I. INTRODUCTION

Information on the thermodynamic properties of supersaturated vapor is of considerable importance for both material science and process engineering applications. For modeling processes in the metastable region, as done in nucleation theories,\textsuperscript{1-6} often predictions of equations of state (EOS) are employed. Since most of these EOS are based on measurements outside the two-phase region only, it is necessary to verify their validity in the metastable region. For nucleation theories predicting the system behavior in the metastable region, the location of the spinodal is of special significance, because at the spinodal the barrier height of nucleation goes to zero, while the nucleation rate goes to infinity.\textsuperscript{7,8} Both quantities are of fundamental relevance and once the location of the spinodal is known, a nucleation theory can be tested by checking whether its expressions for these quantities show the correct behavior at the spinodal.

The lack of experimental data on supersaturated vapor at conditions which are not close to the binodal is due to the short-lived nature of the supersaturated vapor under experimental conditions.\textsuperscript{9} Since a real fluid consists of a large number of molecules, it will generate many clusters with the potential to grow to form a new liquid phase. Thus the induction time, during which a supersaturated vapor exists before it separates into two phases, is short compared to the time needed to measure any properties of the metastable vapor.

In molecular dynamics simulations, fluids consisting only of a very small number of molecules are investigated and the time needed to determine thermodynamic properties is shorter than the induction time for nucleus formation in most cases. This allows investigations up to the vicinity of the spinodal. In the present work, the pressure of the supersaturated vapor of the Lennard-Jones fluid is evaluated and the location of the spinodal is estimated for temperatures covering the range from slightly above the triple temperature to 92\% of the critical temperature. Although the Lennard-Jones model is very basic, it describes the properties of simple real fluids, e.g., methane and the noble gases, with very good accuracy.\textsuperscript{10} Therefore it is used in many computer simulation studies on homogeneous nucleation,\textsuperscript{11-13} which can be compared to experimental studies using Argon or other simple fluids.\textsuperscript{14,15} The method employed here can be used with more complex molecular models in a straightforward fashion.

To the knowledge of the authors of this study, there is only one simulation study which determined some \( p, \rho, T \) data in the metastable region and gives an estimation of the spinodal.\textsuperscript{16} The authors of that study incorporated a few simulated metastable region state points in an EOS for the Lennard-Jones fluid.\textsuperscript{17} This EOS is compared to the present results in Sec. IV.

II. METHOD

All molecular dynamics simulations are started in this work with the molecules placed in a fcc lattice configuration with randomly oriented velocity vectors. In this way the molecules are distributed evenly throughout the volume and no clusters are introduced \textit{a priori}. This initial configuration is extremely unlikely to appear in physical systems, so the beginning of the simulation is characterized by the decomposi-
tion of the initial configuration into a physical distribution of the molecules. This time span is referred to in the following as initial period. After this period, there are three possible cases of fluid behavior depending on the stability state of the fluid.

If the fluid is in a stable state, the system reaches after the initial period a stable one-phase equilibrium. In the second case, the fluid is metastable and the system remains for a certain time after the initial period in a metastable state of supersaturated vapor. This time span is referred to in the following as the induction period, its length as the induction time \( t_i \). After the induction period a phase separation process takes place, which brings the system into its final state, a stable two-phase equilibrium. The unstable case shows the same evolution, but the induction period after the initial period is missing. Instead, the phase separation starts instantaneously.

The metastable state of the supersaturated vapor is characterized by the fluid consisting of a vapor phase at a pressure \( p \) higher than the equilibrium vapor pressure \( p_e \). The vapor contains clusters of molecules with a density much higher than the mean density. These clusters emerge, grow, shrink, and disappear, but the distribution of cluster sizes remains constant apart from statistical fluctuations depending on the system size. The clusters are prototypes of a corresponding liquid phase at the same temperature, which would instantaneously emerge from the supersaturated vapor, were it not for the surface contribution to the cluster formation energy that presents a barrier to phase separation.\(^7,18,19\)

Therefore, the system remains in a metastable state until an energy fluctuation surmounts that barrier to create a cluster large enough to grow and form a new liquid phase. The duration of the metastable state, the induction time, depends on the probability that a sufficiently large energy fluctuation occurs. At the binodal, the induction time goes to infinity, whereas at the spinodal it goes to zero, because there any energy fluctuation is sufficient to initiate a phase separation.

In the present work, the induction period was identified by observing plateau values in the evolution of three characteristic quantities—pressure \( p \), the number of molecules in the largest cluster \( N_c \), and the number of molecules not belonging to any cluster \( N_v \), thus belonging to the ambient vapor phase.

The simulations were conducted in the canonical \( NVT \) ensemble. Therefore, the overall density of the system was constant, whereas the pressure changed with the system undergoing different periods during a simulation run. The pressure \( p \) and the number of molecules which do not belong to any cluster \( N_v \) decrease during both the initial period and the phase separation period. On the other hand, the number of molecules in the largest cluster \( N_c \) increases during the initial and phase separation period. This last criterion, also employed in Ref. 18, is especially useful, because it is a direct indicator of an ongoing phase separation.

