Temperature Effect on Interactions of Oil Droplet with Water-wetted Shale Kerogen at Reservoir Temperatures: Linear Relationships between Temperature, Free Energy, and Contact Angle

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Abstract

Detailed knowledge about the interfacial interactions between oil and kerogen on nanoscales is imperative for unlocking adsorbed hydrocarbon in tight reservoirs, especially in unconventional shale that retain abundant hydrocarbon in kerogen nanopores. In this study, temperature effect on interactions of light oil with a type II kerogen in water was investigated using molecular dynamics simulation. Non-polar and polar light oil droplets were represented by clusters of 30 octane molecules and 30 octanethiol molecules, respectively. The free energy calculations were performed with umbrella sampling at constant temperatures in the range 300–500 K (27–227 °C, 80–440 °F), that are comparable to the reservoir conditions of common shale plays. Our result shows that the adsorption/desorption energy of an oil droplet is a linear function of temperature, which can be described by van ‘t Hoff equation. Comparative simulations using single oil molecule show that the result from single oil molecule cannot qualitatively describe oil droplet. In addition, the most stable contact angles of oil droplets which are associated with the global energy minimum were identified. The cosine of the contact angle can be linearly correlated with the free energy of oil adsorption/desorption. This study provides a thermodynamic insight at molecular level on how temperature affects the oil interactions with kerogen, closing the knowledge gap on unconventional oil recovery.

Keyword: oil/shale interaction, linear relationship, temperature, free energy, contact angle, molecular dynamics

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Introduction

Petroleum is a major energy source for modern civilization and therefore crude oil is a strategic resource for geopolitical influence.\textsuperscript{1–3} Current technology can yield up to 30\%–60\% of the original oil in place, leaving up to 70\% in a reservoir.\textsuperscript{4,5} Unconventional tight reservoirs, especially tight shale plays, have abundant hydrocarbon retained in kerogen nanopores.\textsuperscript{6–9} On nanometer scale, surface can exert a significant influence on the confined fluid through intermolecular interactions.\textsuperscript{10,11} Thus, knowledge about the fluid-surface interactions is particularly crucial for developing unconventional shale oil.\textsuperscript{12–14}

Temperature plays a vital role in thermodynamic processes, including interfacial interactions. Understanding the temperature effect is essential for predicting equilibrium and the rate constant for any chemical systems.\textsuperscript{15} Many oil recovery technologies have applied temperature effects to enhance the thermal recovery process by steam injection, hot water flooding, and in-situ combustion.\textsuperscript{16} However, all these techniques are originally designed for recovering conventional hydrocarbon, especially heavy oil. To effectively transfer these techniques to unconventional shale, it is imperative to gain a fundamental understanding about the temperature effect on oil recovery in shale nanopores.

Direct evidence for the temperature effect on oil/kerogen interactions in shale nanopores is mostly obtained from phenomenon observations using molecular dynamic simulations. Wang et al., 2015 evaluated the temperature effect on the density distribution of octane in kerogen slit (graphene surface) at temperature ranging from 333 to 393 K.\textsuperscript{17} They observed an up to 2\% reduction in the number of adsorbed octane molecules at elevated temperatures. Recently, Yang et al., 2020 examined the temperature effect on the adsorption of hydrocarbon mixtures on a kerogen slit (porous functionalized surface) at temperatures ranging from 280 to 400 K. They observed linear relationships between the temperature and the number of oil compounds confined in the slit.\textsuperscript{18} Because molecular dynamics simulations can only study events of relatively short timescale typically in nanoseconds, determining whether the system has reached equilibrium state is crucial for a reliable simulation, which can be difficult without energy calculations. To the best of our knowledge, no study has been systematically conducted to evaluate the temperature effect on the energetics of oil/kerogen interactions on nanoscales.

We hypothesized that the free energy of oil interactions from shale kerogen can be described as a linear function of temperature. In the present study, the temperature effect on the energy of light oil interactions with shale kerogen surfaces are investigated at given temperatures from 300 to 500 K. The impacts of molecular polarity (polar vs non-polar oil) and molecular clustering (oil droplet vs single oil molecule) to the interaction energetics were taken into account. Because there is no study directly linking the free energy with the contact angel of an oil droplet in a petroleum system, we correlate the free energy with the contact angles of oil droplet using a simple linear equation. Identifying the relationships between free energy, temperature, and contact angle can provide thermodynamic insights into the hydrocarbon behavior and interface wettability on nanoscales.

Computational

Models. Two types of interface system were investigated: a single oil molecule on a water-wetted kerogen surface and an oil droplet on a water-wetted kerogen surface (Figure 1). Details such as the size of the simulation box, number of water molecules, and kerogen slab thickness are tabulated in Table 1. The input structures of water, oil, oil cluster, and kerogen surface were taken from our previous study,\textsuperscript{19} which has been proven to simulate reasonable interfacial phenomena. Hydrocarbons with eight carbons are one of the most abundant compounds in crude tight oil,\textsuperscript{20} especially in the Bakken formation.\textsuperscript{21} Therefore, n-octane (C\textsubscript{8}H\textsubscript{18}) was selected to represent the light oil compound. Given that the sulfur content is crucial to the economic value of crude oil,\textsuperscript{22,23} octanethiol (C\textsubscript{8}H\textsubscript{17}:SH) was modeled as the polar
counterpart of octane to evaluate the impact of molecular polarity. The oil droplets were prepared using 30 molecules of octane and octanethiol to represent the non-polar and polar oil droplets, respectively. A type II kerogen slab was built with 511 kerogen fragment molecules C_{22}H_{13}ON, which is adopted from a type II mature kerogen molecule.24 The assembled kerogen slab has an H/C ratio of 0.59 and an O/C ratio of 0.05, which can be categorized as a type II kerogen. The density of this kerogen slab is 1.15 g/cm^3, in decent agreement with experimental data: 1.18 – 1.89 g/cm^3.25-28 Detailed procedures on how to prepare the kerogen surface were reported in our previous publication.19

