Equivalence between condensation and boiling in a Lennard Jones fluid

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Condensation and boiling are phase transitions highly relevant to industry, geology or atmospheric science. These phase transitions are initiated by the nucleation of a drop in a supersaturated vapor and of a bubble in an overstretched liquid respectively. The surface tension between both phases, liquid and vapor, is a key parameter in the development of such nucleation stage. Whereas the surface tension can be readily measured for a flat interface, there are technical and conceptual limitations to obtain it for the curved interface of the nucleus. On the technical side, it is quite difficult to observe a critical nucleus in experiments. From a conceptual point of view, the interfacial free energy depends on the choice of the dividing surface, being the surface of tension the one relevant for nucleation. We bypass the technical limitation by performing simulations of a Lennard Jones fluid where we equilibrate critical nuclei (both drops and bubbles). Regarding the conceptual hurdle, we find the relevant cluster size by searching the radius that correctly predicts nucleation rates and nucleation free energy barriers when combined with Classical Nucleation Theory. With such definition of the cluster size we find the same value of the surface tension for drops and bubbles of a given radius. Thus, condensation and boiling can be viewed as two sides of the same coin. Finally, we combine the data coming from drops and bubbles to obtain, via two different routes, estimates of the Tolman length, a parameter that allows describing the curvature dependence of the surface tension in a theoretical framework.

I. INTRODUCTION

Understanding first order phase transitions is of great importance to many fields, ranging from biology [1], to atmospheric science [2], physics [3], geology [4] or industry [5, 6].

In the absence of impurities or external surfaces, first order phase transitions start with the emergence of a nucleus of the stable phase in the bulk of the parent metastable phase [7]. A nucleus is “critical” if it is big enough so that it has 50 per cent chances to either grow or redissolve.

Although the emerging phase is more stable, the presence of an unfavourable interface between the nucleus and the parent phase can delay to a great extent the phase transition. Thus, for instance, alkane vapors can be saturated thousands of times over their vapor pressure before condensation takes place [8], alkane liquids can be substantially superheated above the boiling temperature [9, 10] or liquid water can be supercooled up to ~ 60 K below melting until it freezes [11, 12].

Therefore, the surface tension, \( \gamma \), or the free energy per unit area between both phases, plays a key role in the development of first order phase transitions. Whereas \( \gamma \) can be readily measured for a flat interface at equilibrium – at least between fluid phases [13] – it cannot be directly probed for curved interfaces, which is the relevant case for nucleation. Moreover, the fact that critical nuclei are nanoscopic objects makes it very difficult to observe them in experiments, let alone measuring their \( \gamma \). The usual strategy is to infer \( \gamma \) by combining a theoretical description of nucleation with measurements of the nucleation rate (the number of nuclei that appear per unit of time and volume) [7, 17–18]. This approach relies on the validity of theoretical approximations that are difficult to assess.

Computer simulations do have access to the time and length scales relevant for the observation of critical nuclei. However, whereas the methodology and theoretical framework for computing \( \gamma \) for flat interfaces is very well established [20–21], that for curved interfaces is still under development [22–23]. One of the key issues is that \( \gamma \) for curved interfaces depends on the location of the interface, that can be defined in different ways [22–23]. The current situation is that the dependence of \( \gamma \) with the curvature of the interface is contradictory between different groups [18–23, 33–34].

In this work we address fundamental questions regarding the liquid-vapor interface with computer simulations. It has been shown in different simulation works that spherical nuclei can be equilibrated at constant volume and temperature in finite systems [35–38]. Recently, we showed with simulations of bubbles [39] and crystals [40] that nuclei thus equilibrated are critical, in agreement with Density Functional Theory (DFT) predictions [41–45]. On the other hand, we have extensively developed in the past years the so-called Seeding method [56–61] to study nucleation phenomena. This method consists in obtaining with simulations the properties of critical clusters and “plug” them in the Classical Nucleation Theory (CNT) formalism [62–65] to obtain predictions of the nucleation rate and of the \( \gamma \) curvature dependence. This approach has been successful for a wide range of systems [56–58, 60, 61, 64–70] and we use it here for the first time to study condensation. In particular, we apply Seeding at constant volume both to condensation and to cavitation for a Lennard Jones model.

Since Seeding relies on CNT, it is necessary to validate it by comparing its predictions with independent calculations that do not rely on such framework. We do so by...
II. SIMULATION DETAILS

The Lennard-Jones model potential, as well as the simulation details, are the same as in our previous work [54, 70]. In particular, we studied the truncated and force-shifted Lennard-Jones (TSF-LJ) potential [72], a model for which the vapor-liquid transition has been previously investigated [70, 72]:

\[ U_{TSF-LJ}(r) = U_{LJ}(r) - U_{LJ}'(r_c) - (r - r_c)U_{LJ}''(r_c), \]

where \( U_{LJ}(r) \) is the standard 12-6 Lennard-Jones potential and \( U_{LJ}'(r) \) is its first derivative. The interaction potential is truncated and shifted at \( r_c = 2.5\sigma \), being \( \sigma \) the particle’s diameter and \( \epsilon \) the depth of the un-truncated Lennard-Jones potential. Unless otherwise specified, all magnitudes in this work are given in Lennard-Jones reduced units [54]. Thus, the reported temperatures are reduced by \( \epsilon/k_B \), distances by \( \sigma \), densities by \( \sigma^{-3} \), pressures by \( \epsilon/\sigma^2 \), times by \( \tau = \sqrt{m\sigma^2/\epsilon} \) (being \( m \) the particle mass), interfacial free energies by \( \epsilon/\sigma^2 \) and nucleation rates by \( 1/(\tau\sigma^3) \).

