Dynamic Odd–Even Effect in Liquid n-Alkanes near Their Melting Points

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Abstract: n-Alkanes are the textbook examples of the odd–even effect: The difference in the periodic packing of odd- and even-numbered n-alkane solids results in odd–even variation of their melting points. However, in the liquid state, in which this packing difference is not obvious, it seems natural to assume that the odd–even effect does not exist, as supported by the monotonic dependence of the boiling points of n-alkanes on the chain length. Herein, we report a surprising odd–even effect in the translational diffusional dynamic properties of n-alkanes in their liquid states. To measure the dynamics of the molecules, we performed quasi-elastic neutron scattering measurements near their melting points. We found that odd-numbered n-alkanes exhibit up to 30 times slower dynamics than even-numbered n-alkanes near their respective melting points. Our results suggest that, although n-alkanes are the simplest hydrocarbons, their dynamic properties are extremely sensitive to the number of carbon atoms.

n-Alkanes (C\(_n\)H\(_{2n+2}\)) are a well-known example of substances that exhibit an intriguing “odd–even effect”.\([1-3]\) The melting points of n-alkanes show a zig-zag shape rather than a monotonic trend as a function of the number of carbon atoms. This odd–even effect also holds for most of their \(\alpha\)- and \(\alpha_\omega\)-substituents.\([1,4]\) Such an odd–even effect becomes more significant for short chains: the shorter the chain length, the larger the difference in melting points between two n-alkanes differing in length by one carbon atom. Other physical properties characterizing the solid state, such as sublimation enthalpy, solubility, and modulus, display similar odd–even alternation.\([2,4,5]\)

Although this striking odd–even effect was known hundreds of years ago, its molecular origin was only revealed in the last decade. With the help of single-crystal diffraction and controlled crystal growth, the crystalline lattice of n-alkanes was determined.\([5]\) It was confirmed that the intermolecular distances between the end groups, namely, the CH\(_3\) groups, are responsible for the alternation in the densities and melting points. In short, n-alkanes with an even number of carbon atoms pack more efficiently into ordered periodic crystalline structures and thus exhibit higher densities and melt at higher temperatures, whereas n-alkanes with an odd number of carbon atoms do not pack as effectively, and thus their densities are lower, and lower temperatures are needed for melting or freezing. A “packing effect” has been established to explain the odd–even effect as well as the related physical properties in the solid state.

In contrast, the boiling points of n-alkanes increase monotonically as a function of the molecular weight (see Figure 1a), thus suggesting that the odd–even effect does not exist in the liquid state. Ultimately, the dynamics of molecules in the liquid state are determined by their molecular structure and interactions. Although ordered periodic packing is not as well defined in liquids as in solids, the molecular conformation still depends on the chain length of the n-alkane molecules.\([6-8]\) In keeping with this logic, we hypothesized that the odd–even variation of the chain length of n-alkane molecules would also cause an odd–even effect on the dynamic properties in the liquid state.\([9,10]\) Such an odd–even effect may be subtle in terms of thermodynamic and structural quantities because of the transient nature of local structures in the liquid state. However, we show herein that slight structural variation between n-alkanes is manifested in their dynamic and transport properties.

Considering that the odd–even effect of various thermodynamic properties in solid n-alkanes, it is natural to ask first whether such odd–even alternation of those thermodynamic properties exists in the liquid state. For example, at a constant temperature, the density of n-alkanes only shows a monotonic trend as a function of the chain length \(n\); whereas the viscosity of n-alkanes also shows a monotonic trend at different temperatures.\([11,12]\) Therefore, superficially it appears that the odd–even effect does not exist in the liquid state.\([13,14]\) However, these data were obtained and presented at the same temperatures irrespective of the different melting points of n-alkanes. Since this temperature is well above the melting
points of n-alkanes, the odd–even effect may not be apparent, simply because of the large thermal activation, especially for systems with lower melting points. After all, the addition of a CH₃ group will still affect the intermolecular distances between the end groups and the molecular structures in the liquids. Therefore, it is more reasonable to compare the liquid properties with respect to their individual temperature coordinate, marked by their respective melting points.

Near the melting point, the classical Kauzmann–Eyring theory of viscous flow suggested that the viscosities of simple liquids, such as n-alkanes, should have similar values of about 0.002 Pa·s.¹⁴ This prediction is based on the assumption that the number of holes introduced upon melting is the same for all n-alkanes. However, experimentally, the viscosities of n-alkanes at their freezing points are not the same, but exhibit an odd–even effect, and so do their densities (Figure 1b). The variation in density and viscosity is very subtle, with differences less than 0.02 g/mL and 0.002 Pa·s. However, the odd–even trend is clearly observed. To rule out the possibility that the odd–even trends of viscosities and densities are caused by the odd–even effect of the melting points themselves, we interpolated the melting points of the odd-numbered n-alkanes on the basis of those of the even-numbered n-alkanes. When their densities and viscosities were scrutinized along this monotonic temperature line,¹⁵ a weak odd–even effect was still noticeable in the liquid state of n-alkanes near their melting points. Therefore, the Kauzmann–Eyring prediction of the viscosity of n-alkanes at their melting point is only conditionally valid: The values of the normalized viscosities are indeed close to 0.002 Pa·s, but the theory failed to capture the detailed odd–even variation. The differences in these thermodynamic quantities between neighboring n-alkanes are so small that modern measurements with very high accuracy are required to detect them. However, the goal of this study was to show that such an odd–even effect in the liquid state is manifested in the microscopic dynamic properties of the n-alkanes.