Because the kerogen model surface can be highly mobile especially over 300 K, yielding unreliable estimation of free energy. Therefore, unlike our previous study, all the kerogen surfaces in this work were rigid by fixing the position of all kerogen atoms in all directions (X, Y, and Z). To evaluate the impact of using rigid kerogen surface, we evaluated the free energy of a polar oil molecule interactions with the flexible water-wetted kerogen surface at a lower temperature range of 200K to 400K. In Figure S1, the unrestricted flexible kerogen surface produced systematic lower free energy of oil desorption than the rigid one. The reduced energy can be ascribed to the mobile surface of flexible kerogen model, exposing more functional groups to form more dipole – dipole interactions with water. As a result, the flexible kerogen surface became less functionalized after wetting by water compared with the rigid surface, weakening the oil-surface interactions. This postulate is consistent with the observation from methane adsorption simulations that the flexible kerogen can have 57% more methane adsorption than the rigid one.29,30 The interest of this study is the relationship between the free energy and the temperature. Our data in Figure S1 suggest that whether the kerogen surface is rigid or flexible makes no qualitative difference to this relationship.

To date, there is no water model that can represent all water properties accurately.31,32 The qualitative results produced by common water models, however, should be potential-independent.31 Nonetheless, we compared several common water models by replicating the calculation of free energy surfaces of the single polar oil molecule interaction with the wet kerogen surface. Common water models we tested include simple point charge series (SPC, SPC/F, and SPC/E) and transferable intermolecular potential series (TIP3P, TIP4P-Ew, and TIP5P-E). In Figure S2, different water models produced noticeable difference in free energy but qualitatively similar patterns of free energy evolution. The calculation results and performance details are compared in Table S1. The lowest desorption energy by SPC/F is attributed to the large dipole moment of water model induced by the flexible structure.33 Therefore, this study used SPC/F water model owing to its simplicity and the consequent improvement in computational efficiency. Several editions of flexible water model have been proposed.34-37 The SPC/F model in this study is adopted from CLAYFF force field,38 which has been extensively used to describe aqueous solution interactions with mineral surfaces. The parameters of SPC/F potential used in this study are listed as supporting text 1. It is anticipated that using different water models will not alter how the free energy responds to the temperature change, although the absolute values in free energy may vary.

The OPLS-AA force field was applied to describe the organic molecules including octane, octanethiol, and kerogen.39 Their molecular geometries and dipole moments described by this force field are qualitatively consistent with results from density function theory calculation, as shown in Table S2. All these force field potentials have produced reasonable results as demonstrated by our previous study.19

**Molecular Dynamics Simulations and Free Energy Calculations.** Molecular dynamics simulations were carried out by GROMACS (version 2018.4, open-source software).40-46 The free energy surfaces of oil interactions with surfaces were computed using the umbrella sampling. All MD simulations were performed in canonical ensembles (NVT) with the following settings: periodic boundary conditions, time step of 1.0 fs, fast smooth particle-mesh Ewald (SPME) electrostatics with interpolation order of 4,
relative strength of the Ewald-shifted direct potential $10^{-5}$, 0.12 nm fourierspacing, Verlet cutoff-scheme, and a Nosé–Hooer extended ensemble for temperature coupling every 0.41 ps. Five different temperatures were tested, including 300 K, 350 K, 400 K, 450 K, and 500 K. The temperature range is based on the reported data of common shale plays ranging from 305 K to 436 K.\textsuperscript{47}

Using an isothermal-isobaric ensemble (NPT) would be desirable to compare with the experimental results usually obtained under constant pressure and temperature; however, MD simulation of a large multi-phase multi-component system in the NPT ensemble can be challenging for reaching equilibrium. Moreover, umbrella sampling requires that the size of system be large enough to satisfy the minimum image convention. To accommodate this requirement without compromising computation efficiency, the simulation systems were prepared in the NVT ensembles with vacuum space (Figure 1).

All systems initially performed constrained simulations prior to umbrella sampling simulation. In a constrained simulation, the oil was fixed along the direction of the reaction coordinate. Each constrained simulation was run up to 100 ps to allow the system to be reach equilibrium. The settings of umbrella sampling simulation for each system are tabulated in Table 1. Upon the completion of umbrella sampling simulations, weighted histogram analysis method (WHAM) was carried out to compute the free energy surface and error analysis. The errors were estimated using Bayesian bootstrapping. Each bootstrapping used 10 bootstraps.

