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Tolman length and rigidity constants of water and their role in nucleation

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A proper understanding of nucleation is crucial in several natural and industrial processes. However, accurate quantitative predictions of this phenomenon have not been possible. The most popular tool for calculating nucleation rates, classical nucleation theory (CNT), deviates by orders of magnitude from experiments for most substances. We investigate whether part of this discrepancy can be accounted for by the curvature-dependence of the surface tension. To that end, we evaluate the leading order corrections for water, the Tolman length and the rigidity constants, using square gradient theory coupled with the accurate CPA equation of state. The Helfrich expansion is then used to incorporate them into the CNT-framework. For water condensation, the modified framework successfully corrects the erroneous temperature dependence of the nucleation rates given by the classical theory and reproduces experimental nucleation rates.

Nucleation is the rate limiting step in most first order phase transitions, such as boiling, condensation and crystallization. The process starts with the formation of a small embryo of the new phase in the bulk of the metastable phase, which will continue to grow spontaneously only if its size exceeds a certain threshold.[1]

Nucleation of water is perhaps the most popular example in literature, due to its relevance in the industry, for instance in boilers or turbines, in biological systems, or in atmospheric sciences and climate modelling.[2]

Despite of several extensions and theoretical advances, Classical Nucleation Theory (CNT) is still the most widely used theoretical tool to predict nucleation rates.[1,3–5] Even though CNT provides a qualitatively correct picture of nucleation, its quantitative predictions are often orders of magnitude away from experiments. For instance, for the simple case of Argon condensation, CNT deviates more than 20 orders of magnitude from experiments.[6] For homogeneous water condensation, the deviations are significantly smaller, but CNT still predicts the wrong temperature dependence of the nucleation rates. Similar to many other substances, CNT predicts nucleation rates for water that are too low at low temperatures, but overpredicts them at high temperatures.[1,7]

One of the crudest assumptions of CNT is the so-called capillary approximation, which considers the surface of droplets or bubbles to be sharp and to have the same surface tension as the planar interface. Thus, incorporating the curvature dependence of the surface tension is expected to improve CNT-predictions, accounting for parts of the large discrepancies. Many works in the literature have attempted different routes of evaluating and including the contribution from curvature in CNT.[8–17] However, taking into account these curvature effects in real systems is not an easy task. The leading order correction in the curvature expansion of the surface tension is the Tolman length. Neither the magnitude nor the sign of the Tolman length is known for most substances. Even for the simple Lennard-Jones fluid, molecular dynamics (MD) simulations have only recently given a negative value, consistent with predictions from density functional theory.[15,17–22]

Curvature contributions to the surface tension up to second order can be taken into account through the Helfrich expansion:[23]

$$\sigma(H, K) = \sigma_0 - \delta\sigma_0 H + \frac{k}{2}H^2 + \tilde{k}K + ... \qquad (1)$$

where, σ_0 is the surface tension of the flat surface, $H = \kappa_1 + \kappa_2$ is the total curvature, and $K = \kappa_1\kappa_2$ is the Gaussian curvature, with κ_1 and κ_2 being the principal curvatures. The magnitude of the curvature corrections in this expansion are defined by the Tolman length δ, the bending rigidity k and the rigidity constant $\tilde{k}$ associated with the Gaussian curvature.

We recently calculated these constants for the Lennard-Jones fluid, combining Square Gradient Theory (SGT) with a very accurate equation of state, and showed that we could then reproduce the Tolman length and surface tension obtained from MD-simulations.[22] The work also showed that the second order terms, the rigidity constants, were crucial to correctly predict the surface tension of small droplets and bubbles. For water, there are only a few recent (and usually indirect) estimates of the Tolman length and the rigidity constants, often based on simulation models having properties that differ much from real water.[24–27]

In this work, we use SGT combined with the accurate cubic plus association (CPA) equation of state[28–30] to evaluate the Tolman length and the rigidity constants of water. Furthermore, we show that by properly including the curvature-dependence of the surface tension in CNT, it is possible to provide quantitatively accurate predictions of the experimental water nucleation rates with the correct temperature trend. Thus, at least for water, the

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proper incorporation of curvature corrections seems to correct some of the problems in CNT and brings hope that the same is possible for other substances.

