

# Computer Simulations, Nucleation Rate Predictions and Scaling

Barbara N. Hale

*Physics Department, University of Missouri-Rolla, Rolla, MO, 65409USA*

**Abstract.** Computer simulations of atomic and molecular systems relevant to the prediction of nucleation rates have focused primarily on two approaches: (1) calculation of the free energy of formation of the critical embryo (or equivalently  $n$ -cluster probability ratios); and (2) time dependent simulation of embryo formation in a dense parent phase. Excepting a few scope-limited quantum mechanical treatments both these approaches use some form of effective atom-atom pair potentials. Successful nucleation rate prediction demands adequate treatment of entropic effects (configurational sampling) and hence all these approaches employ microscopic statistical mechanics. In Monte Carlo (MC) approaches particle configurations are sampled with a Boltzmann weighting subject to thermodynamic constraints such as constant  $T$ ,  $N$  or  $\mu$ ,  $V$  or  $P$ . In molecular dynamics (MD) inter-atomic forces accelerate the atoms along time trajectories subject to system constraints. Since the mid-1990s, sampling efficiency algorithms, steadily increasing computing power and the ingenuity of young scientists have turned this field into an impressive statistical mechanical study of many body classical systems. The intent of this paper is to generate an initial literature data base relevant to these “nucleation” simulations, to gather the nucleation rate predictions and experimental data into unifying plots and to examine the implications of the scaled supersaturation in comparing the experimental data with the simulation predictions. In particular, homogeneous vapor-to-liquid nucleation rates estimated *via* MC and MD simulations are compared with experimental rate data for argon and for water.

*Key Words:* Homogeneous nucleation, computer simulations, Monte Carlo, molecular dynamics, effective pair potentials, density functional theory, nucleation rate, work of formation, free energy of formation, critical cluster, vapor-to-liquid phase transitions, liquid-to-solid phase transitions, critical nucleus, small cluster properties, cluster definition, microscopic many body interactions, thermodynamic constraints, scaled nucleation rate, scaled temperature dependence, scaling law, effective surface tension, argon, water, TIP4P, Lennard-Jones, scaled supersaturation

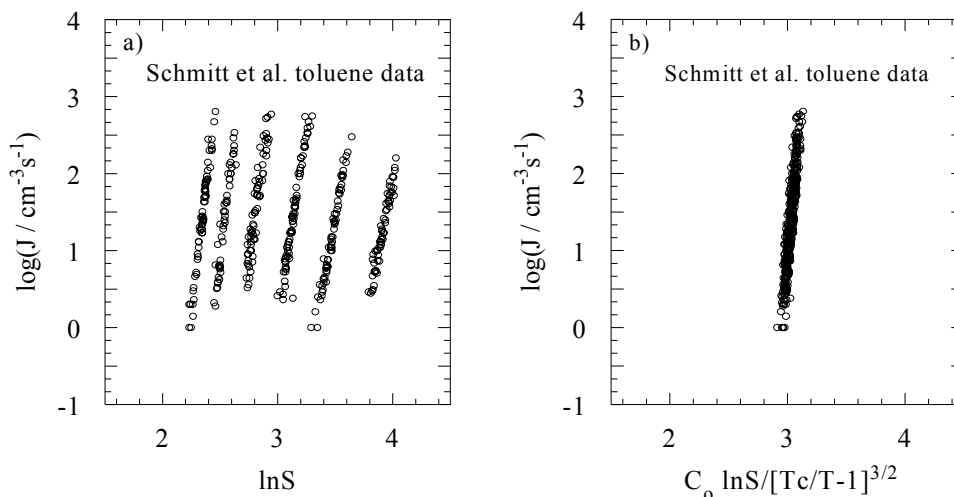
## THE FIRST COMPUTER SIMULATIONS

This summary is intended for the nucleation community. The whole of microscopic simulation literature (much of which has relevance to nucleating systems) is immense. Many of the computer simulations do not predict a nucleation rate, but rather demonstrate techniques and test inter-atomic potentials for their applicability to real systems. Because it is not possible to present all the nucleation-directed computer simulation literature in this article a web site has been set up at <http://web.UMR.edu/~hale/nucleation.html> for those interested in more details. The abstracts for all the articles are included. A more extensive discussion of the simulational details for the Monte Carlo and molecular dynamic methods is given by H. Vehkamäki in this volume.

The history of these simulations begins in the late 1960s and 1970s, when simply to carry out a few hundred thousand step Monte Carlo simulation was a feat. To these early workers<sup>1-41</sup> much is owed: Metropolis<sup>1</sup>, Alder and Wainwright<sup>2</sup>, Wood and Parker<sup>3</sup>, Hoover and Ree<sup>4</sup>, Hansen and Verlet<sup>5</sup>, McDonald<sup>6</sup>, Norman and Filinov<sup>7</sup>, Rahman<sup>8</sup>, Johansson<sup>9</sup>, Stillinger *et al.*<sup>10</sup>, McGinty<sup>11</sup>, Adams and Jackson<sup>12</sup>, Lee, Barker and Abraham<sup>13</sup>, Robertson and Pound<sup>14</sup>, Stauffer *et al.*<sup>15</sup>, and Briant and Burton<sup>16</sup>, to name a few. While many were simulating lattice gases<sup>15,24,28,32,38</sup> or argon Lennard-Jones systems<sup>5-8,11,13,18,23,26,27,29,31,33,34,39-41</sup> because of the generally accepted potential and enhanced computational speed, a few were attempting water systems with a variety of potentials.<sup>10,16,17,19,20,22,30,35,36</sup> The molecular dynamics simulations of liquid water by Stillinger<sup>10</sup> and the water-water potentials developed for these simulations were especially important to subsequent studies focused on the nucleation of atmospheric water and ice<sup>35</sup>.