We use cubic boxes with periodic boundary condition and the Molecular Dynamics (MD) LAMMPS package [73] to perform all simulations of this work. The equations of motion are integrated with a leap-frog algorithm [73].

In the MD Seeding simulations we used a time-step of 0.0012. The system was kept at constant temperature using the Nose-Hoover thermostat [74] with a relaxation time of 0.46.

For the MD simulations used within the Umbrella Sampling scheme we set the time step for the integration of the motion equations to 0.0012. The relaxation times for the Nose-Hoover thermostat and barostat were 0.46 and 1.6 respectively.

All simulations are carried out at \( T = 0.785 \). The co-existence pressure at such temperature for the model is \( p_{coex} = 0.0267 \). We determined this value, refined with respect to that of 0.026 previously published [73], by running long \( (4 \times 10^5 \tau) \) MD NVT simulations with an elongated box \((50 \times 17 \times 17)\) where the vapor and the liquid were put at contact at the temperature of interest. The average pressure normal to the interface in such simulation corresponds to \( p_{coex} \).

III. SEEDING OF CONDENSATION

This work is based on a recent publication where we demonstrate how to compute bubble nucleation rates in an overstretched Lennard-Jones fluid by equilibrating critical bubbles in the NVT ensemble, an approach we call "NVT-Seeding" [54]. The Seeding method, originally developed to study crystal nucleation [58, 61], and more recently applied to vapor cavitation [54, 70, 81], consists in combining CNT [62, 63] with computer simulations to estimate nucleation free energy barrier heights, \( \Delta G_c \), interfacial free energies, \( \gamma \), and, most importantly, nucleation rates, \( J \).

According to CNT, the Gibbs free energy barrier for the nucleation of a spherical liquid drop is given by the following expression:

\[ \Delta G = \gamma A - V \Delta p \]  

(2)

Where \( V \) and \( A \) are the volume and the area of the drop respectively. By maximizing Eq. 2 assuming a spherical drop shape one obtains both the height of the nucleation free energy barrier,

\[ \Delta G_c = \frac{2\pi R_c^3 \Delta p}{3}, \]

(3)

where \( R_c \) is the critical droplet radius and \( \Delta p \) is the pressure difference between the interior of the drop and the surrounding vapor, and the number of particles in the critical drop,

\[ N_c = \frac{(32\pi \rho_l \gamma^3)}{(3\Delta p^3)}, \]

(4)

where \( \rho_l \) is the critical drop number density and \( \gamma \) is the liquid-vapor surface tension. By substituting in the equation above \( N_c \) by the droplet volume \((4/3\pi R_c^3)\) times \( \rho_l \) one recovers the Laplace equation:

\[ \Delta p = \frac{2\gamma}{R_c}. \]

(5)

This derivation shows that the Laplace equation, which is valid when the droplet surface is located at the surface of tension, is implicit in CNT. Consequently, \( R_c \) should be identified with the radius of tension, \( R_s \). This is an important point that we will use later on in the paper.

The CNT prediction for the nucleation rate of drops is given by [52]:

\[ J = A_0 \rho_{vap} \exp \left( \frac{-\Delta G_c}{k_B T} \right), \]

(6)
where $k_B$ is the Boltzmann constant, $\rho_{vap}$ is the density of the vapor phase that multiplied by $\exp\left(-\frac{\Delta G}{k_B T}\right)$ gives the number density of critical clusters and $A_0$ is a kinetic pre-factor.

$A_0$ is computed as the product of the Zeldovich factor, $Z$, and the rate of attachment to the critical nucleus, $f^+$:

$$A_0 = Z f^+.$$  \hspace{1cm} (7)

$Z$ takes into account the establishment of a steady state and, according to CNT, is given by \cite{62, 63}:

$$Z = \sqrt{\frac{\Delta G(N)''|_{N_c}}{2\pi k_B T}} = \sqrt{\frac{\Delta p}{6\pi k_B T \rho_l N_c}} = \sqrt{\frac{\Delta p}{8\pi^2 k_B T \rho_l^2 \cdot R^3_c}}$$  \hspace{1cm} (8)

where $N_c$ is the number of particles in the drop and $|\Delta G_c(N)||_{N_c}$ is the curvature of $\Delta G(N)$ evaluated at the barrier top.

The attachment rate, $f^+$, can be estimated by multiplying the collision frequency of the vapor per unit of wall area given by the kinetic theory of gasses (ktg) by the area of the critical bubble:

$$f_{ktg}^+ = \sqrt{\frac{k_B T}{2\pi m}} \left(\frac{6\sqrt{\pi N_c}}{\rho_l}\right)^{2/3}$$  \hspace{1cm} (9)

where the subscript “ktg” stresses the fact that this expression of the attachment rate is based on the kinetic theory of gasses.

Combining this equation with \cite{54} and \cite{1} the following kinetic pre-factor is obtained:

$$A_0^{ktg} = \sqrt{\frac{\Delta p R_c \rho_{vap}}{\pi m \rho_l}}.$$  \hspace{1cm} (10)

The equations above are quite powerful, because only $R_c$, $\Delta p$ and the density of both phases are required to obtain key nucleation parameters as free energy barriers, interfacial free energies and nucleation rates. The Seeding method consists in performing simulations of a cluster of the stable phase surrounded by the metastable phase (a liquid drop surrounded by supersaturated vapor in our case as shown in Fig. 1) to compute $R_c$, $\Delta p$, $\rho_l$ and $\rho_{vap}$ in order to get “cheap” estimates of $\Delta G_c$, $\gamma$ and, most importantly, $J$ through the expressions above.