Nucleation is an activated process where the phase transition takes place through the formation of critically-sized bubble/droplet (embryo) in a metastable phase. In the context of CNT, the nucleation rate is given by:

$$J = J_0 \exp\left(-\frac{\Delta W^*}{k_{\mathrm{B}} T}\right) \qquad (2)$$

where ΔW^* is the nucleation barrier (i.e. the work of formation of the critical embryo), k_{B} is Boltzmann's constant, T is the temperature and J_0 is the kinetic prefactor which can be calculated from kinetic gas theory, using for instance the prescription by Becker and Döring:[31]

$$J_0 = \frac{1}{\rho_l}\sqrt{\frac{2\sigma_0}{\pi m}}\left(\frac{P_g}{k_{\mathrm{B}} T}\right)^2 \qquad (3)$$

where ρ_l is the liquid-phase molecular density, m is the mass of a water molecule and P_g is the pressure of the gas. Since the nucleation rate depends exponentially on the nucleation barrier, it is crucial to predict this correctly to obtain quantitative nucleation rates.

We will focus our analysis on the homogeneous nucleation of a perfectly spherical embryo of radius r in a single-component fluid in the NPT ensemble (i.e. constant total number of molecules N, pressure P, and temperature, T). The subtle thermodynamics of bubble/droplet formation in CNT has been worked out nicely in several references, especially by Abraham[32] and by Ono and Kondo,[33] and we refer to them for details, since we will only provide the main results. We will use the equimolar as our choice of dividing surface. In that case, the properties of the critical embryo, which is a stationary solution of the Gibbs energy, are given by the equality of the chemical potential for all phases and the generalized Laplace relation[1,32]

$$P_{\mathrm{i}} - P_{\mathrm{o}} = \frac{2\sigma(r_{\mathrm{e}}^*)}{r_{\mathrm{e}}^*} + \left(\frac{\partial \sigma(r)}{\partial r}\right)_{r=r_{\mathrm{e}}^*} \qquad (4)$$

where subscript "i" denotes the bubble/droplet, subscript "o" denotes the exterior phase, and r_{e}^* is the radius of the critical embryo using the equimolar dividing surface. Following Abraham,[32] the work of formation for the critical embryo is given by

$$\Delta W^* = \frac{4\pi r_{\mathrm{e}}^{*2}}{3}\left(\sigma(r_{\mathrm{e}}^*) - r_{\mathrm{e}}^*\left(\frac{\partial \sigma(r)}{\partial r}\right)_{r=r_{\mathrm{e}}^*}\right) \qquad (5)$$

The curvature dependence of the surface tension is then assumed to follow the Helfrich-expansion (Eq. 1), which for a perfectly spherical droplet/bubble is:

$$\sigma(r) = \sigma_0 - \frac{2\delta\sigma_0}{r} + \frac{k_s}{r^2} + \mathcal{O}\left(r^{-3}\right) \qquad (6)$$

where $k_s = 2k + \tilde{k}$, r is the radius which, by definition, is positive for a droplet and negative for a bubble, and terms beyond second order are neglected. Using Eq. 6 in Eq. 4, we obtain:

$$P_{\mathrm{i}} - P_{\mathrm{o}} = \frac{2\sigma_0}{r_{\mathrm{e}}^*}\left(1 - \frac{\delta}{r_{\mathrm{e}}^*}\right) \qquad (7)$$