## DATA ANALYSIS AND THE SCALED SUPERSATURATION

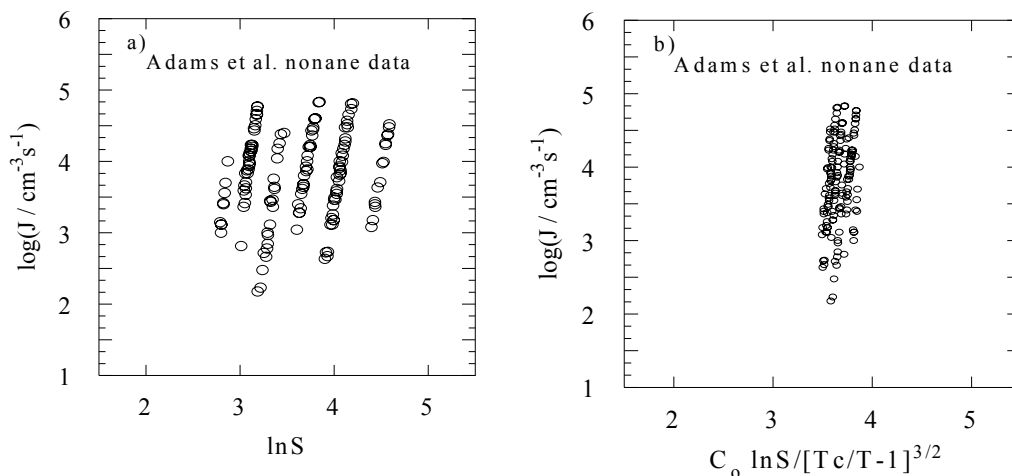
In 1980s homogeneous nucleation experiments<sup>42-45</sup> began to provide more detailed information about the dependence of the nucleation rate,  $J$ , on temperature,  $T$ , and supersaturation ratio,  $S$ . The data of Schmitt *et al.*<sup>44</sup> for toluene is plotted in Fig. 1a.



**Figure 1.** The homogeneous toluene nucleation rate data of Schmitt *et al.*<sup>44</sup> plotted a) vs.  $\ln S$  and b) vs. the scaled supersaturation<sup>46</sup>,  $\ln S / [T_c/T - 1]^{3/2}$ . The constant  $C_0 = [T_c/240 - 1]^{3/2}$ .

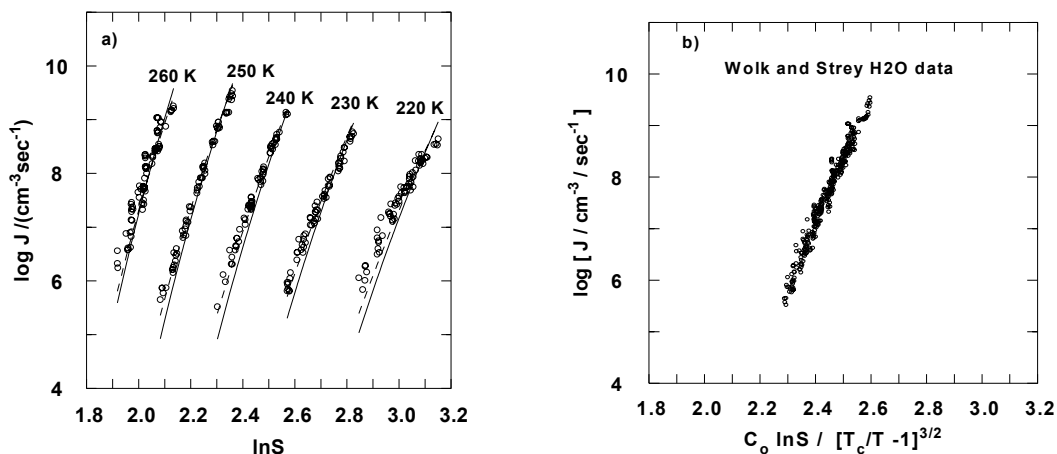
Fig. 1b shows  $\log J$  plotted as a function of the scaled supersaturation<sup>46,47</sup>,  $\ln S_{\text{scaled}}$ , where  $\ln S_{\text{scaled}} = \ln S / [T_c/T - 1]^{3/2}$ . This scaled supersaturation is similar to that first proposed by Binder<sup>48</sup> and is taken from the scaling law<sup>46</sup> we developed in 1986. One can see the effect of the scaling as it collapses all the “temperature data lines” in Fig. 1a onto a single line. Assuming that the data holds no unexpected surprises, this effect is one that should not be missed. It suggests the specific combination of  $S$  and  $T$  upon which the nucleation rate data depends:  $J_{\text{exp}} = J(\ln S / [T_c/T - 1]^{3/2})$ . This method of plotting the data permits a check for consistency (and scaling) without resorting to *ad*

*hoc* parameters. The data for nonane of Adams *et al.*<sup>42</sup> (Fig. 2) also exhibits this scaling, though to a less satisfactory degree.



**Figure 2.** The homogeneous nonane nucleation rate data of Adams *et al.*<sup>42</sup> plotted a) vs.  $\ln S$  and b) vs. the scaled supersaturation<sup>46</sup>,  $\ln S / [T_c/T - 1]^{3/2}$ . The constant,  $C_0 = [T_c/240 - 1]^{3/2}$ .

Probably most surprising is the scaling of the homogeneous nucleation rate data for water, a polar substance of considerable complexity. This is shown in Fig. 3. for the data of Wölk and Strey<sup>45</sup>.



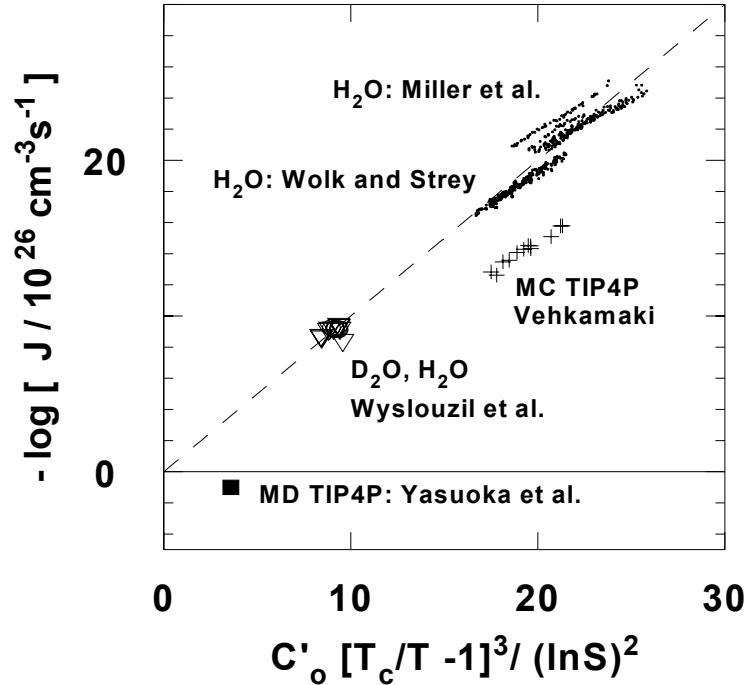
**Figure 3.** The homogeneous water nucleation rate data of water, Wölk and Strey<sup>45</sup> plotted vs. a)  $\ln S$  and b) the scaled supersaturation<sup>46</sup>,  $\ln S / [T_c/T - 1]^{3/2}$ . The constant,  $C_0 = [T_c/240 - 1]^{3/2}$ .