During the induction period, all these quantities are constant, apart from small fluctuations, and the pressure can be determined as the average pressure during the whole induction period. This was done in several series of simulations for different temperatures starting near the binodal, with stepwise increased densities towards the spinodal. The density at the spinodal point was determined by the simulation where for the first time no induction period could be observed.

Near the spinodal, extremely short induction times and fluctuations in the pressure and molecule numbers due to the small-system size occasionally made the identification of the induction period by only one of the criteria described above difficult. Then, by comparison of all three criteria the identification was possible. Further evidence of the approximate location of the induction period could be gathered from simulations at neighboring densities. Since an isotherm in the pressure-density diagram has a maximum at the spinodal, the spinodal pressure could be determined with much higher accuracy than the spinodal density. Additionally, the fluctuations in the induction time due to the stochastic nature of the nucleation process and the fact that the initial period conceals the fluid’s behavior in the first moments of the simulations contribute to the uncertainty of the spinodal density. As a consequence, multiple simulations in the neighborhood of the spinodal were performed.

In Fig. 1, three typical evolutions of the characteristic
quantities, the pressure $p$, the number of molecules in the largest cluster $N_c$, and the number of molecules not belonging to any cluster $N_s$ are shown. The pressure obtained from the simulation was filtered using a 16th-order zero-phase digital lowpass filter with the cutoff frequency $f_c = 0.025$. At low supersaturations near the binodal, the induction period lasts longer than the simulation time, and no phase separation is observed. At a higher supersaturation, the initial period is followed by the induction period characterized by constant quantities, after which the beginning phase separation period is indicated by decreasing $p$ and $N_s$ but increasing $N_c$. Finally, at a density beyond the spinodal point, an instantaneous phase separation takes place. No induction period is observed.

### III. Simulation Details

In the present work the behavior of spherical Lennard-Jones fluids was studied by molecular dynamics simulations. The spherical Lennard-Jones potential is

$$u_{LJ}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right],$$

where $r$ is the distance between two molecules. The size and energy parameters are denoted by $\sigma$ and $\varepsilon$, respectively.

A large cutoff radius $r_c = 10\sigma$ (in a few cases $r_c = 7.5\sigma$) for the nonshifted potential was chosen to take the inhomogeneous molecule distribution, as a result of the cluster formation, explicitly into account. Outside the cutoff radius the effect of the inhomogeneous density distribution was assumed to vanish and standard long-range corrections were employed.

Molecular dynamics simulation runs were performed at seven temperatures $kT/\varepsilon = 0.7, 0.75, 0.8, 0.9, 1.0, 1.1,$ and $1.2$ covering the range from slightly above the triple temperature ($kT_{trip}/\varepsilon = 0.68$) to $92\%$ of the critical temperature ($kT_c/\varepsilon = 1.31$). The equations of motion were solved numerically using a velocity-Verlet integration scheme in order to compensate the energy fluctuations due to the decomposition of the initial configuration quickly. After that, a Nosé-Hoover chain thermostat consisting of three elements with $Q_1 = 7.6\sigma^2/(12.6,33\ ms)$ and $Q_3 = Q_2 = Q_1/N$ was used to keep the temperature constant.

Four system sizes $N = 2048, 4000, 5324,$ and $6250$ were used for the simulations. In order to maximize the induction time, the sizes were chosen as small as possible, however large enough that a physically realistic cluster distribution could develop. For the temperatures $kT/\varepsilon = 0.7, 0.75, 0.8, 0.9, 1.0,$ and $1.1$ the largest clusters occurring during the induction period contained less than about 300 molecules, which means that a number of $N = 2048$ is sufficiently large to allow a realistic cluster distribution. In order to verify that the simulations were not subject to small-system effects, also simulations with $N = 4000$ and $N = 6250$ were conducted for some test points. Only at the temperature $kT/\varepsilon = 1.2$, clusters of more than 1000 molecules appeared, so for that temperature the system size was chosen to $N = 4000$, in some cases to $N = 5324$.

In the longest simulation runs usually 100 000 time steps were used, which is sufficient to determine the average pressure during the metastable state. In simulations near the spinodal, the induction period is shorter than 100 000 time steps, so the simulations were terminated earlier.

The supersaturated pressure was measured using the standard virial theorem and averaged over the induction time. This method is also valid for inhomogeneous systems, since the pressure obtained by the virial theorem is the pressure a system containing clusters exerts on container walls.

Initially, the molecules were positioned in a fcc lattice configuration, and their velocities were assigned randomly and rescaled once such that the temperature had the desired value. Typically, it took 6000–7000 time steps until the initial configuration was decomposed. In order to accelerate the decomposition of the lattice configuration and thus to shorten the initial period, some simulations near the spinodal were started at a higher temperature, where the fluid was in a stable vapor state. After 5000 time steps the lattice configuration was assumed to be decomposed and the system was cooled down by rescaling the velocities in one step to the desired temperature, taking the fluid to a metastable state. By that, the initial period was shortened to about 2000 time steps.