For the equimolar dividing surface, the second order terms in the Helfrich expansion in Eq. 7 cancel out. Using Eq. 6 in Eq. 5, the nucleation barrier becomes:

$$\Delta W^* = \frac{4\pi\sigma_0 r_{\mathrm{e}}^{*2}}{3}\left(1 - \frac{4\delta}{r_{\mathrm{e}}^*}\right) + 4\pi k_s. \qquad (8)$$

which agrees with and generalizes the work by McGraw and Laaksonen[12], where they implicitly assumed $\delta = 0$. We can simplify further by introducing $r_{\mathrm{CNT}}^* = 2\sigma_0/(P_{\mathrm{i}} - P_{\mathrm{o}})$. Solving Eq. 7 for r_{e}^* and expanding gives:

$$r_{\mathrm{e}}^* = r_{\mathrm{CNT}}\left(1 - \frac{\delta}{r_{\mathrm{CNT}}} - \frac{\delta^2}{r_{\mathrm{CNT}}^2} + \mathcal{O}\left(r_{\mathrm{CNT}}^{*-3}\right)\right) \qquad (9)$$

which can be introduced in Eq. 8. The final expression for the nucleation barrier is then:

$$\Delta W^* = \frac{4\pi\sigma_0 r_{\mathrm{CNT}}^{*2}}{3}\left(1 - \frac{6\delta}{r_{\mathrm{CNT}}^*}\right) + 4\pi\left(k_s + \delta^2\sigma_0\right) \qquad (10)$$

The above equation is also valid for bubbles, but the radius is then negative according to the convention of the Helfrich expansion. With the common assumptions in CNT of ideal vapor and an incompressible droplet, we get the following approximate formulas for the CNT-radii:[1,32]

$$r_{\mathrm{CNT}}^* = 2\sigma_0/(\rho_{l,\mathrm{eq}} k_{\mathrm{B}} T \ln S) \qquad \text{droplet} \qquad (11)$$

$$r_{\mathrm{CNT}}^* = 2\sigma_0/(P_{\mathrm{eq}} - P_{\mathrm{o}}) \qquad \text{bubble} \qquad (12)$$

where subindex "eq" refers to properties along the coexistence-line, and S is the supersaturation, $S = P_{\mathrm{o}}/P_{\mathrm{eq}}$. To distinguish Eq. 10 from the standard expressions in CNT with the capillarity approximation, we shall call the modified framework curvature corrected-CNT, or simply c-CNT, and we will investigate to what extent these curvature corrections affect the predictions from CNT and bring them closer to experiments.

We demonstrated in previous work that it was crucial to use an accurate equation of state to get accurate estimates of the coefficients in the Helfrich expansion with square gradient theory.[22] Unfortunately, we cannot combine square gradient theory with the most accurate equation of state for water (IAPWS),[34] since it fails for densities between the spinodals. We shall instead use the CPA equation of state,[28–30] which provides an accurate representation of the equilibrium properties of water away from the critical point, as shown and discussed in the supplementary information (SI).[35] We have also included in the SI a comparison of SGT with MD-simulations made using the water models TIP4P/2005

and SPC/E (Fig. SI. 1). The results are not expected to coincide since only TIP4P/2005 gives surface tensions which agree with experiments, and both water-models fail to predict the equlilibrium vapor pressure accurately.

The CPA equation of state consists of a cubic part (subscript C) which accounts for the physical forces, and an association part (subscript A), which accounts for hydrogen bonding and other chemical forces.[29] This gives for the Helmholtz energy density:

$$f_{\text{eos}} = f_{\text{eos,C}} + f_{\text{eos,A}} \tag{13}$$

from which other relevant properties such as pressure, entropies and enthalpies can be derived. We used the same CPA-formulation and parameters as Queimada et al.[30] The square gradient model solution is a stationary state of the following functional of the density profile $\rho(\mathbf{r})$:

$$\overline{\Omega}_{\text{sgm}} = \int d\mathbf{r} \left[f_{\text{eos}}(T, \rho(\mathbf{r})) - \mu\rho(\mathbf{r}) + \frac{\eta(T)}{2} |\nabla\rho(\mathbf{r})|^2 \right] \tag{14}$$