Actually it has been known for some time that the classical Becker-Döring nucleation rate model has the wrong temperature dependence. Recently, Wölk *et al.*<sup>49</sup>, developed an empirical temperature fitting function which alters the Becker-Döring nucleation rate,  $J_{BD}$ , to agree with the experimental water data. It was noted that upon this conversion,

$J_{BD}$  becomes nearly identical to the scaled nucleation rate model<sup>46,47</sup>. It was a demonstration of this which motivated the scaled supersaturation plots in Figs. 1-3.<sup>47</sup>

## EXPERIMENTS AND SIMULATIONS: WATER

The scaling of  $J$  permits comparison of a range of numerical simulation data with experimental data taken under different conditions. Molecular dynamics simulations of vapor-to-liquid systems are often carried out in dense vapor systems at relatively high temperatures,<sup>50-54</sup> where experimental data is lacking. In 1998 Yasuoka and Matsumoto<sup>52</sup> carried out a large scale molecular dynamics simulation on a system of 5000 carrier gas atoms and 5000 water molecules interacting via the TIP4P water-water potential. The system temperature was thermostated at 350K via the carrier gas atoms after the quench. Vapor depletion reduced the initial supersaturation of 14.6 to an average value near  $S = 7.3$ , corresponding to the observed nucleation rate of  $9.62 \cdot 10^{26} \text{ cm}^{-3} \text{ s}^{-1}$ ; the critical nucleus was in the range of 30- 45 water molecules. Although the nucleation rate is larger than any observed, it can be compared roughly with the nozzle data of Heath *et al.*<sup>54</sup> and the expansion chamber data of Wölk and Strey<sup>45</sup> on a scaled plot. This is shown in Fig. 4., where  $\log[10^{26}/J]$  is plotted vs.  $[T_c/T - 1]^3 / (\ln S)^2$ .



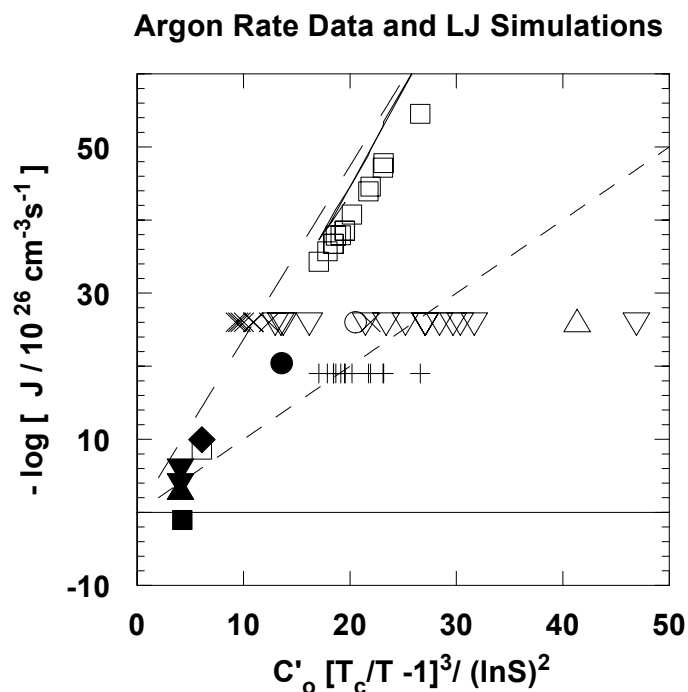
**Figure 4.** The  $\log [10^{26} / J]$  vs.  $[T_c/T - 1]^3 / (\ln S)^2$  for the water data of Miller *et al.*<sup>55</sup>, the fast expansion chamber data of Wölk and Strey<sup>45</sup>, the nozzle data of Wyslouzil *et al.*<sup>56-58</sup>, the MD simulation of TIP4P water by Yasuoka and Matsumoto<sup>52</sup>, and the MC TIP4P calculations of Merikanto *et al.*<sup>112</sup> The constant,  $C'_o = [16\pi/3]\Omega^3 / \ln 10$  with  $\Omega = 1.47$ . The dashed line is the scaled model prediction<sup>46</sup> using  $\Omega = 1.47$ ; see also TIP4P MCDS model simulations of Hale and DiMattio<sup>87</sup>.

The molecular dynamics result for  $J$  does not fall on the line predicted by the experimental data. However, the simulation assumes a TIP4P model for water which does not reproduce the experimental surface tension. The Monte Carlo simulations of Merikanto *et al.*<sup>112</sup> using TIP4P water appear to have the right temperature dependence but the predicted nucleation rates are too large by a factor of about  $10^4$ .

## EXPERIMENTS AND SIMULATIONS: ARGON

A large number of computer simulations beginning in the 1990s have used the Monte Carlo method to sample the configuration space of atoms (or molecules) in small clusters.<sup>59-95</sup> Several techniques can be used to determine the critical cluster size,  $n^*$ , and calculate  $n$ -cluster energies of formation. One can determine a steady state nucleation rate from  $\frac{1}{J} = \sum_{n=1}^{2n^*} \frac{1}{J_n}$  where  $J_n$  is the equilibrium forward rate for size  $n$ ; or one

can insert the calculated energy of formation and vapor pressure into the classical model. Most of these simulations have been focused on the rare-gas, Lennard-Jones (LJ) system. Computationally this has considerable advantage. But experimental argon



**Figure 5.** The  $\log [10^{26} / J]$  vs.  $[T_c/T - 1]^3 / (\ln S)^2$  for the experimental argon data of Zahoransky<sup>78</sup> ( $\nabla$ ), Fladerer<sup>113</sup> (+), Wu *et al.*<sup>114</sup> (X), Matthew and Steinwandl<sup>115</sup> ( $\Delta$ ), and Stein<sup>116</sup> ( $\circ$ ). The theoretical predictions are: Yasuoka and Matsumoto<sup>106</sup> ( $\blacksquare$ ), ten Wolde and Frenkel<sup>73, 82</sup> using  $S = 1.53$  ( $\bullet$ ), Hale<sup>68</sup> for  $S$  and  $T$  corresponding to Fladerer data ( $\square$ ), Senger *et al.*<sup>81</sup> ( $\blacktriangledown$ ), Oh and Zeng<sup>86</sup> ( $\blacktriangle$ ), Chen *et al.*<sup>90</sup> ( $\blacklozenge$ ), and CNT with Zeldovich factor for  $S$  and  $T$  corresponding to Fladerer data (— solid line). The  $C'_o = [16\pi/3](\Omega)^3/\ln(10)$  with  $\Omega = 1.5$ . The scaled model prediction with  $\Omega = 1.5$  (short-dashed line) passes through the Fladerer data. The long-dashed line shows the scaled model prediction<sup>46</sup> with  $\Omega = 2.1$ , the bulk experimental excess surface entropy/k per molecule, as determined from the surface tension.

vapor-to-liquid nucleation rates have proven more difficult to measure. In Fig. 5 is a scaled supersaturation plot of simulation results for Lennard-Jones compared with some of the experimental argon rate data.