We performed quasi-elastic neutron scattering (QENS) experiments to measure the relaxation dynamics of the liquid n-alkanes. The high-resolution incoherent QENS technique benefits from the exceptionally large incoherent cross section of hydrogen atoms, and thus is suitable for studying single-particle self-motion with sub-picosecond resolution. Various dynamic processes, ranging from fast segment relaxation to slower translational and rotational diffusion, exist in n-alkanes.²¹–²⁴ In contrast to the bulk quantities, the microscopic dynamic properties are more sensitive and thus can directly reflect the subtle differences between individual n-alkanes in the series.²⁵

QENS spectra measured with the disk chopper time-of-flight spectrometer (DCS) at the NIST Center for Neutron Research are shown in Figure 2. We chose the incident neutron wavelength to be 8 Å, which provided an elastic energy resolution of approximately 30 μeV full width at half maximum (FWHM). We measured the QENS spectra slightly (3 K) above the melting point of each n-alkane (Tₘ + 3 K). This temperature set was chosen to decouple the melting-temperature odd–even effect from the dynamic properties of the individual n-alkane as well as to ensure that the n-alkanes remained in the liquid state throughout the data-acquisition process (about 6 h per sample). For comparison, we also measured the QENS spectra for all n-alkane samples at a constant temperature of 246 K. This temperature (246 K) was chosen in accordance with the highest temperature (the melting point of decane plus 3 K) used in first temperature set.

The dependence of the scattered neutron intensity on the wave-vector transfer Q and energy transfer E, essentially the double differential cross section, is described by the Fourier transform of the self-intermediate scattering function:

\[ I(Q, E) = N F_{s}(Q, t) \otimes R(Q, E) \]  

(1)

in which N is the normalization factor, \( F_{s}(Q, t) \) is the self-intermediate scattering function, and \( R(Q, E) \) is the Q-dependent energy-resolution function. The term \( F_{s}(Q, t) \) can be further decoupled as the product of the translational correlation function \( F_{t}(Q, t) \) and the rotational correlation function \( F_{r}(Q, t) \) of the hydrogen atoms of the n-alkanes:

\[ F_{s}(Q, t) = A(Q) F_{t}(Q, t) F_{r}(Q, t) \]  

(2)

\( A(Q) \) represents the fraction of mobile atoms that are within the time window of the measurements. \( A(Q) \) is fixed at unity because of its coupling with the normalization factor N. \( F_{t}(Q, t) \) represents the contribution from the translational relaxation. For a glass-forming liquid, it can be described by

![Figure 1.](Image 52x803 to 92x825)  

- Figure 1. a) Melting points and boiling points of n-alkanes (n = 5–10) as a function of their backbone length n. b) Density and viscosity of n-alkanes near their respective melting points (Tₘ + 3 K). Error bars herein represent one standard deviation.
The measured QENS spectra can be described well with the above-described model at all measured \( Q \) values and temperatures for all samples. Even more remarkably, the data can be fitted well with the translational contribution alone in most \( Q \) values. Only at larger \( Q \) values, the addition of rotational and intramolecular contributions is needed to improve the fitting (see the Supporting Information). Therefore, to minimize the number of fitting parameters and at the same time not to lose generality, we present the analysis herein with only the translational relaxation contribution (see the Supporting Information for analysis with the complete model). The fitting of the QENS spectra of all samples with only the translational model is demonstrated in Figure 2. This model is able to capture the key features in the measured QENS spectra in all \( Q \) ranges and fit all the data with only two parameters: the translational diffusional relaxation time \( \tau \) and the stretching exponent \( \beta \). The three \( Q \) values presented in Figure 2 were chosen to show their similar behavior. Analysis with the more detailed model with additional parameters did not change our conclusion (see the Supporting Information).

The inverse of the extracted translational relaxation time \( 1/\tau \) and the stretching exponent \( \beta \) were plotted as a function of \( Q \) and \( Q \), respectively (Figure 3a,b). For \( Q = 0.52 \text{ Å}^{-1} \), the relaxation time \( \tau \) for the translational diffusion of \( n \)-alkanes is in the order of 10 ps. All even-numbered \( n \)-alkanes have smaller \( \tau \) values than odd-numbered \( n \)-alkanes, as readily identified by the apparent separation between the blue curves (odd-numbered \( n \)-alkanes) and red curves (even-numbered \( n \)-alkanes) in Figure 3a. A consistent trend was also observed in the plot of \( \beta \) versus \( Q \) (Figure 3b): The even-numbered \( n \)-alkanes have similar \( \beta \) values at different \( Q \) values, whereas the odd-numbered \( n \)-alkanes have smaller \( \beta \) values. At the very small \( Q \) values measured, we found that the value \( \beta \) did not converge towards the hydrodynamic limit, probably because of two factors: 1) The liquid dynamics is getting close to the resolution of the instrument at small \( Q \) values, thus leading larger uncertainties in the measurement, and 2) The internal motions of the molecules contribute relatively more to the spectral “background”, which is not fully resolved in the measured dynamic range. Despite these systematic errors, the odd–even trend is still clearly observed.