The main drawback of Seeding is that the definition of $R_c$ is not unique. Therefore, the resulting free energy barrier depends on the specific definition of $R_c$. This contrasts with rigorous simulation methods like Umbrella Sampling \cite{73, 82} or with theoretical approaches like DFT \cite{83, 85} where the nucleation free energy does not depend on the criterion chosen to measure the nucleus size, which can be estimated \textit{a posteriori} via, e. g. the nucleation theorem \cite{54, 88} (although in the particular case of DFT an approximate functional needs to be proposed so that the results do also contain approximations). To assess the suitability of our choice to compute $R_c$ we complement Seeding with Umbrella Sampling simulations.

We use the NVT ensemble to run the simulations of the drops given that in such ensemble critical nuclei are naturally equilibrated and stabilised for long times \cite{54, 55}. We equilibrate drops in 10 different systems. The edge of the cubic simulation box, $L$, and the total number of particles in each system, $N_T$, are reported in Table I. A large number of particles is used to minimize finite size effects \cite{52, 54, 89}. Each system was simulated for about $10^6$ Lennard Jones times of equilibration and $2 \cdot 10^5$ of production.

To prepare the initial configuration we cut a spherical liquid drop from a bulk liquid simulation and insert it in a bulk vapor box removing the overlapping vapor particles. The liquid drop is cut with a certain tentative radius, but the precise number of particles in each phase is not crucial given that equilibrium is reached along the course of the NVT simulation.

From a simulation of a drop surrounded by supersaturated vapor one can obtain an average radial density profile starting from the center of the drop as that shown in Fig. 2 (to find the drop centre in each configuration we use a similar strategy to that described in our previous work \cite{51} consisting in this case in identifying the maxima of density profiles computed along each cartesian coordinate). Following Refs. \cite{54, 70}, we obtain $R_c$ from such density profile as the distance at which the density is average between the liquid and the vapor plateaux. This is indicated with a vertical dashed line in Fig. 2. We refer to this way of obtaining $R_c$ as the “equi-density” criterion. The $R_c$’s thus obtained in our NVT-Seeding simulations are also reported in Table I.

![Figure 1](image-url)
tions of $R_c$ are in principle as valid as the equi-density criterion \[70, 84, 85\]. We argue later on in the paper that our $R_c$ definition is a good one because it makes Seeding predictions consistent with independent calculations of $\gamma$, $J$ or $\Delta G_c$.

**FIG. 2.** Density profile of a critical drop equilibrated in the NVT ensemble at $T=0.785$ surrounded by supersaturated vapor. The droplet radius, indicated by a red vertical line in the figure, is given by the point at which $\rho(r)$ takes an average value between both plateaux (equi-density criterion). The density profile corresponds to the system labelled as IV in table I.

To get $\Delta p = p_l - p_{vap}$ we obtain first the vapor density, $\rho_{vap}$, by counting the number of particles outside a sphere concentric with the drop but with a larger radius (we use a sphere radius $7\sigma$ larger than that of the drop, but we have checked for a few selected cases that any value beyond $\sim 5\sigma$ gives the same result). $\rho_{vap}$ is given by the number of particles outside the sphere divided by the $L^3$ minus the sphere volume. We then use the bulk vapor equation of state to infer $p_{vap}$ from $\rho_{vap}$.

**FIG. 3.** Box volume versus time in NpT simulations starting from 40 configurations taken from the NVT-Seeding simulation labelled as IX in Table I. The imposed pressure is the average viral pressure of the NVT-Seeding run.

We report $p_{vap}$ and $\rho_{vap}$ in table I. We have checked for all studied systems that $p_{vap}$ coincides with the overall

**FIG. 4.** (a) $\gamma$ vs vapor pressure obtained from NVT-Seeding data of droplets surrounded by supersaturated vapor. The surface tension at coexistence ($p=0.0267$) is included \[70\]. (b) $\Delta G_c$ vs vapor pressure. NVT-Seeding and US data are compared. Empty black symbols correspond to Seeding predictions when the Gibbs dividing (equi-molar) –instead of the equi-density– surface is employed to identify the cluster radius. (c) Nucleation rate versus vapor pressure as obtained from NVT-Seeding, US and spontaneous nucleation.
virial pressure of the system. On the other hand, \( p_t \) is obtained, as in our previous work \[54, 70\], by assuming equal chemical potential between the critical drop and the surrounding vapor:

\[
\int_{p_{\text{coex}}}^{p_{\text{vap}}} \frac{1}{\rho_{\text{vap}}(p)} dp = \int_{p_{\text{coex}}}^{p_t} \frac{1}{\rho(p)} dp \tag{11}
\]

where \( p_{\text{coex}} \) is the coexistence pressure and \( \rho_{\text{vap}}(p) \) and \( \rho(p) \) are the bulk vapor and bulk liquid number densities at pressure \( p \). In table I we report \( p_t \) and \( \Delta p \) for all studied systems. Once \( p_t \) is known, \( \rho_t \), also reported in the table, can be easily computed from the bulk liquid equation of state. In all cases, this computation of \( \rho_t \), based on the equality of chemical potential between both phases, is consistent with that obtained from the density profiles. For instance, for system IV we get \( \rho_t = 0.0680 \), which is fully consistent with the first plate observed in the density profile shown in Fig. 2. This means that the mechanical pressure and the thermodynamic pressure inside the drop coincide, a matter of current debate for solid-liquid nucleation [60].