To determine the number of molecules belonging to a cluster, a simple criterion following Refs. 11, 18, and 27 was employed: A molecule with at least four neighboring molecules within a radius of $1.5\sigma$ was considered to be inside a cluster, as well as the neighboring molecules, regardless if they had at least four neighbors themselves. It can be argued that this is a rather crude method to determine the number of molecules in a cluster. However, in the present work molecule numbers were only used as indicators to identify the different periods.

### IV. Results

Table I shows the $p, v, T$ data for the metastable Lennard-Jones fluid obtained in the present work by molecular dynamics simulation. In Fig. 2 these $p, v, T$ data are shown graphically. Also depicted are isotherms for the different temperatures generated from the theoretically based EOS of Mecke et al., and Kolafa and Nezbeda, as well as the empirical EOS of Boltachev and Baidakov, which was parametrized also taking into account metastable state points. The simulation results show a van der Waals-like course up to the spinodal. The comparison with the EOS reveals systematic deviations, with the simulation results lying constantly below all EOS except for the highest temperature. Towards the spinodal, the difference increases, with a maximum deviation of about 7% at the spinodal. The deviations are shown in Fig. 3 for the EOS of Mecke et al. For higher temperatures, the EOS of Boltachev and Baidakov exhibits lower pressures than the two other EOS, showing the same tendency as the simulation results of the present study. Such a negative deviation can be expected, because for
The construction of the two theoretically based EOS only data from outside the two-phase region were used, and effects due to the inhomogeneous density distribution caused by local transient density fluctuations in the form of clusters were not taken into account. Therefore it is understandable that the simulation results and the EOS are in good accordance for low supersaturations near the binodal, where only a small fraction of the molecules are concentrated in clusters. Towards the spinodal, an increasing number of molecules are part of clusters, resulting in a less dense gas yielding lower supersaturated pressures. The two theoretically based EOS do not take this effect into account, but treat the supersaturated vapor as homogeneous phase. The EOS of Boltachev

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**FIG. 2.** Pressure-density diagram for the supersaturated vapor of the Lennard-Jones fluid. Simulation results (solid line) compared to the EOS of Mecke et al. [Ref. 28] (dashed line), Kolafa and Nezbeda [Ref. 29] (dotted line), and Boltachev and Baidakov [Ref. 17] (dotted-dashed line). The dew line was determined by the EOS of Mecke et al. [Ref. 28].

**FIG. 3.** Deviation plot comparing the pressure obtained from the EOS of Mecke et al. [Ref. 28] to the results from the present simulations as a function of the density divided by the corresponding dew density $\rho^*$ at seven different temperatures: $kT/e=0.7$ (solid line), 0.75 (open circle), 0.8 (open triangle), 0.9 (open square), 1.0 (solid square), 1.1 (open square), 1.2 (open circle).
The \( p,\rho,T \) data of the Lennard-Jones supersaturated vapor were determined up to the spinodal for a range of temperatures from slightly above the triple temperature to 92\% of the critical temperature. In spite of short averaging time due to early phase separation, it was possible to determine the \( p,\rho,T \) data also in the vicinity of the spinodal by incorporating information from the neighboring points. An estimate of the location of the spinodal is presented.

The comparison with EOS for the Lennard-Jones fluid shows systematic deviations. The simulation results are mostly lower than those of the EOS, the deviations get larger when the spinodal is approached, and are about 7\% at their maximum. We assume that this is caused by EOS treatment of the supersaturated vapor as a homogeneous phase, whereas in the simulations the inhomogeneous density distribution due to local transient density fluctuations in the form of clusters yields a lower pressure.

V. CONCLUSION

The authors thank Guido Fuchs, Technical University of Vienna, for fruitful discussions.

\[ kT/e \quad \rho \ \sigma^3 \quad p \ \sigma^4/e \]

\begin{array}{ccc}
0.70 & 0.046(1) & 0.0160(5) \\
0.75 & 0.055(4) & 0.0195(5) \\
0.80 & 0.064(5) & 0.0247(6) \\
0.90 & 0.090(5) & 0.0345(10) \\
1.00 & 0.105(8) & 0.0475(12) \\
1.10 & 0.155(10) & 0.0650(10) \\
1.20 & 0.190(10) & 0.0910(10) \\
\end{array}

and Baidakov\textsuperscript{17} was parametrized also to a few metastable supersaturated vapor state points for higher temperatures, yielding lower pressures there.

In Table II the spinodal pressures and densities are given for the investigated temperatures. As discussed above, the density values are subject to relatively large uncertainties.

**ACKNOWLEDGMENT**

The authors thank Guido Fuchs, Technical University of Vienna, for fruitful discussions.