where $\mathbf{r}$ is the position and η is the temperature-dependent influence parameter. The stationary density-profiles across the interface are found by solving the corresponding Euler-Lagrange equations. Furthermore, the coefficients in the Helfrich-expansion can be defined analytically in terms of density expansion functions,[36] which can be found by solving a coupled set of differential equations. We have solved these equations for water using a methodology presented previously, and refer to that work for further information about the explicit equations, and the numerical routines.[22]

The resulting Tolman length and rigidity constants for water are reported in Fig. 1, and their values are also tabulated in the SI (Tab. SI. 1).[35] A linear extrapolation was used to obtain the coefficients below T=273.15K (red dashed line) where many of the nucleation experiments for water have been performed (SI). Most of the non-linearity in Fig. 1b comes from the normalization with $k_{\text{B}}T$.

Our results indicate that the Tolman length of water is negative and weakly temperature-dependent, having a small value of about -0.05 nm. This result compares well with previous estimates in the literature.[24–26] For instance, as shown in Fig. 1a, the Tolman length from SGT is within the error bars of the Tolman length from recent Monte Carlo/MD-simulations using the TIP4P/2005 model.[26] Sedlmeier and Netz found a negative Tolman length about twice that value, using the SPC/E water model to investigate water interfaces in the presence of hydrophobic solutes.[24] Even though the exact value of the Tolman length from the SPC/E model is expected to be inaccurate since the model fails to reproduce the experimental surface tension, it is interesting to note that its magnitude increases with temperature similar to Fig. 1a.[24] Other indirect estimates of the Tolman length for water have been obtained from nucleation experiments. In particular, Holten et al. estimated it using nucleation experiments in an expansion wave tube and reported positive values.[37] Azouzi. et al. using cavitation
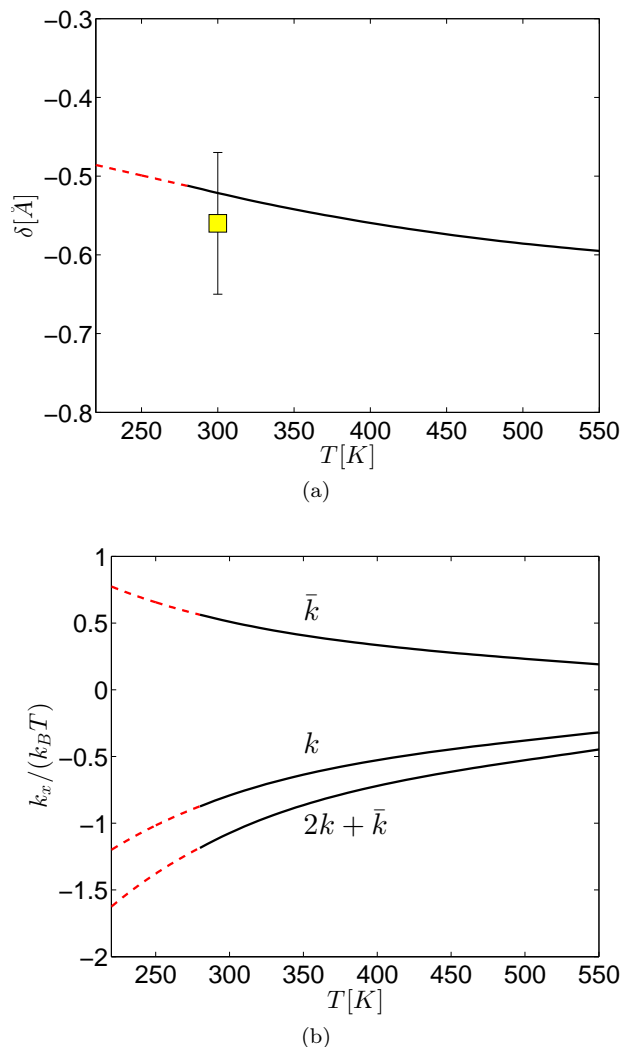