Data visualization and analysis. The simulation data were visualized by VMD (version 1.9.3, free to non-commercial use).\textsuperscript{48} VMD was also used to analyze the surface area of interfaces and the quantity of adsorbed oil atoms in the first layer on surface through Tcl/tk scripting (Supporting Text 2). The surface area was measured using solvent-accessible surface area (SASA) algorithm with a probe radius of 0.14 nm. Oil atoms within 0.36 nm radius of the kerogen surface were counted as the first layer adsorbates, considering the maximum range of non-bonded interactions is approximate to 0.36 nm in these simulations. The contact angles of oil droplets were measured by Fiji ImageJ (version 1.52p, open source)\textsuperscript{49} using contact angle plugin developed by Marco Brugnara. Circle best-fit algorithm was applied. The reported surface areas and contact angles were averaged from the estimation of 11 trajectory snapshots from simulations corresponding to the free energy minimum. The contact angle measurements were listed in the Supporting Information as Table S3.

Results

Entropy and enthalpy calculation. The free energy directly calculated from the NVT ensemble is Helmholtz free energy ($\Delta A$). The pressure changes along the reaction coordinates in all simulated systems are well within the fluctuation range of measured pressures. All simulation systems have local vacuum and fixed volume. For the above reasons, the energy contribution from pressure and volume can be ignored. The Helmholtz free energy calculated from these NVT ensembles can be treated as Gibbs free energy ($\Delta G$) given that $G = A + PV$.

In this study, oil molecules can move in both directions at the surface: move away from surface (desorption) and move towards surface (absorption). Despite the presence of vacuum, oil molecule and droplets in all simulations were constantly being fully submerged in water. No phase changes have been observed during these simulations. Thus, thermodynamic properties of desorption obtained from free energy calculations should coincide with the properties of adsorption.\textsuperscript{50} If the free energy of oil adsorption/desorption is a linear function of the temperature, the entropic and enthalpic contributions can be described by van`t Hoff equation:

$$\Delta G = \Delta H - T\Delta S$$  \hspace{1cm} (1)
where $\Delta G$ is the change of Gibbs free energy (kJ/mol), $\Delta H$ is the enthalpic contribution (kJ/mol), $T$ is the temperature (K), and $\Delta S$ is the entropic contribution (J/mol/k). Such linear relationship suggests that the entropic contribution is temperature independent. Previous study suggests that entropies of alkane adsorption on acidic zeolites can be insensitive over a moderate temperature range up to 450 K. The reported reservoir temperatures of common shale plays are between 305 K and 436 K, which gives a temperature range less than 150 K.

Moreover, because there is no phase change, nor any chemical reactions at the simulated interfaces in this study, the adsorption process should be the reverse of desorption. There should be no difference in the absolute values of free energy, enthalpy, and entropy between adsorption and desorption. All the simulation systems exhibited gains in free energy, enthalpy, and entropy during oil desorption, whereas they exhibited losses during oil adsorption. For the purpose of convenience, free energy, enthalpy, and entropy below refer to the desorption which all have positive values.

**Oil droplet.** The free energy, entropy, and enthalpy of the desorption of oil droplet are shown in Figure 2 and Table 2. Increasing temperature reduces the desorption energy of an oil cluster, which exhibits entropic gains of 22.7 (1.4) J/mol/k and 26.3 (3.2) J/mol/k for each molecule in the polar and non-polar oil droplets, respectively. The enthalpic gains are 14.3 (0.5) kJ/mol and 15.0 (1.3) kJ/mol per molecule for polar and non-polar droplets, respectively. The increase in enthalpy indicates oil cluster desorption from wet kerogen is an endothermic reaction.

**Single oil molecule.** The free energy, entropy, and enthalpy of the desorption of single oil molecule are compared in Figure 3 and Table 2. Changing temperature has substantially less impact on the desorption energy for both polar and non-polar single oil molecules than for oil droplet. The entropic gains are 6.6 (3.7) J/mol/k and 8.2 (11.4) J/mol/k for polar and non-polar oil molecule, respectively. The enthalpic gains are 21.6 (1.5) kJ/mol and 20.6 (4.8) kJ/mol for polar and non-polar oil, respectively. The errors in entropy and enthalpy are relatively large because the small systems of a single oil molecule are more susceptible to statistical errors than are the large systems of an oil droplet. The gaining in enthalpy indicates oil desorption from wet kerogen is an endothermic reaction.

**Contact angle.** The contact angles of both polar and non-polar oil clusters on the kerogen surfaces increased as temperature increased (Figure 6). The contact angles of an oil droplet range from 48° to 64° and 50° to 74° for polar and non-polar oil, respectively. We also reported the number of oil atoms adsorbed on the kerogen surfaces. Below 500K, the differences in the contact angle and the fraction between polar and non-polar oil droplets are negligible (well within error bars, Figure S3). At 500K, these differences became noticeable, which also reflected in the corresponding Gibbs free energy at 500K (Figure 5). Despite the large error bars, the contact angles of polar oil are systematically smaller than those of non-polar oil under the same temperature. In general, the variations of contact angle are consistent with the changes in free energy.

