0\( \sigma \), respectively) is identified as the third intramolecular neighbor in a gauche conformation. A hint of such a peak can also be seen in Fig. 4(a) but is just barely visible. The small peak at about 1.15\( \sigma \) can also be attributed to the gauche conformation, which manifests itself in Fig. 4(a) as a shoulder. The inset in Fig. 4(b) shows the intermolecular correlation. It shows less structure than the intermolecular correlation in the inset of Fig. 4(a) for the linear n-hexadecane.

Figure 5(a) exhibits the summed results for all six layers for n-hexadecane. In addition to the intramolecular peaks similar to those seen in Fig. 3(a) for a single molecular layer, Fig. 5(a) shows the striking feature of stripes of peaks and valleys running parallel to the series of intramolecular peaks, demonstrating the predominant parallel intermolecular packing. Comparison of Fig. 5(a) and Fig. 3(a) shows that the number of intermolecular peaks is twice that of an individual layer and the separation between the peaks is half that for an individual layer. This suggests a hexagonal packing structure for the backbone of the alkane molecules. Such structure can be clearly seen in Fig. 5(b), where a perspective view of the same configuration of Fig. 3(a) is shown. It should be pointed out, however, that the structure is far from perfectly
where molecules \( i \) as in analogy to the two-particle positional correlation function illustrated in Fig. 5 for the entire film for 2,6,11,15-tetramethylhexadecane is compared with a bulk solid material. The structure in Fig. 5 shows that, unlike the linear \( n \)-hexadecane, there is little or no interlayer correlation in the confined \( n \)-hexadecane, due to the high energetic cost of packing the \( n \)-hexadecane molecule.

\[ f(\theta) = \frac{1}{n} \left( \sum_i \sum_{j \neq i} \delta(\cos \theta_{ij} - \cos \theta) \right). \tag{1} \]

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