There has been much simulation, theoretical and experimental work devoted to study the formation of nuclei confined at constant volume \[32, 44, 48, 91–99\]. In Refs. \[54, 55\] we showed with simulations that nuclei equilibrated in the NVT ensemble are critical because they have equal chances to grow or shrink when simulated in the NpT ensemble at the same temperature and at the average pressure along the NVT run. Based on this result, we opted to study here drop nucleation in the NVT ensemble, where statistics is better because clusters remain stable for very long times \[54\]. Stabilising nuclei to gain time to study their properties is something quite desirable. An alternative strategy to the use of constant volume simulations is to pin the nucleus to a heterogeneous solid substrate [100].

Despite having already shown the equivalence between stable (NVT) and critical (NpT) nuclei for cavitation [54], we check here for one of the NVT-Seeding simulations if the drops equilibrated at constant volume and temperature do correspond to a Gibbs free energy maximum. In Fig. 3 we show the evolution of the box volume in NpT simulations started from 40 independent configurations gathered along the NVT-Seeding trajectory labelled as IX in Table I. The imposed pressure is the average virial pressure along the NVT-Seeding run. Roughly, in 50 per cent of the cases the box expands (the drop dissolves) and in the other half of the cases the box shrinks (the drop grows). This result supports the use of NVT to study drop condensation in the same manner we did for bubble cavitation and crystal nucleation [51, 55]. Furthermore, the equivalence between clusters equilibrated at constant volume and critical nuclei has been recently proven with DFT theoretical arguments for crystallization (see supplementary material of Ref. [57]).

Having computed \( R_c, \Delta p \) and \( \rho_{\text{vap}} \) and \( p_t \) we have everything needed to obtain \( \gamma, \Delta G_c \) and \( J \) according to the equations presented in section III. We report the values for these variables in table I and plot them in fig. I (a)-(c) versus the vapor pressure with black dots. In the following section we comment each of these graphs.

### B. \( \gamma, \Delta G_c \) and \( J \)

#### 1. \( \gamma \)

As shown in Fig. I (a) the prediction we obtain from Seeding is that \( \gamma \) decreases as the vapor supersaturation increases. This trend is in agreement with previous work [32, 44]. Accordingly, using the capillarity approximation (i. e., that \( \gamma \) is pressure independent) would be erroneous. The green square in Fig. I (a) corresponds to the surface tension at coexistence [70] obtained through the pressure tensor \[101\] in an NVT simulation of a liquid and a vapor at contact. The trend of the Seeding data is fully consistent with the coexistence value, as shown by the linear fit in the figure. This is a good consistency test, although the \( \gamma \) values provided by Seeding could still be incorrect despite the fact that they extrapolate correctly to coexistence. Therefore, a test for Seeding predictions away from coexistence is needed.

#### 2. \( \Delta G_c \)

To further test our Seeding results we compare \( \Delta G_c \) obtained with Seeding with that computed via Umbrella Sampling. In Fig. I (b), where we plot \( \Delta G_c \) versus the vapor pressure, black solid dots correspond to Seeding and red ones to US (details on US calculations are described in section IV). Whereas Seeding predictions rely on the validity of CNT and on a proper definition of \( R_c \), Umbrella Sampling calculations are rigorous and independent on the criterion to identify the nucleus size [72]. On the other hand Seeding is much “cheaper” than US from a computational point of view. As a matter of fact, Seeding has access to much higher nucleation barriers than US. The accordance between Seeding and US shown in Fig. I is excellent, which gives us great confidence on Seeding predictions. The choice of the equi-density surface to identify the drop radius has proven correct. If we use another criterion, such as the Gibbs (equi-molar) dividing surface, the agreement between Seeding and Umbrella Sampling deteriorates (empty black symbols in Fig. I (b)). To compute \( R_c \), the radius associated to the Gibbs dividing surface, we use \( N_T = N_l + N_{\text{vap}} \) where \( N_l = 4/3\pi R_c^3 \rho_l \) and \( N_{\text{vap}} = |V_T - (4/3\pi R_c^3)\rho_{\text{vap}}| \), where \( V_T \) is the volume of the simulation box and the densities \( \rho_l \) and \( \rho_{\text{vap}} \) are obtained as described in Sec. III.

In a recent publication on cavitation (nucleation of bubbles instead of drops) we compared the performance of different criteria to identify the cluster radius and found that the equi-density criterion also made Seeding predictions consistent with other rigorous calculations.
Therefore, identifying the critical drop radius with the equi-density distance seems to be quite general for condensation-evaporation transitions.

3. \( J \)

Once \( \Delta G_c \) is known computing \( J \) via Eq. 6 is quite straightforward. The kinetic pre-factor \( A_0 \) given by the kinetic theory of gases, Eq. 10, depends on parameters we already have under control: \( \Delta p \), \( R_e \) and the density of both phases. The values of \( A_0 \) computed via Eq. 10, \( A_0^{kg} \), are reported in Table I.

These \( A_0 \) values are approximate since they rely on the validity of the kinetic theory of gases to estimate the attachment rate (see section III). We therefore have to check \( A_0^{kg} \) by computing the attachment rate with an alternative approach. Following the work by Auer and Frenkel 102, the attachment rate can be computed from the diffusion of \( N \), the number of particles in the liquid drop, around the critical drop 102:

\[
 f_{af}^+ = \frac{\langle (N(t) - N(0))^2 \rangle_{N_c}}{2t},
\]

where the average is performed over several trajectories starting from a critical drop configuration. The \( af \) subscript stresses the fact that this expression of the attachment rate is based on the work by Auer and Frenkel.