**Discussion**

**Enthalpy and entropy contributions to free energy.** The differential enthalpy $\Delta H$ is a quantitative indicator of the strength of the binding between adsorbate (e.g. oil) and adsorbent (e.g. kerogen surface). In this study, all the calculated values of $\Delta H$ and $\Delta S$ are positive for oil desorption and negative for oil adsorption. Positive $\Delta H$ indicates the desorption process is endothermic, and therefore heat is absorbed as the oil molecules are desorbed from kerogen surface, or vice versa. The positive $\Delta S$ indicates oil molecule will gain entropy upon desorption because of less restriction to the molecular mobility in solution than on surface. Surface adsorption has no impact on the vibration of a short chain alkane with less than ten carbons. The oil molecules, octane and octanethiol, have eight carbons. Therefore, the
entropy changes in adsorption/desorption are mostly through the translation and the rotation of oil molecules. The differential entropy indicates that the oil molecules will have substantial losses in the degrees of freedom of translational and rotational motion during adsorption, and the oil molecules will gain entropy due to both translational and rotational motions during desorption process. This result provides thermodynamic insights on how the kerogen surface affects the molecular dynamics of oil compounds.

**Effect of polarity of oil molecules.** There are noticeable differences in free energy and entropy between polar and non-polar oil droplets, whereas these differences are less apparent for a single oil molecule. Nevertheless, the impact caused by oil polarity has a distinct pattern on the free energy and entropy during surface interactions either with an oil droplet or with a single oil molecule: polar oil exhibited larger changes in free energy and entropy than non-polar oil. However, the differential enthalpies of polar oil are comparable to those of non-polar oil (Table 2).

The differences in the free energy and entropy can be attributed to the presence of the polar functional group thiol -SH in polar oil molecule: octanethiol. Polar oil molecules can form strong dipole-dipole interactions with the kerogen surface through polar functional groups since the kerogen model molecule also has polar functional groups such as hydroxyl -OH and amine -NH. The strong interactions of polar oil molecule with kerogen surface leads to higher level of free energy for desorption and higher extent of mobility loss than that of non-polar oil.

The differences in the differential enthalpy are negligible. The differential enthalpy is a function of the quantity of absorbates. Because the numbers of absorbed oil molecules are the same between the polar and the non-polar oil either for the single molecule adsorption or for the oil droplet adsorption. It is reasonable that the differential enthalpies of both polar and non-polar oil are statistically identical.

Overall, it appears that the molecular polarity makes no substantial differences in free energy, entropy, and enthalpy. Since the kerogen surface is highly heterogeneous and contains both polar and non-polar functional groups, one may argue the kerogen surface could interact equivalently with polar and non-polar oil owing to the presence of these functional groups. Our previous study simulated the adsorption of single oil molecule on wet and dry kerogen surfaces, and showed that the surface water clearly changes the energetics of oil-water interactions. On dry kerogen, a polar oil molecule requires nearly two times higher energy to desorb than that of non-polar one. On wet kerogen, water molecules were competing against oil molecules for surface adsorption, suppressing interaction energetics of both polar and non-polar oil to approximately the same level. Therefore, the surface water negates the effect of molecular polarity, suggesting the fluid composition can complicate the oil-surface interactions. This complexity indicates the fluid composition (e.g. water content and polar compounds) needs to be properly modeled in order to simulate hydrocarbon system that can represent a natural one.

**Effect of molecular clustering.** The free energy per molecule is higher for the single oil molecule than for the oil droplet; the enthalpy, higher; and the entropy, lower. One main difference between a single molecule and an oil droplet is that different types of intermolecular interactions are involved in the interface of the oil interactions with the kerogen surface. When an oil droplet is adsorbed, only a portion of the 30 oil molecules is closely attached to the surface. Each oil molecule is subjected to non-bonded intermolecular interactions with other oil molecules, surface kerogen molecules, and water molecules. For an individual oil molecule in the droplet, the net results of these interactions are highly dependent on the surrounding environment. In general, intermolecular forces from surrounding water molecules would oppose the forces from surface molecules; and the net contribution from oil-oil interactions should be
negligible to oil-surface interactions. Likewise, when the adsorbate is a single oil molecule, the oil molecule is only affected by the surrounding water and surface molecules.

The degree of the opposing effect from water on the oil-surface interactions depends on the number of water molecules in the effective proximity of the adsorbed oil. Since a droplet absorbate has proportionally fewer water molecules in the vicinity than the single molecule absorbate, the opposing effect from water is stronger for a single molecule absorbate than for an oil droplet. This difference leads to higher free energy per molecule for desorbing a single molecule than for an oil droplet.

Interestingly, the differential enthalpy of the oil droplet containing 30 molecules is not proportional to that of a single oil molecule. The difference in enthalpy indicates that the enthalpic effect on a single molecule adsorbate cannot be linearly scaled up to describe absorbate of a molecular cluster. Further study is required to examine the size effect on enthalpy.

In terms of entropy, the entropy gain of an oil droplet is substantially higher than that of a single molecule. This significant difference is attributed to the presence of oil-oil interactions. Oil is immiscible with water due the formation of oil droplet, indicating oil-oil interactions are substantially stronger than oil-water interactions. Therefore, the mobility of oil molecules within the droplet absorbate should be lower than that in the single molecule absorbate. Because mobility loss mostly occurs in translational and rotational motions. The single oil molecule absorbate can still perform noticeable movement translationally and rotationally on the surface, whereas the oil droplets move substantially less due to the strong oil-oil interactions. This distinction suggests that the single molecule model of oil cannot qualitatively reflect all the interfacial properties of oil cluster.