The experiments generally quote data for “onset” nucleation conditions. For all but one set of the experimental data a rate of  $1 \text{ cm}^{-3}\text{s}^{-1}$  is used in making the plot. For the data of Fladerer<sup>113</sup> an approximate rate of  $10^{7 \pm 2} \text{ cm}^{-3}\text{s}^{-1}$  is used. At large scaled supersaturations (small values of the abscissa in Fig. 5) the Monte Carlo simulations of Senger *et al.*<sup>81</sup>, Oh and Zeng<sup>86</sup>, Chen *et al.*<sup>90</sup>, and Hale<sup>68</sup> are at temperatures near 85K and  $S = 5$ . These data predict nucleation rates of the order of  $10^{17}$ -  $10^{22} \text{ cm}^{-3}\text{s}^{-1}$ . The prediction of ten Wolde and Frenkel<sup>73,82</sup> at  $T = 88.9\text{K}$  and  $S = 1.53$  is  $10^5 \text{ cm}^{-3}\text{s}^{-1}$ . This simulation uses a truncated LJ potential with surface tension about 30% smaller than the untruncated LJ potential. The scaled supersaturation for this point was determined from reduced  $T_c = 1.085$  and  $T = 0.741$ . The MD result of Yasuoka and Matsumoto<sup>106</sup> is larger ( $10^{27} \text{ cm}^{-3}\text{s}^{-1}$ ) and is at  $T = 80\text{K}$ ,  $S=7.2$ . The values of  $S$  for the theoretical data are calculated from the ratio of Lennard-Jones potential model vapor densities,  $\rho_v / \rho_v^0$ , where  $\rho_v^0$  is the vapor density in equilibrium with the liquid. Unfortunately, no experimental data exist at the large scaled supersaturations. In the smaller scaled supersaturation region of the experimental data, the MC simulations<sup>68</sup> and the classical nucleation theory (CNT) give rates of  $10^{-10} \text{ cm}^{-3}\text{s}^{-1}$  and  $10^{-13} \text{ cm}^{-3}\text{s}^{-1}$ , respectively --- about a factor of  $10^{-17}$  to  $10^{-20}$  smaller than the “onset” nucleation indicated by the experimental data. These data are at  $T = 50\text{-}59\text{K}$  and  $S = 8\text{-}16$ . In the small scaled supersaturation region the energies of formation are large; and for large scaled supersaturations the energies of formation are small, giving larger rates. The scaled model<sup>46</sup> with  $\Omega = 1.5$  (dashed line) passes roughly through the Fladerer data. This value of  $\Omega$  (the excess surface entropy/k per molecule) is about 30% smaller than the bulk experimental value of 2.1 as determined from  $-k^{-1}\rho_{\text{liq}}^{-2/3}[\partial\sigma/\partial T]$ , where  $\sigma$  is the bulk surface tension and  $\rho_{\text{liq}}$  is the liquid number density. The prediction of the scaled model with  $\Omega = 2.1$  is indicated in Fig. 5 by the long-dashed line. Clearly for argon, challenges remain for both theorist and experimentalist.

A number of studies have used the density functional approach.<sup>96-98</sup> Zeng and Oxtoby<sup>97</sup> note that their density functional treatment of the Lennard-Jones system gives good agreement with the experimental gas to liquid nonane data. Their non-classical nucleation rate,  $J_{\text{NCL}}$ , is about four orders of magnitude larger than the classical nucleation theory ( $J_{\text{CNT}}$ ). Computer simulations of liquid-solid homogeneous nucleation<sup>99-111</sup> are also noted here because of the great interest the atmospheric community has in ice formation.

## COMMENTS AND CONCLUSIONS

The simulation results have made great progress, particularly in the last six years. Experimental determination of homogeneous nucleation rates remains a challenge, especially in the case of argon for which the simulational treatment holds the most advantage. There appears to be a general need for those reporting simulation results to include predicted nucleation rates, so that the many calculations can be tied

together and compared with the experimental data. At the high temperatures and large  $S$ , the non-ideality of the vapor needs to be taken into account. Finally, it is suggested that the scaling properties of the nucleation rate might prove helpful to the theorists in their simulations as well as to the experimentalists in probing the temperature dependence of the data.