To compute \( N \) we follow 103. We count as neighbors all particles within a 1.625 distance of a tagged particle. Particles with 8 or more neighbors are labelled as “liquid”. Two liquid particles belong to the same drop if their mutual distance is less than 1.625. An example of the calculation of \( f^+ \) according to equation 12 is illustrated in Fig. 5. Typically, \( \langle N(t) - N(0) \rangle_{N_c} \) is obtained by averaging 20 NpT runs started from independent configurations of the critical drop, coming either from NVT-Seeding or from Umbrella Sampling simulations (see section IV). In these runs, the pressure is fixed to the virial value of the simulations were the critical clusters were previously equilibrated. According to Eq. 12, the slope of Fig. 5 divided by 2 gives \( f^+ \). Multiplying such \( f^+ \) by the Zeldovich factor we get an estimate of the kinetic pre-factor, \( A_0^{kg} \), that does not rely on the kinetic theory of gases. \( A_0^{kg} \) is reported in table II for a couple of critical clusters generated with NVT-Seeding (systems IV and VI). \( A_0^{kg} \) is very close to \( A_0^{bg} \). This agreement suggests the validity of the kinetic theory of gases to estimate the attachment rate and makes the theoretical framework that supports the Seeding technique quite powerful given that, since \( A_0^{bg} \) can be used, only \( R_e \), \( \Delta p \) and the density of both phases are required to get accurate estimates of \( J \) in a wide range of orders of magnitude. Note in Fig. 4(c) that Seeding (black dots) has access to \( J \) values many orders of magnitude lower than US (red dots).

The green dots in Fig. 4(c) correspond to rate estimates obtained in brute force NPT molecular simulation runs performed at high supersaturations where condensation occurs spontaneously from an unseeded vapor. In such cases the nucleation rate can be estimated as \( J = 1/(t < V >) \), where \( < V > \) is the average volume before nucleation and \( t \) is the nucleation time averaged over a number of independent trajectories (typically 20 in our case). \( N_T \), \( V \), the vapor pressure and density, and \( J \) for the two states where we studied spontaneous condensation are reported in Table I. In Fig. 4(c) we show that \( J \) estimates from Seeding and from spontaneous nucleation are consistent with each other, which further indicates the ability of Seeding to predict nucleation rates. It is worth mentioning here that NVT-Seeding and spontaneous nucleation are complementary techniques. On the other hand, the former does not have access to such
TABLE III. Data corresponding to the US calculations.

| Label | L    | N_T | ΔG_c/(k_BT) | A_0/l | log_{10}(J) |
|-------|------|------|-------------|-------|------------|
| US-1  | 39.112 | 4000 | 17.7        | 0.041 | -10.3      |
| US-2  | 38.501 | 4000 | 40.7        | 0.039 | -20.3      |

high supersaturations given the difficulty to equilibrate small clusters in the NVT ensemble 54, 55. That said, it would be nonsense using Seeding where nucleation occurs spontaneously in a straightforward manner. On the other hand, spontaneous nucleation is limited to a narrow window of nucleation rates (that enabled by computational time) whereas Seeding has access to extremely low rates.

We would like to end this section by discussing finite size effects, which could be present if a nucleus sees its replica through periodic boundary conditions. On the one hand, we made sure that the density of the outer box side of system X is more than twice than those of the other systems. By looking at Figs. 4(a), (b) and (c) one can see that the results from system X are fully consistent with those inferred from the other systems, which strongly supports the absence of noticeable finite size effects in our simulations.

IV. UMBRELLA SAMPLING

As previously indicated, to validate the Seeding results we used the US technique. We followed Refs. 103, 104 to compute ΔG_c for two different vapor pressures: p=0.031 and p=0.033. Details on the simulation box size and number of particles in the systems used to perform the US calculations are given in table III.

The free energy associated to the formation of an N particle cluster drop can be obtained from:

$$\Delta G(N) = -k_BT \ln [P(N)],$$

where P(N) is the probability distribution of N. Our criterion to compute N is described in Section III B 3. It is important to note that even though different criteria may give different N for a given configuration, the height of an US free energy barrier does not depend on the criterion to determine the cluster size 73. Therefore, contrary to what happens in Seeding, the US method does not depend on the specific criterion to determine the nucleus size. This is why it is important to validate the Seeding method with other techniques such as US.

With conventional NpT simulations at the selected pressures P(N) can only be sampled up to N ~ 40 while the critical cluster is much larger in this regime. To sample the rest of the free energy barrier a biasing potential, U_{bias}, is added to the original Hamiltonian:

$$U_{bias} = \frac{1}{2} k_{bias} (N - N_0)^2,$$

where N_0 controls the cluster size around which the sampling will be centred and k the width of such sampling. Tens of overlapping sampling “windows” centered at different N_0 values are required to reconstruct the whole free energy barrier. The effect of the bias potential on the calculation of the free energy barrier is removed as follows [71]:

$$\Delta G(N) = -k_BT \ln \left( \frac{\chi_N}{e^{-U_{bias}/(k_BT)}} \right) + C$$

where χ_N is the fraction of clusters with N particles that appear within a certain window and C is a constant. The constant is obtained by gluing together the first part of the energy barrier evaluated without the biasing potential (Eq. 13) with the rest of the windows. The result is the whole free energy barrier.

To compute each window we use the hybrid Molecular Dynamics-Monte Carlo scheme labelled as HMC(nM-NpT)/US in Ref. 104. From the starting configuration, random velocities are assigned to every particle according to a Maxwell-Boltzmann distribution and a short (Δt 19.2 Lennard Jones times) MD simulation is run for generating a new configuration, which is accepted with probability min[1, exp[−(U_{bias}(Δt) − U_{bias}(0))/(k_BT)]]. Either in case of acceptance or rejection new random velocities are assigned at the beginning of each short MD cycle. For each window, 10000 of such cycles were performed for equilibration and 60000 to obtain the free energy barrier. We used k_{bias} = 0.04k_BT in the biasing potential (Eq. 13), which gives an acceptance rate of ~ 25%.