**Correlating contact angle with free energy.** All contact angles of both polar and non-polar oil measured in this study are within 90°. Therefore, the kerogen surface can be considered as oil-prone at the given temperatures ranging from 300K to 500K. The measured contact angles corresponded to the global minimum of the Gibbs free energy of the system, which are the most stable contact angles.\(^{55}\) The reported contact angles should be free from the complication caused by the contact angle hysteresis: the difference between advancing and receding contact angles due to the presence of metastable states.\(^{55,56}\)

The surface tension (\(\gamma\)) equals the free energy (\(F\)) per surface area (\(a\)).\(^{57-59}\) The free energy here can either be Helmholtz free energy (\(A\)) or Gibbs free energy (\(G\)).

\[
\gamma = (\partial A/ \partial a)_{n,V,T} = (\partial G/ \partial a)_{n,P,T}
\]

Therefore, in this study

\[
dF = \gamma_{ij} \cdot da_{ij} \tag{3}
\]

where \(i\) and \(j\) denote the components in the simulations including water, surface, oil, and vacuum.

It is reasonable to assume that the surface areas of vacuum, kerogen, and water remain constant since all the umbrella sampling simulations were performed at steady/equilibrium state.

Given that the contact angle (\(\theta\)) can be described by the Young’s equation on the nanoscale.\(^{60,61}\)

\[
\gamma_{\text{water-kerogen}} - \gamma_{\text{oil-kerogen}} = \gamma_{\text{oil-water}} \cdot \cos \theta \tag{4}
\]

The desorption energy (\(\Delta F\)) can be expressed as

\[
\Delta F = \gamma_{\text{oil-water}} \cdot (a_{\text{oil-water, free}} - a_{\text{oil-water, adsorbed}} + a_{\text{oil-kerogen, adsorbed}} \cdot \cos \theta) \tag{5}
\]
A detailed description about the derivation of equation (5) is provided in supporting text 3.

One may wonder why not treat the free droplet as a geometric sphere and the adsorbed droplet as a spherical dome. This approximation has been applied for describing large droplets with over $10^4$ particles at room temperatures on nanoscales. However, the simulation trajectory shows the geometry of oil droplets in this study is far from ideal, especially at elevated temperatures. The increasing temperature will lead to noticeable increase in the surface area of both free and adsorbed droplet due to the geometric deformation. Therefore, the surface areas of the actual model geometry were measured (Table S5) instead of those of the conceptual geometry.

The oil-water surface tension calculated by Equation (5) is plotted with respect to the temperature in Figure 7. Data points of both polar and non-polar oil droplets show good linear regression with coefficients of determination over 0.9. There is no reported data of surface tension under the same conditions to compare the calculated surface tension. The surface tension of oil-water interface is a function of temperature and pressure. The system pressure average in this study ranged from 2.0 kilobar to 2.5 kilobar (Table S4). Owing to the presence of a vacuum in the simulation and the simulation size, the measured pressure may not accurately reflect the pressure at the interface. Nevertheless, the slope of the regression line (0.070) of $\gamma_{\text{octane-water}}$ is comparable to that of the experimental measurements taken at atmospheric pressure (0.082). Another factor that can affect the surface tension is the line tension at the three-phase contact region, and line tension can affect the contact angle of a droplet at nanometer scale. We are aware that an accurate prediction of the surface tension requires strict control on factors such as force field potentials, pressure, and line tension. However, the focus of this study is to establish the intrinsic relationships between free energy, temperature, and contact angle. We believe our interpretations offer a comprehensive analysis consistent with the experimental observations.

In addition, the calculation of Equation (5) shows that the values of $\Delta F/\gamma_{\text{oil-water}}$ are fluctuating in the range of 20 to 27 nm$^2$ for polar oil and 17 to 22 nm$^2$ for non-polar oil, respectively. Considering the statistical error, the $\Delta F/\gamma_{\text{oil-water}}$ can be treated as a constant. According to Zisman theory, the $\gamma_{\text{oil-water}}$ can be a linear function of $\cos \theta$. This empirical correlation indicates that the free energy ($\Delta F$) can be approximated with a linear function of $\cos \theta$. Therefore,

$$\Delta F = c_1 \cdot \cos \theta + c_2$$  \hspace{1cm} (6)

in which $c_1$ and $c_2$ are fitting parameters with constant value.

Indeed, plotting $\Delta F$ against $\cos \theta$ clearly demonstrates the presence of such linear relationship, yielding a coefficient of determination over 0.99 for non-polar oil and 0.76 for polar oil (Figure 8). The fitting accuracy of polar oil is reduced because the polar oil is less homogeneous than the non-polar oil. The proposed simple equation would be suitable to describe a relatively homogenized droplet on nanoscales by correlating the contact angle with free energy or free energy related terms.

**Conclusion**

This study applied molecular dynamics simulations to study the temperature effect on the interactions of light oil with water-wetted shale kerogen. This computational approach can obtain the free energy, enthalpy, and entropy of oil adsorption/desorption as well as the contact angle of oil droplet on surface. The key takeaway messages include:

1. The free energy of oil/shale interactions is a linear function of temperature at shale reservoir temperatures. This relationship provides a molecular thermodynamic approach in estimating hydrocarbon reserves and in developing thermal stimulation techniques for unconventional shale.
2. The most stable contact angles ($\theta$) of an adsorbate droplet can be linearly correlated with the free energy ($\Delta F$) as $\Delta F = c_1 \cdot \cos \theta + c_2$ in which $c_i$ is the fitting parameter. This correlation can immediately aid the wettability study on nanoscales by correlating the contact angle with free energy or free energy related parameters, which is particularly useful to special core analysis in formation evaluation.