FIG. 1. The coefficients in the Helfrich expansion for water from square gradient theory combined with the CPA equation of state (solid lines) and from a linear extrapolation (red dashed lines), where k_x is used to denote all the rigidity constants. The Tolman length for TIP4P/2005-water is also included (square).[26]

experiments in quartz inclusions at $\sim 320K$ obtained an estimate of the Tolman length of -0.047 nm, a value which agrees well with our results.[25] However, in both cases, the contribution from the rigidity constants is ignored, and their inclusion would change their estimates significantly. For small bubbles/droplets it is crucial to include also the rigidity constants in the analysis to obtain the correct surface tension, since both density functional theory and MD-simulations agree that the surface tension is a concave parabolic function of the curvature.[17,24]

Arguably the most important application of the Tolman length and the rigidity constants is in the context of nucleation. We analyze their influence on water nucleation rates, by comparing to a large amount of experimental data from different experimental techniques
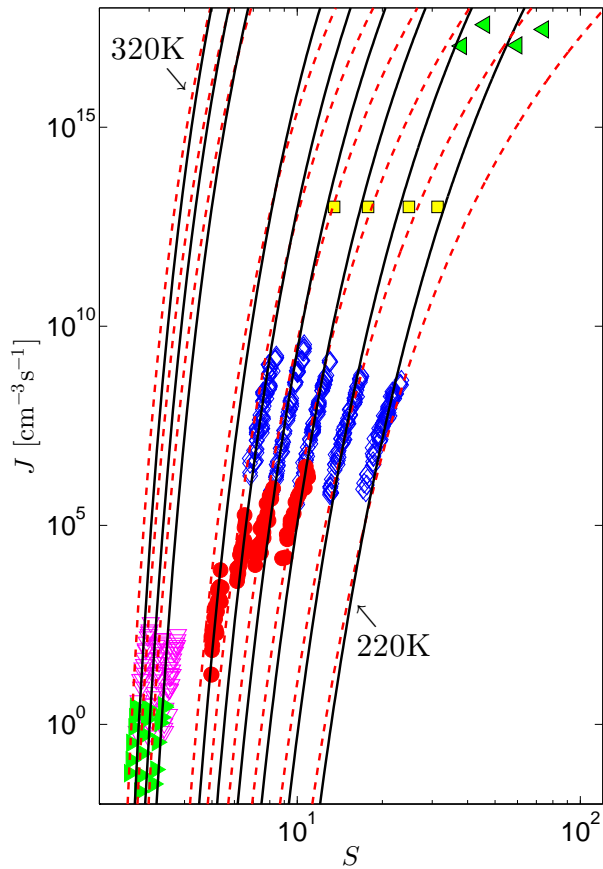
FIG. 2. Experimental nucleation rates from Wölk and Strey (blue diamonds),[7] Manka et al. (red circles),[38] Brus et al. (pink and green triangles),[39,40] Manka (yellow squares),[41] and from Wyslouzil et al.[42] for the temperatures T(K)={320, 310, 300, 270, 260, 250, 240, 230, 220}, compared to CNT (red dashed lines) and c-CNT (solid lines).

covering a wide range of temperatures, supersaturations and nucleation rates.[7,38–43] An excellent overview of the available experiments on homogeneous water-nucleation was recently given by Wölk et al.[44] Moreover, based on their experiments from 2001, Wölk and Strey devised an empirical formula for water to correct the predictions from CNT.[7] This formula, which we will use for comparison, has been found to correspond well with most of the experiments, and has been adopted as a benchmark for homogeneous-water-nucleation.[44]

While the standard CNT typically predicts the correct dependence of nucleation rates on supersaturation, it gives the wrong temperature-dependence. For substances such as water and 1-pentanol, this has been well documented,[1,7,45] and it is also evident from comparing the red dashed lines in Fig. 2 with the experimental results. The figure shows that c-CNT (solid line) gives results which are closer to experiments, both at low and high nucleation rates, where the magnitude of the rates spans 20 orders of magnitude.