## References

1. Metropolis, N., and Ulam, S. "The Monte Carlo Method", *J. Am Stat. Ass.* 44, 1949, pp. 335-41; Metropolis, N., Rosenbluth, A. W., Rosenbluth, M. N., Teller, A. H. and Teller, E., "Equation of state calculations by fast computing machines", *J. Chem. Phys.* 21, 1953, p. 1087.
2. Alder, B. J., and Wainwright, T. E., "Phase transitions for a hard sphere system", *J. Chem. Phys.* 27, 1957, p1208-9.
3. Wood, W. W., and Parker, F. R., "Monte Carlo equation of state of molecules interacting with the Lennard-Jones potential: A supercritical isotherm at about twice the critical temperature". *J. Chem. Phys.*, 27, 1957, p720-33.
4. Hoover, W. G., and Ree, F. H., "Melting transition and communal entropy for hard spheres", *J. Chem. Phys.* 49, 1968, p3609-17
5. Hansen J-P, Verlet L. "Phase transitions of the Lennard-Jones system", *Phys. Rev. A*, 184, 1969, pp.151-61.
6. McDonald, I. R., "Monte Carlo calculations for one- and two-component fluids in the isothermal-isobaric ensemble", *Chem. Phys. Lett.* 3, 1969, p. 241-3.
7. Norman, G. E., Filinov, V. S., "Investigations of phase transitions by a Monte Carlo method", *Teplofizika Vysokikh Temperature*, 7, 1969, pp.233-40. USSR. (*High Temperature (USA)*),7, 1969, pp.216-22.)
8. Rahman, A., "Computer studies of condensed matter", *Rivista del Nuovo Cimento*, 1, spec. issue., 1969, pp.315-27, Italy
9. Johannesson, T., Persson, B. "Computer simulation of nucleation and growth of atom clusters in thin films", *Physica Scripta*,2, 1970, pp.309-12; Johannesson T, Persson B. "Computer simulation of epitaxial nucleation", *Physica Status Solidi A*, 3., 1970, pp.k251-4
10. Rahman A, Stillinger FH, "Molecular dynamics study of liquid water". *J. Chem. Phys.*, 55, 1971, pp.3336-59.; Stillinger FH, Rahman A. "Improved simulation of liquid water by molecular dynamics", *J. Chem. Phys.*,60, 1974, pp.1545-57.; Lemberg HL, Stillinger FH., "Central-force model for liquid water", *J. Chem. Phys.*, 62, 1975, pp.1677-90.; Rahman A, Stillinger FH, Lemberg HL., "Study of a central force model for liquid water by molecular dynamics", *J. Chem. Phys.*, 63, 1975, pp.5223-30.; Stillinger FH, Rahman A., "Revised central force potentials for water" *J. Chem. Phys.*,68, 1978, pp.666-70.
11. McGinty, D. J., "Vapor phase homogeneous nucleation and the thermodynamic properties of small clusters of argon atoms", *J. Chem. Phys.*,55, 1971, pp.580-88
12. Adams, A. C., Jackson, K. A., "Computer simulation of vapor deposition", *Journal of Crystal Growth*, 13-14, 1972, pp.144-7. Netherlands
13. Lee, J. K., Barker, J. A., Abraham, F. F., "Theory and Monte Carlo simulation of physical clusters in the imperfect vapor", *J. Chem. Phys.*, 58, 1973, pp.3166-80.
14. Robertson, D., Pound, G. M., "Numerical simulation of heterogeneous nucleation and growth", *Journal of Crystal Growth*, 19, 1973, pp.269-84; Robertson D, Pound GM. "Heterogeneous nucleation and film growth", *Critical Reviews in Solid State Sciences*, 4, 1974, pp.163-204..
15. Stauffer D., Binder, K., Wildpaner, V., "Structure of binary solution droplets: continuum theory and Monte Carlo simulation", *Water, Air, & Soil Pollution*, 3, 1974, pp.515-25
16. Briant C. L., Burton, J. J., "Effective potential for water-ion interactions in prenucleation embryos", *J. Chem. Phys.*, 60, 1974, pp.2849-55; "Molecular dynamics study of water microclusters", *J. Chem. Phys.*, 63, 1975, pp.3327-33; "A molecular model for the nucleation of water on ions", *J. Atmos. Sci.*,

- 33, 1976, pp.1357-61; "Molecular dynamics study of the effects of ions on water microclusters", *J. Chem. Phys.*, 64, 1976, pp.2888-95.
17. Hale B. N., Plummer, P. L. M., "On nucleation phenomena. I. A molecular model", *J. Atmos. Sci.*, 31, 1974, pp.1615-21; "Molecular model for ice clusters in a supersaturated vapour", *J. Chem. Phys.*, 61, 1974, pp.4012-19; Hale BN, Plummer PLM. "Molecular model for ice clusters in a supersaturated vapour", *J. Chem. Phys.*, 61, 1974, pp.4012-19.
  18. Rowley, L. A., Nicholson D., Parsonage, N.G., "Monte Carlo grand canonical ensemble calculation in a gas-liquid transition region for 12-6 argon", *Journal of Computational Physics*, 17, 1975, pp.401-14.
  19. Abraham FF., "Monte Carlo simulation of physical clusters of water molecules", *J. Chem. Phys.*, 61, 1974, pp.1221-5; Binder, K., Abraham, F. F., Barker, J. A., "Monte Carlo simulation of physical clusters of water molecules. Reply to K. Binder's comments on Monte Carlo simulation of physical clusters", *J. Chem. Phys.*, 63, 1975, pp.2265-7.
  20. G. M. Torrie and J. P. Valleau, "Monte Carlo free energy estimates using non-Boltzmann sampling: Application to the sub-critical Lennard-Jones fluid", *Chem. Phys. Lett.* 28, 1974, p.578
  21. Gilmer, G. H., "Simulation of crystal growth from the vapor", *Proceedings of the 1976 International Conference on Computer Simulation for Materials Applications*. Nat. Bur. Standards. Part II, 1976, pp.964-74. Washington, DC, USA
  22. Mruzik, M. R., Abraham, F. F., Schreiber, D. E., Pound, G. M., "A Monte Carlo study of ion-water clusters", *J. Chem. Phys.*, 64, 1976, pp.481-91.
  23. Rusanov, A. I., Brodskaya, E. N., "The molecular dynamics simulation of a small drop", *Journal of Colloid & Interface Science*, 62, 1977, pp.542-55.
  24. Binder, K., "Computer experiments on nucleation processes in the lattice gas model", *Advances in Colloid & Interface Science*, 7, 1977, pp.279-324. 25.
  25. Bauchspiess, K. R., Stauffer D. "Use of percolation clusters in nucleation theory", *Journal of Aerosol Science*, 9, 1978, pp.567-77.
  26. Rao, M., Berne, B. J., "Nucleation in finite systems: theory and computer simulation", *Astrophysics & Space Science*, 65, 1979, pp.39-46.
  27. Hsu, C. S., Rahman, A., "Crystal nucleation and growth in liquid rubidium", *J. Chem. Phys.*, 70, 1979, pp.5234-40; "Interaction potentials and their effect on crystal nucleation and symmetry", *J. Chem. Phys.*, 71, 1979, pp.4974-86.
  28. Binder, K., Kalos, M. H., "Critical clusters' in a supersaturated vapor: Theory and Monte Carlo simulation", *J. Stat. Phys.*, 22, 1980, pp.363-96.
  29. Garcia, N., Torroja, J. M. S., "Monte Carlo Calculation of Argon Clusters in Homogeneous Nucleation", *Phys. Rev. Letters* 47, 186-190 1980.
  30. Swope, W. C., Andersen, H. C., Berens, P. H., Wilson, K. R., "A computer simulation method for the calculation of equilibrium constants for the formation of physical clusters of molecules: application to small water clusters", *J. Chem. Phys.*, 76, 1982, pp.637-49.
  31. Hale, B. N., Ward, R. C., "A Monte Carlo method for approximating critical cluster size in the nucleation of model systems", *J. Stat. Phys.*, 28, 1982, pp.487-95.
  32. Stauffer, D., Coniglio, A., Heermann, D.W."Monte Carlo experiment for nucleation rate in the three-dimensional Ising model", *Phys. Rev. Letters*, 49, 1982, pp.1299-302.
  33. Polymeropoulos, E. E., Brickmann, J., "Molecular dynamics study of the formation of argon clusters in the compressed gas", *Chemical Physics Letters*, 92, 1982, pp.59-63.
  34. LaViolette, R. A., Pratt, L. R., "Free energy of nucleating droplets via cluster-integral series", *Phys. Rev. A*, 28, 1983, pp.2482-90
  35. Ward, R. C., Hale, B. N., Terrazas, S., "A study of the critical cluster size for water monolayer clusters on a model AgI basal substrate", *J. Chem. Phys.*, 78, 1983, pp.420-3; Deutsch P, Hale BN, Ward RC, Reago DA Jr. "Structural studies of low temperature ice  $h$  using a central force potential model". *J. Chem. Phys.*, 78, 1983, pp.5103-7.
  36. Weber, T. A., Stillinger, F. H., "Molecular dynamics study of ice crystallite melting", *J. Phys. Chem.*, 87, 1983, pp.4277-81.
  37. Kelton, K. F., Greer, A. L., Thompson, C. V., "Transient nucleation in condensed systems", *J. Chem. Phys.*, 79, 1983, pp.6261-76.
  38. Penrose, O., Buhagiar, A., "Kinematics of nucleation in a lattice gas model: microscopic theory and simulation compared", *J. Stat. Phys.*, 30, 1983, pp.219-41