In figure 5 we plot both free energy barriers, being ΔG_c = 17.7k_BT for p=0.033 and ΔG_c = 40.7k_BT for
p=0.031 (also reported in table IV). As already discussed, the agreement between US and Seeding is excellent (see Fig. 4(b)).

Additionally, we compute the kinetic pre-factor \( A_0^{c,f} \) (Eq. 7) to obtain the nucleation rate (Eq. 8). To do that, we launch tens of unbiased trajectories from independent configurations at the barrier top in order to compute the attachment rate via Eq. 12. The Zeldovich factor (Eq. 8) can be obtained by numerically calculating the curvature of \( \Delta G(N) \) at the barrier top. We report \( A_0^{c,f} \) thus calculated and the corresponding \( J \) in table III. As previously discussed, \( J \) from US is fully consistent with that coming from Seeding (see Fig. 4(c)).

In summary, we have compared Seeding, that relies on the theoretical assumptions by CNT and \( ktg \) and depends on the criterion employed to determine the cluster size, with US, that does not have these limitations. We have obtained an excellent agreement between both techniques. This is very good news because Seeding is much more efficient than US and has access to much lower values of the nucleation rate.

![Graph](image)

**FIG. 6.** Free energy for two different pressures (p=0.031 and p=0.033) versus the number of particles in the drop as obtained from US calculations. The different colours represent the different windows performed.

### V. CONDENSATION VS BOILING

#### A. Comparison for a given \( R_c \)

We have studied quite recently the nucleation of bubbles for the same Lennard Jones model employed here. Since the study was performed at the same temperature, the question that naturally arises is whether bubbles and drops with the same radius have the same interfacial properties. To establish the comparison we have repeated the analysis performed in Ref. 54 because in such work we used 0.026 as the coexistence pressure instead of 0.0267. We took the 0.026 value from a paper published more than a decade ago 75. However, we have recomputed more carefully the coexistence pressure at \( T = 0.785 \) and obtain \( p = 0.0267 \) instead, which is the value we use in this work. The difference is subtle, but given that the pressure inside the nucleating phase is obtained by integrating from the coexistence pressure (see Eq. 11) it is very important to use an accurate value for the latter.

The simulation data for different bubbles equilibrated at \( T=0.785 \) in the NVT ensemble are reported in table IV. The values of \( R_c \) corresponding to each system (obtained with the equi-density criterion as discussed in section III A and in Ref. 54) are very close to those recently reported by ourselves 74. However, the values of \( \Delta \) \( p \) here reported are not identical to those of Ref. 54 due to the coexistence pressure issue discussed above. In Fig. 7(a) we plot \( \Delta \) \( p \) vs \( 1/R_c \) for bubbles and and drops at \( T=0.785 \). Drops and bubbles of the same size have the same \( \Delta \) \( p \), which is perhaps the most important result of the paper. Note that, for a given \( R_c \), the pressures of the external and the internal phases are not the same if one compares cavitation and condensation. What is the same is the pressure difference between the internal and the external phases. For instance, let’s focus on the case of drop VII and bubble II, both with \( R_c \approx 8.5 \). In Fig. 8 we compare their radial density profiles. The density of the liquid inside the drop is different from that of the liquid outside the bubble. Also, the density of the vapor inside the bubble is different from that of the vapor outside the drop. The bubble is surrounded by a liquid of pressure -0.01914 whereas the drop by a vapor of pressure 0.0301: the pressures of the external phases do not even have the same sign. The bubble and the drop also have very different pressures: 0.02398 and 0.07432 respectively. Despite the fact that the external and the internal pressures are very different, \( \Delta \) \( p \) is not: 0.043 and 0.044 for the bubble and the drop respectively.

According to the Laplace equation, that \( \Delta \) \( p(R_c) \) is the same for drops and bubbles, implies that \( \gamma \) must be the same also regardless the identity of the internal and the external phases. In Fig. 7(b) we plot \( \gamma \) vs \( 1/R_c \) for bubbles and drops and find that, indeed, they have the same \( \gamma \) within our statistical noise. Of course, attending to Eq. 3 \( \Delta G_c \), that only depends on \( R_c \) and \( \Delta \) \( p \), is also the same for a given \( R_c \), as illustrated in Fig. 7(c).

The nucleation rate for bubbles with a given \( R_c \) is close to the corresponding drop, but is not exactly the same, given that the kinetic pre-factor is not identical. In the case of bubble nucleation we have carefully assessed that the following expression by Blander and Katz (BK) provides a good approximation for \( A_0 \):

\[
A_0^{BK} = \frac{\Delta \rho R_c}{\pi m},
\]

(16)

which is very similar, but with a missing \( (\rho_{vap}/\rho_0) \) factor with respect to the \( ktg \) expression we use for drop condensation (Eq. 10). The \( A_0^{BK} \) values we use in our Seeding predictions of bubble cavitation are reported in...
with the nucleus inside or, more easily, computing it requires either computing the free energy of a system are two sides of the same coin in the sense that they share the relevant conclusion that condensation and cavitation is an important finding of our work. This leads to the equi-density surface both for cavitation and condensation. We believe that identifying the surface of tension with the arbitrariness of establishing a location for the interface. In our case, we found in a recent work by “trial and error” that the equi-density surface gives good results for cavitation. However, there are only few cases in which has been compared for a given temperature as a function of the droplet/bubble size as we do in this work. Establishing such comparison in experiments is difficult because it is not possible to detect the critical nucleus. In simulations the nucleus can be visualized, but computing is a hard task. It requires either computing the free energy of a system with the nucleus inside or, more easily, computing the nucleus size and using a theory to infer as we do in this work. In either approach, one has to deal with the arbitrariness of establishing a location for the interface.