To have a clearer picture of the quality of agreement

between the predictions and the experiments at different temperatures, Fig. 3 compares the average ratio between the different approaches and the experimental nucleation rates. As expected, the mean deviation between CNT (red circles) and experiments increases nearly linearly with temperature. However, both the empirical formula and c-CNT are close to experiments and seem to have the correct temperature trend, at least up to $T = 280K$. The slightly higher deviations at 300K, 310K and 320K are probably due to inaccuracies in the experiments. This claim is supported by a comparison between the nucleation rates obtained by Brus et al. using two different experimental techniques, showing similar deviations.[39,40] It is quite remarkable that the empirical formula by Wölk and Strey (crosses) which has been fitted to experiments, display almost the same deviations with experimental results as a function of temperature, as c-CNT (diamonds), specially taking into account that the curvature corrected CNT depends only on the Tolman length and the rigidity constants from SGT, and has no a priori information about experimental nucleation rates. This strongly suggests that including the curvature dependence of the surface tension corrects the wrong temperature-dependence given by the classical theory, at least for the case of water. At the lowest temperatures, c-CNT gives a slightly too steep curve for the nucleation rates as a function of supersaturation (see Fig. 2), which is most likely due to the linear extrapolation of the Tolman length and the rigidity constants below T=273.15K.

As commonly occurring in the context of nucleation, the excellent quantitative agreement between the c-CNT predictions and the experimental rates may be partially accidental, since the actual values of the nucleation rates might change slightly if one takes into account non-idealities, the compressibility of the liquid phase or uses a different model for the kinetic prefactor. However,
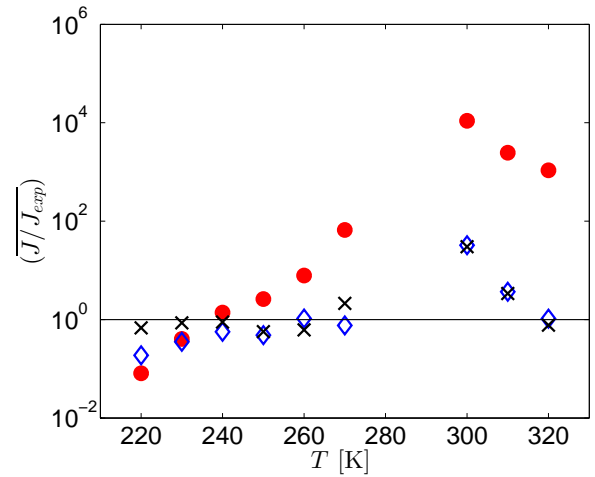

FIG. 3. The average deviation between experiments in Refs.[7,38–40,43] ($J_{exp} < 10^{10}$) and nucleation rates predicted from the empirical formula by Wölk and Strey (black crosses),[7] CNT (red circles) and c-CNT (blue diamonds).

all these modifications typically shift the rates by an approximately constant factor.[7,46] The really important outcome of this work is thus that including the curvature dependence of the surface tension corrects the wrong temperature-dependence given by the classical theory, at least for water.

In summary, we have calculated the Tolman length and rigidity constants of water using SGT combined with the accurate CPA equation of state. Using these constants, it is then possible to incorporate the curvature-dependence of the surface tension into the CNT-framework. The resulting predictions correct the wrong temperature dependence of the nucleation rates given by the classical theory and also improve the agreement with experiments. Thus, this procedure offers a promising way to alleviate the problems of CNT and obtain quantitatively accurate predictions, which hopefully is possible also for other substances.

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