39. Honeycutt, J. D., Andersen, H. C., "The effect of periodic boundary conditions on homogeneous nucleation observed in computer simulations", *Chemical Physics Letters*, 108, 1984, pp.535-8
40. Mountain, R. D., Brown, A. C., "Molecular dynamics investigation of homogeneous nucleation for inverse power potential liquids and for a modified Lennard-Jones liquid", *J. Chem. Phys.*, 80, 1984, pp.2730-4
41. Freeman, D. L., Doll, J. D. "Quantum Monte Carlo study of the thermodynamic properties of argon clusters: the homogeneous nucleation of argon in argon vapor and 'magic number' distributions in argon vapor", *J. Chem. Phys.*, 82, 1985, pp.462-71
42. Adams GW, Schmitt JL, Zalabsky RA. The homogeneous nucleation of nonane. *J. Chem. Phys.*, 81, 1984, pp.5074-8. USA.
43. Wagner PE, Strey R. Measurements of homogeneous nucleation rates for n-nonane vapor using a two piston expansion chamber. *J. Chem. Phys.*, 80, 1984, pp.5266-75.
44. Schmitt JL, Zalabsky RA, Adams GW. Homogeneous nucleation of toluene. *J. Chem. Phys.*, 79, 1983, pp.4496-501. USA
45. Wölk, J, Strey, R. "Homogeneous nucleation of H/sub 2/O and D/sub 2/O in comparison: the isotope effect", *J. Chem. Phys.*, 105, 2001, pp.11683-701; Y. Viisanen, R. Strey and H. Reiss, *J. Chem. Phys.* 99, 4680 (1993); 112, 8205 (2000)..
46. Hale, B. N., "Application of a scaled homogeneous nucleation-rate formalism to experimental data at  $T \ll T_c$ ", *Phys. Rev A*, 33, 1986, pp.4156-63; Hale, B.N., "Scaled Models for Nucleation", *Lecture Notes in Physics*, 309, 1988 pp.323-349; Hale, B. N., "The scaling of nucleation rates", *Metallurgical Transactions A-Physical Metallurgy & Materials Science*, 23A, 1992, pp.1863-8.; Hale, B. N., Kemper, P, Nuth, J. A., "Analysis of experimental nucleation data for silver and SiO using scaled nucleation theory", *J. Chem. Phys.*, 91, 1989, pp.4314-17.
47. Hale, B. N., to be published.
48. Binder, K, Stauffer, D. "Statistical theory of nucleation, condensation and coagulation", *Advances in Physics*, 25, 1976, pp.343-96.
49. Wölk J, Strey R, Heath CH, Wyslouzil BE. "Empirical function for homogeneous water nucleation rates", *J. Chem. Phys.*, 117, 2002, pp.4954-60.
50. Zhukhovitskii, D. I., "Molecular dynamics study of cluster evolution in supersaturated vapor", *J. Chem. Phys.* 103, 1995, 9401.
51. Ikeshoji T. "Molecular dynamics simulation for the (magic number) size effect in nucleation and evaporation of clusters". *Science Reports of the Research Institutes Tohoku University Series A-Physics Chemistry & Metallurgy*, 43, 1997, pp.43-6. Publisher: Tohoku Univ, Japan
- Yasuoka K, Matsumoto M. "Molecular dynamics of homogeneous nucleation in the vapor phase. I. Lennard-Jones fluid", *J. Chem. Phys.*, 109, 1998, pp.8463-70.
52. Yasuoka K, Matsumoto M., "Molecular dynamics of homogeneous nucleation in the vapor phase. II. Water." *J. Chem. Phys.*, 109, 1998, pp.8463-70.  
Kinjo T, Ohguchi K, Yasuoka K, Matsumoto M., "Computer simulation of fluid phase change: vapor nucleation and bubble formation dynamics", Elsevier. *Computational Materials Science*, 14, 1999, pp.138-41
53. Ohguchi K, Yasuoka K, Matsumoto M. "Molecular mechanism of vapor-liquid nucleation", *Yukawa Inst. Theor. Phys. & Phys. Soc. Japan. Progress of Theoretical Physics Supplement*, 138, 2000, pp.257-8. Japan
54. Toxvaerd S. "Molecular-dynamics simulation of homogeneous nucleation in the vapor phase", *J. Chem. Phys.*, 115, 2001, pp.8913-20.
55. Miller, R. C., Anderson, R. J, Kassner, J, L Jr, Hagen, D. E. "Homogeneous nucleation rate measurements for water over a wide range of temperature and nucleation rate", *J. Chem. Phys.* 78, 1983, pp.3204-11
56. Heath CH, Streletzky K, Wyslouzil BE, Wölk, J, Strey R. "H<sub>2</sub>O-D<sub>2</sub>O condensation in a supersonic nozzle", *J. Chem. Phys.*, 117, 2002, pp.6176-85;
57. Khan, A., Heath, C.H., Diergsweiler, U. M , Wyslouzil, B. E., Strey, R. "Homogeneous nucleation rates for D/sub 2/O in a supersonic laval nozzle", *J. Chem. Phys.* 119, 2003, pp.3138-47;
58. Kim, Y. J., Wyslouzil, B. E., Wilemski, G., Wölk, J, Strey, R., "Isothermal Nucleation Rates in Supersonic Nozzles and the Properties of Small Water Clusters", *J. Phys. Chem.* in press.
59. Ellerby, H. M., Weakliem, C. L., Reiss, H., "Toward a molecular theory of vapor-phase nucleation. I. Identification of the average embryo", *J. Chem. Phys.*, 95, 1991, pp.9209-18..