Plotting of the extracted translational relaxation time \( \tau \) and the stretching exponent \( \beta \) as a function of the number of carbon atoms \( n \) for all samples at three representative \( Q \) values (Figure 3c,d) shows a very clear odd–even trend of the dynamics of \( n \)-alkanes. The three \( Q \) values were chosen to show the consistent trend across the accessible \( Q \) range. Given that all data were acquired in the liquid state, they show a dynamic odd–even effect at the molecular level, to the best of our knowledge for the first time for \( n \)-alkanes. The
odd-numbered n-alkanes showed longer relaxation times than their neighboring even-numbered species; in other words, pentane, heptane, and nonane move more slowly than hexane, octane, and decane. Interestingly, all even-numbered n-alkanes showed very similar relaxation times (e.g. about 3 ps at 0.97 Å⁻¹) near their melting point, whereas the relaxation time of the odd-numbered n-alkanes varied across the Q range.

Unlike the density and viscosity, the amplitude of the dynamic odd–even effect goes beyond the simple odd–even trend of the melting points of n-alkanes. Taking hexane and heptane, for example, the difference between their melting points is only 4 K, whereas their translational relaxation time differs by a factor of more than two. The extreme case is nonane, which shows much slower dynamics than octane. Although the melting points are only 3 K apart, the dynamics of nonane is more than 30 times slower than that of octane at 0.52 Å⁻¹. Although the small stretching exponent of nonane is partially responsible for its slow dynamics, this result is still extremely surprising given that the structural difference between nonane and octane is only one methylene group.

The stretching exponent β also shows a similar odd–even trend. The common expectation is that n-alkanes behave very differently from a supercooled liquid because of their low viscosities; however, our measurements revealed a highly stretched nature of the relaxational behavior of liquid n-alkanes above their melting points.

In contrast, for all samples measured at the same temperature of 246 K, the relaxation time τ and the stretching exponent β did not show any odd–even trend. The extracted parameters 1/τ and β are plotted in Figure 4 in the same way as in Figure 3. Since 246 K is well above the melting point of most n-alkanes in the series, the relaxation time τ for translational motion is smaller than 10 ps at Q = 0.52 Å⁻¹. The Q-dependence curves (Figure 4a,b) can no longer be separated into two groups, and thus both the translational relaxation time τ and the stretching exponent β only follow a monotonic order. It is even more clear that the dynamics of n-alkanes measured at the same high temperature only show a monotonic trend from a plot of the extracted τ and β values as a function of the number of carbon atoms n (Figure 4c,d). As expected, the heavier n-alkanes move more slowly in terms of translational motion. This result is in accordance with the trends of other thermodynamic properties of liquid n-alkanes at the same temperature, where no odd–even alternation is observed.

In summary, with high resolution QENS measurements, we discovered a surprising dynamic odd–even effect in liquid n-alkanes near their melting points. Our observations firmly established that the odd–even effect does exist in the liquid state and is more prominent in dynamic quantities than in thermodynamic quantities. Furthermore, they suggest that mechanisms other than periodic packing should be scrutinized to gain a more thorough understanding of the odd–even effect. At this stage, it is tempting to make speculations about the observed dynamic odd–even effect. It is known that the symmetries of odd and even n-alkane molecules in all-trans forms are different (C₃ᵥ symmetry versus Cᵥ symmetry). Although all-trans forms are not favorable configurations in liquids, we speculate that an extra CH₃ group switches the structural symmetry of neighboring n-alkanes and thus affects the local packing structures of the n-alkane molecules.

Figure 3. a, b) Dependence of the inverse of the relaxation time 1/τ (a) and the stretching exponent β (b) of n-alkanes near their respective melting points on Q. The values for odd-numbered n-alkanes are plotted in blue and those for even-numbered n-alkanes are plotted in red. Both graphs clearly show odd–even alternation, as blue curves and red curves are separated into two groups. c, d) Dependence of the extracted translational relaxation time τ (c) and the stretching exponent β (d) of liquid n-alkanes near their respective melting points on the number of carbon atoms n for three representative Q values. A clear dynamic odd–even effect is observed.
their melting point, the local configuration of molecules, although too small to detect conveniently, may resemble the packing structure of the solids, which fundamentally leads to the alternating trend of the transport properties. Therefore, we anticipate that the dynamic odd–even effect disappears gradually as the temperature is raised, which could be verified in the future. In any case, the exact mechanism responsible for the discovered dynamic odd–even effect of liquid \(n\)-alkanes requires high-precision simulations and careful reexamination and extension of the classical theories of molecular viscous flow. The transport properties of \(n\)-alkanes are fundamental to petroleum science and knowledge about these properties is important for a wide spectrum of chemical processes, such as lubrication, diffusion through porous media, and heat transfer.\[31–35\]

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