In our case, we found in a recent work by “trial and error” that the equi-density surface gives good results for cavitation. By “good results” we mean that Seed predictions of nucleation are consistent with those coming from independent methods that do not rely on a precise definition of the nucleus size. In this work we have demonstrated that the same criterion to locate the interface is successful in condensation. Therefore, one of our main findings is that the equi-density surface is the one that provides good predictions when CNT is used both for cavitation and for condensation. This means that the equi-density surface can be identified with the surface of tension, which is the one for which CNT works and the Laplace equation holds (see section ). We believe that identifying the surface of tension with the equi-density surface both for cavitation and condensation is an important finding of our work. This leads to the relevant conclusion that condensation and cavitation are two sides of the same coin in the sense that they share the same surface tension.

In Ref. , was found to be quite different for both phenomena, but the comparison was not established for the surface of tension but for the equimolar surface. In Ref., however, the comparison was established for the first time for the surface of tension and, although was similar for condensation and cavitation, there were significant differences that need to be further investigated in order to match our work with that of Ref. .

| Label | $L$ | $N_f$ | $\rho_{\text{eqap}}$ | $\rho_l$ | $\rho_{\text{ap}}$ | $\rho_t$ | $\Delta p$ | $R_c$ | $\gamma$ | $\Delta G_c/(k_B T)$ | $A_0^{BK}$ | log$_{10}(\gamma)$ |
|-------|-----|-------|-----------------|--------|-----------------|--------|-----------|------|--------|-----------------|----------|---------------|
| I     | 36.731 | 30795 | 0.03765 | 0.6453 | 0.02365 | -0.02601 | 0.0497 | 7.35 | 0.1826 | 52.7 | 0.341 | -23.5 |
| II    | 36.731 | 30342 | 0.03834 | 0.6484 | 0.02398 | -0.01914 | 0.0431 | 8.50 | 0.1832 | 70.6 | 0.342 | -31.3 |
| III   | 36.731 | 29760 | 0.03875 | 0.6501 | 0.02419 | -0.01503 | 0.0392 | 9.53 | 0.1869 | 90.6 | 0.345 | -40.0 |
| IV    | 36.731 | 29034 | 0.03907 | 0.6514 | 0.02433 | -0.01191 | 0.0362 | 10.52 | 0.1906 | 112.5 | 0.348 | -49.5 |
| V     | 36.731 | 28147 | 0.03949 | 0.6530 | 0.02453 | -0.00776 | 0.0323 | 11.50 | 0.1857 | 131.1 | 0.344 | -57.6 |
| VI    | 36.731 | 27082 | 0.03972 | 0.6539 | 0.02464 | -0.00558 | 0.0302 | 12.45 | 0.1881 | 155.7 | 0.346 | -68.3 |

**TABLE IV.** NVT-Seeding data for the different bubbles studied in this work at $T=0.785$.

B. Comparison for a given metastability degree

In Ref. it was proposed in a DFT study that the work of formation of critical bubbles studied at different temperatures collapse when plotted against the metastability degree, $X_m$, quantified as:

$$X_m = \frac{\mu_{\text{nuc}} - \mu_{\text{coex}}}{\mu_{\text{spinodal}} - \mu_{\text{coex}}} \quad (17)$$

where $\mu_{\text{nuc}}$ is the chemical potential of the parent phase at the conditions where nucleation is studied, $\mu_{\text{coex}}$ is the coexistence chemical potential at the same temperature and at coexistence pressure, and $\mu_{\text{spinodal}}$ is the chemical potential at the same temperature but at the pressure where spinodal decomposition takes place. To estimate the spinodal pressure we run NpT simulations of the bulk liquid and vapor phases with 4000 particles. We estimate the spinodal decomposition pressure as that for which we the system undergoes a phase transition without any induction period, right after the start of the simulation. Both chemical potential differences in Eq. can be easily obtained by numerically integrating the molar volume along pressure at constant temperature. The denominator is the maximum possible metastability whereas the numerator is the actual metastability of the state where nucleation is studied. Therefore, $X_m$ varies from 0 at coexistence, to 1 at spinodal decomposition. The metastability degree above described can be computed for drop as well as for bubble nucleation. Therefore, we have the chance to compare nucleation free energy barriers for drops and bubbles as a function of $X_m$. The comparison, shown in Fig. , reveals the interesting conclusion that $\Delta G_c$ for bubble and drop nucleation is the same for a given metastability degree. Therefore, not only nucleation barriers at different temperatures can be collapsed via the metastability degree as proposed in Ref. , but also bubble and drop nucleation data match for a given metastability degree.
C. Tolman Length