60. Ellerby, H. M., Reiss, H., "Toward a molecular theory of vapor-phase nucleation. II. Fundamental treatment of the cluster distribution", *J. Chem. Phys.*, 97, 1992, pp.5766-72.
61. J. S. van Duijneveldt and D. Frenkel, "Computer simulation study of free energy barriers in crystal nucleation", *J. Chem. Phys.* 96 1992, p.p 4655
62. Li Weakliem C, Reiss H., "Toward a molecular theory of vapor-phase nucleation. III. Thermodynamic properties of argon clusters from Monte Carlo simulations and a modified liquid drop theory", *J. Chem. Phys.*, 99, 7, 1 1993, pp.5374-83.
63. Gregory, V. P., Schug, J. C., "Clustering of Lennard-Jones particles below the critical temperature" *Molecular Physics*, 78, 1993, pp.407-20
64. Weakliem, CL, Reiss H. "Toward a molecular theory of vapor phase nucleation. IV. Rate theory using the modified liquid drop model", *J. Chem. Phys.*, 101, 1994, pp.2398-406.
65. Wright D, El-Shall MS. "Monte Carlo simulation of acetonitrile clusters (CH<sub>3</sub>/sub 3/CN)N, N=2-256: melting transitions and even/odd character of small clusters (N=2-9), heat capacities, density profiles, fractal dimension, intracluster dimerization, and dipole orientation", *J. Chem. Phys.*, 100, 1994, pp.3791-802
66. ten Wolde, P. R., Ruiz-Montero, M. J, Frenkel, D., "Numerical evidence for BCC ordering at the surface of a critical FCC nucleus", *Physical Review Letters*, 75, 1995, pp.2714-17.
67. Zapadinsky, E. L, Kulmala M., "Helmholtz free energy of a cluster on the coherent substrate: Monte Carlo calculations", *J. Chem. Phys.*, 102, 1995, pp.6858-64.
68. Hale, B. N., "Monte Carlo calculations of effective surface tension for small clusters", *Australian Journal of Physics* 49, 1996, pp.425-34.
69. Hettema H, McFeaters JS., "The direct Monte Carlo method applied to the homogeneous nucleation problem", *J. Chem. Phys.*, 105, 1996, pp.2816-27
70. Guan Hua Chen, Guang-Wen Wu. "Multi-dimensional entropy sampling Monte Carlo method and free energy landscape of Ar<sub>13</sub>", *Chemical Physics Letters*, 281, 1997, pp.343-51
71. Oh, K. J, Zeng, X. C., Reiss, H. "Toward a molecular theory of vapor-phase nucleation. V. Self-consistency in the decoupled dimer limit", *J. Chem. Phys.*, 107, 1997, pp.1242-6.
72. Oh KJ, Gao GT, Zeng XC. "The effect of a uniform electric field on homogeneous vapor-liquid nucleation in a dipolar fluid. I. Stock er fluid", *J. Chem. Phys.*, 109, 1998, pp.8435-41
73. ten Wolde, P.R., Frenkel, D. "Computer simulation study of gas-liquid nucleation in a Lennard-Jones system", *J. Chem. Phys.*, 109, 1998, pp.9901-18; ten Wolde, P.R., Ruiz-Montero, M. J., Frenkel, D. "Numerical calculation of the rate of homogeneous gas-liquid nucleation in a Lennard-Jones system", *J. Chem. Phys.*, 110, 1999, pp.1591-99
74. Kusaka, Z.-G. Wang, and J. H. Seinfeld, "Binary nucleation of sulfuric acid-water: Monte Carlo simulation", *J. Chem. Phys.*, 108, 1998, pp.6829-48.
75. J. H. Vlugt, M. G. Martin, B. Smit, J. I. Siepmann, and R. Krishna, "Improving the efficiency of the configurational-bias Monte Carlo algorithm", *Mol. Phys.* 94, 1998, p 727.
76. Kusaka I, Wang Z-G, Seinfeld JH. "Direct evaluation of the equilibrium distribution of physical clusters by a grand canonical Monte Carlo simulation", *J. Chem. Phys.*, 108, 1998, pp.3416-23
77. Shen VK, Debenedetti PG. "A computational study of homogeneous liquid-vapor nucleation in the Lennard-Jones fluid", *J. Chem. Phys.*, 111, 1999, pp.3581-9
78. Zahoransky, RA, Hoschele J, Steinwandel J. "Formation of argon clusters by homogeneous nucleation in supersonic shock tube flow", *J. Chem. Phys.*, 103, 1995, pp.9038-44; Zahoransky, RA, Hoschele J, Steinwandel J., "Homogeneous nucleation of argon in an unsteady hypersonic flow field", *J. Chem. Phys.*, 110, 1999, pp.8842-3.
79. Kusaka I, Oxtoby DW. Identifying physical clusters in vapor phase nucleation. *J. Chem. Phys.*, 110, 1999, pp.5249-61.
80. Oh, K.J, Zeng, X.C., "Formation free energy of clusters in vapor-liquid nucleation: A Monte Carlo simulation study", *J. Chem. Phys.* 110, 1999, p 4471-4476
81. Senger B, Schaaf P, Corti DS, Bowles R, Pointu D, Voegel J-C, Reiss H. "A molecular theory of the homogeneous nucleation rate. II. Application to argon vapor", *J. Chem. Phys.*, 110, 1999, pp.6438-50.
82. Kathmann SM, Schenter GK, Garrett BC. "Dynamical nucleation theory: Calculation of condensation rate constants for small water clusters", *J. Chem. Phys.*, 111, 1999, pp.4688-97
83. G. T. Gao, K. J. Oh, and X. C. Zeng. "Effect of uniform electric field on homogeneous vapor-liquid nucleation and phase equilibria. II. Extended simple point charge model water", *J. Chem. Phys.*, 110, 1999, pp.2533-8