3. A single molecule cannot represent an oil droplet because of the absence of oil-oil molecular interactions. This finding suggests that an adsorption model without consideration of the intermolecular interactions in the adsorbate can make inaccurate prediction on nanoscales.

Our work demonstrates that molecular dynamics simulation is capable of filling the knowledge gap between experimental observation and theoretical calculation. For more realistic simulations, one can consider using NPT ensemble for pressure control and applying water models such as SPC/E and TIP4P-Ew (whose surface tension values are in good agreement with experiments[^2]).

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Figure 1. Simulation snapshot of a polar oil droplet (left) and a single polar oil molecule (right) on water-wetted kerogen surfaces. Each simulation box contains water, oil, and kerogen molecules. Different types of molecules are depicted with different styles for visual clarity. White represents hydrogen; green, carbon; yellow, sulfur; blue nitrogen; and red, oxygen.
Figure 2. Temperature effect on the free energy of oil droplets on kerogen surfaces. The orange triangles (pointing upwards) represent free energy per molecule of a polar oil droplet, while the blue triangles (pointing downwards) denote the free energy of non-polar droplet. The fitting equations are $f(x) = 14.3 - 22.7x$ and $f(x) = 15.0 - 26.3x$ for polar and non-polar oil droplets, respectively. The coefficients of determination are 0.99 and 0.96 for polar and non-polar oil droplets, respectively. Standard errors are illustrated with error bars.
Figure 3. Temperature effect on the free energy of single oil molecules on kerogen surfaces. The orange triangles (pointing upwards) represent the polar oil, while the blue triangles (pointing downwards) denote the non-polar oil. The fitting equations are $f(x) = 21.6 - 6.6x$ and $f(x) = 20.6 - 8.2x$ for polar and non-polar oil droplets, respectively. The coefficients of determination are 0.54 and 0.05 for polar and non-polar oil droplets, respectively. Standard errors are illustrated with error bars.
Figure 4. Temperature effect on the contact angle of polar and non-polar oil droplet on wet kerogen surfaces. The orange triangles (pointing upwards) represent the polar oil, while the blue triangles (pointing downwards) denote non-polar. Standard errors are illustrated with error bars.
Figure 5. Calculated surface tension of water-oil with respect to temperature. The orange triangles (pointing upwards) represent the surface tension of water/polar oil, the blue triangles (pointing downwards) denote surface tension of water/non-polar oil, the hollow blue triangles (pointing downwards) stand for the experimental measurements at atmospheric pressure. The fitting equations are \( f(x) = 34.1 - 0.0564x \) and \( f(x) = 39.6 - 0.0703x \) for water/polar oil and water/non-polar oil, respectively. The coefficients of determination are 0.95 and 0.98 for water/polar oil and water/non-polar oil, respectively. The fitting equation for experimental data of surface tension of water/non-polar oil is \( f(x) = 75.6 - 0.0821x \) with a coefficient of determination 1.00.
Figure 6. Linear correlation between the free energy with respect to the cosine of contact angle ($\theta$). The orange triangles (pointing upwards) represent the polar oil, while the blue triangles (pointing downwards) denote non-polar. The fitting equations are $f(x) = 436.4x - 63.5$ and $f(x) = 465.2x - 81.6$ for polar and non-polar oil droplets, respectively. The coefficients of determination are 0.76 and 0.99 for polar and non-polar oil droplets, respectively. Standard errors are illustrated with error bars.
### Table 1. Specification of simulation systems, which includes simulation box size, number of water molecules, kerogen slab thickness, total number of atoms, number of configurations for umbrella sampling, the spacing between windows, harmonic potential, and production time of each configuration.

| System                  | Single oil molecule | Oil droplet (30 molecules) |
|-------------------------|---------------------|----------------------------|
| Box dimension (X × Y × Z, nm) | 8.1 × 7.9 × 14.0    | 8.1 × 7.9 × 16.0          |
| Water molecules          | 3950                | 10000                     |
| Slab thickness (nm)      | 3.54                | 3.54                      |
| Total number of atoms    | 3.0 × 10⁵           | 5.0 × 10⁵                 |
| Configurations           | 261                 | 361                       |
| Spacing (nm)             | 0.01                | 0.01                      |
| Harmonic potential (kJ/mol / nm²) | 5000              | 5000                      |
| Production time (ns)     | 0.2                 | 0.1                       |

### Table 2. Changes of free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) calculated from the oil interactions with wet kerogen surfaces under different temperatures. * The ΔG, ΔH, and ΔS of oil droplets are normalized as per molecule for comparison. Their original values, based on the whole oil cluster, are divided by 30, the total number of molecules in the oil clusters.