Since bubbles and drops of the same radius have the same interfacial properties, we can use the data coming from both systems altogether in order to compute the Tolmann Length, $\delta_T$, which is defined as \[34, 74]\:

$$\delta_{Tolman} = \lim_{R_c \to \infty} (R_c - R_s)$$

(18)

where $R_c$ is the Gibbs equi-molar radius and $R_s$ is the radius of the surface of tension. We identify $R_c$ with $R_c$ (the equi-density radius) given that (i) we obtain good predictions of nucleation when we use $R_c$ and (ii) $R_s$ is the radius that enters CNT \[17, 49, 52, 102\]. To underline the fact that we identify $R_c$ with $R_c$ we label $R_c$ as $R_{s=c}$ in the following figures. $R_c$ can be easily computed from the radial density profiles \[52, 70\]. In Fig. \[10]\(a)\) we show $R_c - R_{s=c}$ versus $1/R_{s=c}$ for all data (either bubbles or drops) coming from this work. The extrapolation to $1/R_{s=c} = 0$ provides an estimate of $\delta_{Tolman}$, indicated with an empty blue dot in the figure. We obtain $\delta_{Tolman} = 0.15 \pm 0.02$. We showed in a recent paper, in which we analysed spherical hard sphere crystals in equilibrium with the fluid, that $\delta_{Tolman}$ can be also estimated by fitting $\gamma$ to the following expression:

$$\gamma = \gamma_0 \left(1 - 2\frac{\delta_T}{R_s}\right)$$

(19)

where $\gamma_0$ is the value of $\gamma$ at coexistence at the temperature of interest and $\delta_T$ is the fitting parameter that serves as an estimate for $\delta_{Tolman}$ \[52\]. This approach is similar in spirit to those that include $\gamma$ given by Eq. \[16\] in CNT to fit free energy barriers obtained by rare event methods \[84, 110\]. Again, we identify here $R_c$ with $R_c$. Consequently, we use the $\gamma$ data coming from such radius (that reported in tables \[II\] and \[LV\]) to obtain an estimate of $\delta_T$ with the expression above. The data of $\gamma$ vs $1/R_{s=c}$ are shown in green in Fig. \[10]\(b)\). The solid line is a linear fit of $\gamma$ vs $1/R_{s=c}$ which includes $\gamma_0$ (the green square in the figure). The $\delta_T$ value coming from such fit, $\delta_T = 0.21 \pm 0.03$, is shown with a red dot in Fig. \[10]\(a)\). Both values, $\delta_{Tolman}$ obtained via Eq. \[16\] (blue dot in Fig. \[10]\(a)\)) and $\delta_T$ coming from Eq. \[19\] (red dot the same figure), are consistent with each other within the statistical uncertainty of our estimates. This corroborates the idea, recently checked for the first time for hard sphere crystals \[52\], that the Tolman length can be obtained either from Eq. \[19\] or from Eq. \[16\]. Hence, this idea seems to be a general one pertaining not only to the crystal-fluid equilibrium but also to the liquid-vapor one.

This study may shed some light in the intense literature debate about the magnitude and sign of the Tolman length \[18, 30, 32, 34, 14\]. We obtain a Tolman length of about twenty per cent the particle diameter. Its sign is positive, which means that $\gamma$ decreases when one moves away from coexistence at constant temperature.

VI. CONCLUSIONS

The main conclusions we draw from our work are the following:

1. We have used NVT-Seeding to investigate droplet nucleation in a supersaturated Lennard-Jones vapor. The results obtained from this technique are consistent with: (i) independent calculations of the nucleation free energy barrier performed with Umbrella Sampling (ii) the surface tension of a flat interface obtained from the pressure tensor in a vapor-liquid coexistence simulation (iii) the drop nucleation rate obtained both with US and in brute force spontaneous nucleation simulations.

2. NVT-Seeding requires defining the radius of a droplet equilibrated in the NVT ensemble. The radius definition that passes the consistency tests mentioned in the previous paragraph is that given by the surface where the density is average between that of the interior and that of the exterior phases. Such radius definition was also successful in our earlier studies of bubble nucleation \[54, 74\]. Therefore, we identify this “equi-density” radius with the radius of tension, $R_s$.

3. The good performance of Seeding strongly supports the use of CNT to describe nucleation. However, the capillarity approximation (that $\gamma$ is curvature independent) does not provide good results. A $\gamma$ dependent on the curvature of the critical nucleus must be plugged into the theory. Therefore, the theory, although powerful, requires the involvement of simulations given that the $\gamma$-curvature dependence is obtained by computing the size of the critical cluster at different pressures.

4. The kinetic theory of gases provides very good estimates of the kinetic pre-factor of the condensation nucleation rate. This makes the theoretical framework very powerful given that only the size of the critical cluster, the density of the external phase and the bulk phases equations of state are needed to estimate nucleation rates.

5. We compare NVT-Seeding results of droplets with those obtained for bubbles and find that, for a given temperature, bubbles and droplets of the same radius have, within the accuracy of our method, the same pressure difference with the surrounding medium. Therefore, bubbles and droplets of the same size have the same surface tension and the same nucleation free energy barrier. In this respect, condensation and boiling can be seen as two sides of the same coin. Such duality is only verified if the size of the critical nucleus (either a bubble or a drop) is determined with the equi-density radius (our empirical definition of the surface of tension).
6. We estimate the Tolman length, $\delta_T$, by extrapolating to infinite-size drops/bubbles the difference between the equimolar radius, $R_e$, and $R_s$. Such $\delta_T$ is consistent with that obtained by linearly fitting $\gamma(1/R_c)$, in accordance with our recent work of hard sphere crystals.

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FIG. 7. (a) $\Delta p$ vs. $1/R_c$, (b) $\gamma$ vs. $1/R_c$, (c) $\Delta G_c$ vs. $R_c$, and (d) $\log_{10} J$ vs. $1/R_c$ for droplets (black symbols) and bubbles (red symbols) as obtained from NVT-Seeding.
FIG. 8. Radial density profiles of drop VII and bubble II, compared. They have almost identical radius, $R_c$.

FIG. 9. Nucleation free energy barrier for drops and bubbles (see legend) as a function of the metastability degree, $X_m$, defined in Eq. 17.

FIG. 10. (a) $R_e - R_{s=c}$ and (b) $\gamma$ vs. $1/R_{s=c}$ for drops and bubbles together.
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