84. K. J. Oh and X. C. Zeng, "Formation free energy of clusters in vapor-liquid nucleation: A Monte Carlo simulation study", *J. Chem. Phys.* 110, 1999, p 4471.
85. Oh KJ, Zeng XC. "A small-system ensemble Monte Carlo simulation of supersaturated vapor: Evaluation of barrier to nucleation", *J. Chem. Phys.*, 112, 2000, pp.294-300
86. Wonzak S., Strey, R., Stauffer, D. "Confirmation of classical nucleation theory by Monte Carlo simulations in the 3-dimensional Ising model at low temperature", *J. Chem. Phys.*, 113, 2000, pp.1976-80.
87. Hale, B. N., DiMattio, D. J. "A Monte Carlo discrete sum (MCDS) nucleation rate model for water", *Nucleation and Atmospheric Aerosols 2000*, Ed. B. N. Hale and M. Kulmala, AIP Conference Proceedings Vol 534, 2000, pp 31-34.
88. Kathmann, S.M., Hale, B.N., "Monte Carlo simulations of small sulfuric acid-water clusters", *J. Phys. Chem. B*, 105, 2001, pp.11719-28
89. Oh, K. J., Zeng XC. "Effect of carrier-gas pressure on barrier to nucleation: Monte Carlo simulation of water/nitrogen system", *J. Chem. Phys.*, 114, 2001, pp.2681-6.
90. Chen, B., Siepmann, J. I, Oh, K.J, Klein, M.L. "Aggregation-volume-bias Monte Carlo simulations of vapor-liquid nucleation barriers for Lennard-Jonesium", *J. Chem. Phys.*, vol.115, 2001, pp.10903-13.
91. Oh KJ, Gao GT, Zeng XC. "Nucleation of water and methanol droplets on cations and anions: the sign preference", *Phys. Rev. Letters*, 86, 2001, pp.5080-3
92. Chen, B., Siepmann, J.I., Oh, K.J., Klein, M.L., "Simulating vapor-liquid nucleation of n-alkanes" *J. Chem. Phys.*, 116, 2002, pp.4317-29.
93. Kusaka I. "System size dependence of the free energy surface in cluster simulation of nucleation", *J. Chem. Phys.*, 119, 2003, pp.3820-5.
94. ter Horst JH, Kashchiev D. "Determination of the nucleus size from the growth probability of clusters", *J. Chem. Phys.*, 119, 2003, pp.2241-6.
95. Reguera D, Reiss H. "Nucleation in confined ideal binary mixtures: the Renninger-Wilemski problem revisited", *J. Chem. Phys.*, 119, 2003, pp.1533-46.
96. Oxtoby D. W., Evans, R., "Nonclassical nucleation theory for the gas-liquid transition", *J. Chem. Phys.* 89, 1988 pp. 7521.
97. Zeng, X. C., Oxtoby, D. W. "Gas-liquid nucleation in Lennard-Jones fluids", *J. Chem. Phys.* 94, 4472 (1991).
98. McGraw, R., Laaksonen, A. "Interfacial curvature free energy, the Kelvin relation, and vapor-liquid nucleation rate", *J. Chem. Phys.* 106, 1997 5284
99. Swope WC, Andersen HC. "10<sup>6</sup>-particle molecular-dynamics study of homogeneous nucleation of crystals in a supercooled atomic liquid", *Phys. Rev. B*.41, 1990, pp.7042-54
100. Stillinger, F. H., Stillinger, D. K., "Computational study of transition dynamics in 55-atom clusters". *J. Chem. Phys.*, 93, 1990, pp.6013-24.
101. Shimin, Xu, Bartell, L. S., "Molecular dynamics studies of melting and solid-state transitions of TeF<sub>6</sub> clusters", *J. Phys. Chem.*, 97, 1993, pp.13550-6.
102. Shimin, Xu, Bartell, L. S., "Molecular dynamics studies of melting and solid-state transitions of TeF<sub>6</sub> clusters", *J. Phys. Chem.*, 97, 1993, pp.13550-6.
103. Svishchev, I. M, Kusalik, P. G. "Crystallization of liquid water in a molecular dynamics simulation". *Physical Review Letters*, 73, 1994, pp.975-8; "Crystallization of molecular liquids in computer simulations: carbon dioxide", *Phys. Rev. Letters*, 75, 1995, pp.3289-92.
104. Borzsak I, Cummings PT. "Electrofreezing of water in molecular dynamics simulation accelerated by oscillatory shear", *Phys. Rev. E*. 56, 1997, pp.R6279-82
105. Huang, J., Zhu, X, Bartell, L. S., "Molecular dynamics studies of the kinetics of freezing of (NaCl)<sub>108</sub>". *J. Phys. Chem. A.*, 102 1998, pp.2708-15.
106. Yasuoka, K., Matsumoto, M., "Molecular dynamics of homogeneous nucleation in the vapor phase. I. Lennard-Jones fluid.", *J. Chem. Phys.*, 109, 1998, pp.8451-8462.
107. Yasuoka, K., Matsumoto, M., "Molecular dynamics of homogeneous nucleation in the vapor phase. II. Water.", *J. Chem. Phys.*, 109, 1998, pp.8463-8470.
108. Chushak, Y. G, Bartell, LS. "Simulations of spontaneous phase transitions in large, deeply supercooled clusters of SeF<sub>6</sub>", *J. Phys. Chem. B*, 103, 1999, pp.11196-204.
109. Chushak Y, Bartell LS. "Crystal nucleation and growth in large clusters of SeF<sub>6</sub> from molecular dynamics simulations", *J. Phys. Chem. A*, 104, 2000, pp.9328-36
110. Jinfan Huang, Bartell LS. "Molecular dynamics simulation of nucleation in the freezing of molten potassium iodide clusters", *J. Phys. Chem.* .106, 2002, pp.2404-9.

111. Matsumoto M, Saito S, Ohmine I. "Molecular dynamics simulation of the ice nucleation and growth process leading to water freezing", *Nature*, 416, 2002, pp.409-13.
112. Merikanto, J., Vehkamäki, H., Zupanski, "Monte Carlo simulations of critical cluster sizes and nucleation rates of water:" *J. Chem. Phys.* in press, 2004.
113. Fladerer, A. Dissertation, "Nucleation and Condensation in a Supersaturated Argon Vapor", University of Köln, 2002.
114. Wu, B.J.C., Wegener, P.P, Stein, G.D., "Homogeneous nucleation of argon carried in helium in supersonic nozzle flow", *J. Chem. Phys.* 69, 1978, pp.1776-7.
115. Matthew, M.W., Steinwandel, J., "An experimental study of argon condensation in cryogenic shock tubes", *J. Aerosol Sci.*, 14, 1983, pp.755-63.
116. Stein, G. D. "Argon Nucleation in a Supersonic Nozzle", NTIS-Report No. ADA007357 (1974).