| System                  | 300K  | 350K  | 400K  | 450K  | 500K  | ΔH  | ΔS  |
|-------------------------|-------|-------|-------|-------|-------|-----|-----|
| Polar molecule          | 20.1 (3.9) | 19.1 (3.6) | 18.7 (3.4) | 18.1 (3.4) | 18.9 (3.7) | 21.6 (1.5) | 6.6 (3.7) |
| Non-polar molecule      | 16.9 (1.9) | 17.7 (2.3) | 21.2 (2.6) | 17.2 (1.7) | 15.6 (1.5) | 20.6 (4.8) | 8.2 (11.4) |
| Polar droplet *         | 7.73 (0.20) | 6.10 (0.21) | 5.17 (0.24) | 4.19 (0.20) | 3.04 (0.22) | 14.3 (0.5) | 22.7 (1.4) |
| Non-polar droplet *     | 7.09 (0.20) | 5.39 (0.20) | 4.99 (0.18) | 3.60 (0.24) | 1.49 (0.19) | 15.0 (1.3) | 26.3 (3.2) |
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Supporting Information

Temperature Effect on Interactions of Oil Droplet with Water-Wetted Shale Kerogen at Reservoir Temperatures: Linear Relationships between Temperature, Free Energy, and Contact Angle

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Supporting Information

Supporting Text 1. Parameterization of SPC/F water model.

[ moleculetype ]
; molname nrexcl
SOL 2

[ atoms ]
; nr type resnr residue atom cgnr charge mass
 1 OW 1 SOL OW 1 -0.820 15.99940
 2 HW 1 SOL HW1 1 0.410 1.00800
 3 HW 1 SOL HW2 1 0.410 1.00800

[ bonds ]
; i j funct length force.c.
 1 2 1 0.09572 502080.0 ; OW HW
 1 3 1 0.09572 502080.0 ; OW HW

[ angles ]
; i j k funct angle force.c.
 2 1 3 1 109.50 627.600 ; HW-OW-HW
Supporting Information

Supporting Text 2. Tcl/tk script for VMD
Scripts and instruction are available at https://github.com/er1czz/vmd

Supporting Text 3. Equation derivation.

Free energy ($F$) can be expressed as a function of surface tension ($\gamma$) and surface area ($a$), which can be applied for both the Helmholtz and the Gibbs free energy. In the equation below, “o” denotes oil; “s”, surface; “w”, water; and “v”, vacuum. And “’” and “” stand for a system with the free oil droplet and a system with the adsorbed oil droplet, respectively.

For both systems, $dF = \gamma_{ij} \cdot da_{ij}$ can be expanded as

$$dF = \gamma_{sv} \cdot da_{sv} + \gamma_{vw} \cdot da_{vw} + \gamma_{ow} \cdot da_{ow} + \gamma_{os} \cdot da_{os}$$ (s1)

For systems in steady/equilibrium state, the surface areas of water-vacuum and surface-vacuum contact regions should be unchanged. Therefore

$$0 = da_{wv} = da_{sv}$$ (s2)

Given that the free energy of desorption

$$\Delta F = F^o - F'$$ (s3)

Combine s1, s2, and s3 to obtain

$$\Delta F = (\gamma_{ow} \cdot a^o_{ow} + \gamma_{sw} \cdot a^o_{sw}) - (\gamma_{ow} \cdot a'_{ow} + \gamma_{sw} \cdot a'_{sw} + \gamma_{os} \cdot a'_{os})$$ (s4)

Since kerogen surface is rigid, its total surface area should be a constant value

$$a^o_{sw} = a'_{sw} + a'_{os}$$ (s5)

Substituting for $a^o_{sw}$ in s4 gives

$$\Delta F = \gamma_{ow} \cdot (a^o_{ow} - a'_{ow}) + (\gamma_{sw} - \gamma_{os}) \cdot a'_{os}$$ (s6)

According to the Young’s equation

$$\gamma_{sw} - \gamma_{os} = \gamma_{ow} \cdot \cos \theta$$ (s7)

Now substitute for $\gamma_{sw} - \gamma_{os}$ in s6 we obtain

$$\Delta F = \gamma_{ow} \cdot (a^o_{ow} - a'_{ow} + a'_{os} \cdot \cos \theta) \quad \text{QED.}$$ (s8)
Figure S1. Comparison between the free energy of a single polar oil molecule desorption from a fixed (rigid) kerogen surface and from an unrestricted (flexible) kerogen surface under different temperatures. The energies of oil desorption from unrestricted kerogen surfaces are systematically lower than those from fixed kerogen surfaces. Standard errors are illustrated with error bars.
Figure S2. The free energy profiles of a single polar oil molecule on a rigid kerogen surfaces wetted with different water models. The distance is measured from the center of mass of the oil molecule to that of the kerogen slab. These free energy profiles are qualitatively identical. The deviation in energy minimum position is reasonable, and is attributed to the heterogeneity of kerogen surfaces and the asymmetric geometry of the polar oil molecule.
Figure S3. Fraction of number of atoms in oil droplets affected by the kerogen surface. The fraction is the percentage of oil atoms within 0.36 nm of the surface out of the total number of atoms in the oil droplet. The orange bars represent polar oil droplets, while the blue bars (with stripe pattern) denote the non-polar oil droplets. Standard errors are illustrated with error bars.
Figure S4. Surface areas of different contact regions on adsorbed oil droplets. Orange, yellow, sky blue, and blue squares denote contact areas between polar oil and water, polar oil and kerogen surface, non-polar oil and water, and non-polar oil and kerogen surface, respectively. Standard errors are illustrated with error bars.
Supporting Information

| Model    | Description                                      | Dipole       | Hours | Efficiency % | ∆G (kJ / mol) |
|----------|--------------------------------------------------|--------------|-------|--------------|---------------|
| SPC/F    | Flexible Simple Charge Point, 3 sites            | 2.39 – 2.4612| 48    | 100          | 19.08 (3.57)  |
| SPC      | Simple Charge Point, 3 sites                     | 2.273        | 49    | 98           | 27.99 (3.36)  |
| SPC/E    | Extended Simple Charge Point, 3 sites            | 2.354        | 49    | 98           | 27.85 (2.70)  |
| TIP3P    | Transferable Intermolecular Potential, 3 sites   | 2.355        | 49    | 98           | 24.85 (2.61)  |
| TIP4P-Ew | 4 sites, Ewald summation                         | 2.325        | 54    | 89           | 30.41 (3.21)  |
| TIP5P-E  | 5 sites, Ewald summation                         | 2.297        | 62.5  | 77           | 29.60 (3.00)  |

Table S1. Description and performance of water models SPC/F, SPC, SPC/E, TIP3P, TIP4P-Ew, and TIP5P-E. The benchmark tests were conducted at NERSC using 64 cores on Cori Intel Xeon Phi (KNL) node. Each calculation computed a free energy surface at 350 K of a single polar oil molecule interacting with a fixed kerogen surface in the presence of 3950 water molecules. Each free energy surface was derived from 121 configurations. 200 ps umbrella sampling was performed on each configuration.

| Compound      | Dipole Moment (Debye) | MD      | PM7      | DFT      |
|---------------|-----------------------|---------|----------|----------|
| water         |                       | 1.13    | 2.130    | 2.094514 |
| octane        |                       | 0.00    | 0.003    | 0.000161 |
| octanethiol   |                       | 1.05    | 2.218    | 2.025873 |
| kerogen       |                       | 1.27    | 0.490    | 0.645501 |

Table S2. Molecular dipole moment of water, octane, octanethiol, and kerogen. Molecular dynamics simulation (MD) were carried out by Avogadro.8,9 Semi-empirical calculations were conducted by MOPAC with PM7 Hamiltonian.10,11 Density function theory (DFT) calculations were performed by GAMESS with 6-31G* basis set,12,13 B3LYP functional,14,15 and a SCF convergence of 10^-5 of the density matrix. Please note that all these calculations are based on single molecule models in vacuum. The optimized kerogen structure can be downloaded from https://github.com/er1czz/md

| Temperature (K) | Contact angle (degree) | Polar oil | Non-polar oil |
|----------------|------------------------|-----------|---------------|
| 300            |                        | 48.27 (2.26) | 50.37 (1.62) |
| 350            |                        | 56.35 (3.12) | 59.05 (3.27) |
| 400            |                        | 54.38 (2.42) | 61.33 (2.10) |
| 450            |                        | 67.29 (1.27) | 65.24 (1.98) |
| 500            |                        | 63.72 (2.92) | 74.12 (2.42) |

Table S3. Contact angles of polar and non-polar oil droplets at different temperatures. “()” denotes standard error.

| Temperature (K) | Polar oil droplet system pressure (bar) | Non-polar oil droplet system pressure (bar) |
|----------------|----------------------------------------|------------------------------------------|
|                | Free   | Adsorbed | Free   | Adsorbed |
| 300            | 2.00E+03 | 1.98E+03 | 2.03E+03 | 2.01E+03 |
| 350            | 2.08E+03 | 2.04E+03 | 2.14E+03 | 2.13E+03 |
| 400            | 2.18E+03 | 2.15E+03 | 2.21E+03 | 2.19E+03 |
| 450            | 2.32E+03 | 2.28E+03 | 2.34E+03 | 2.31E+03 |
| 500            | 2.49E+03 | 2.45E+03 | 2.51E+03 | 2.48E+03 |

Table S4. System average pressures of free oil droplet simulations and adsorbed oil droplet simulations at different temperatures.
Supporting Information

| Temperature | Free droplet Oil-water | Adsorbed droplet Oil-water | Adsorbed droplet Oil-kerogen | Free droplet Oil-water | Non-polar oil (nm²) Adsorbed droplet Oil-water | Non-polar oil (nm²) Oil-kerogen |
|-------------|------------------------|-----------------------------|-----------------------------|------------------------|-----------------------------------------------|----------------------------------|
| 300 K       | 36.27 (0.44)           | 28.66 (0.30)                | 22.18 (0.37)                | 34.84 (0.49)           | 28.71 (0.18)                                  | 21.71 (0.35)                     |
| 350 K       | 37.66 (1.14)           | 29.86 (0.37)                | 22.59 (0.48)                | 35.66 (0.35)           | 28.76 (0.24)                                  | 20.49 (0.43)                     |
| 400 K       | 43.39 (1.02)           | 32.06 (0.73)                | 24.98 (0.90)                | 40.14 (1.00)           | 31.63 (0.49)                                  | 24.32 (0.96)                     |
| 450 K       | 45.48 (1.02)           | 32.86 (0.64)                | 22.36 (0.78)                | 45.24 (1.22)           | 32.51 (1.25)                                  | 22.20 (0.99)                     |
| 500 K       | 55.77 (1.06)           | 40.39 (0.91)                | 25.48 (0.95)                | 49.42 (1.59)           | 35.40 (0.66)                                  | 21.46 (1.16)                     |

Table S5. Surface areas of different contact regions on oil droplets. “()” denotes standard error.
Reference

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