

## Nucleation of a liquid on aerosol nanoparticles

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**Abstract.** - Nucleation of liquid water in the Earth's atmosphere occurs via heterogeneous nucleation on aerosol particles. We consider nucleation on both water insoluble and water soluble aerosol particles. We find that, for particles of the same radius, nucleation on soluble particles dominates. Soluble particles dissolve in the liquid phase and form a droplet even at coexistence. The radius of this droplet essentially determines the supersaturation at which nucleation occurs: the larger the droplet the smaller the supersaturation required before it nucleates to form the bulk liquid. We find that the supersaturation is best measured by the Kelvin radius, which is the radius of a droplet of pure liquid that coexists with vapour of a given supersaturation. We show that nucleation occurs at a universal value of the ratio between the radius of the droplet at coexistence and the Kelvin radius.

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**Introduction.** – Clouds are a key part of the Earth's atmosphere [1, 2]. They are of course composed of water droplets, and these droplets form when a part of the Earth's atmosphere becomes supersaturated with water. This can occur when warm humid air rises and cools. Thus we need to understand the process of droplet formation in order to understand and predict the behaviour of the Earth's atmosphere and hence its climate. This is a very important and topical problem. Now the formation of liquid water in air supersaturated with water vapour is of course a first-order phase transition. Like other first-order phase transitions, it proceeds via nucleation and growth [3, 4]. Nucleation in the atmosphere occurs at low supersaturations, the chemical potential of liquid water is perhaps only  $0.01$  to  $0.02kT$  below that in the supersaturated vapour. At these low supersaturations, homogeneous nucleation is prevented by huge barriers and so is irrelevant [1]. The nucleation is in fact occurring on aerosol particles in the atmosphere. Motivated by this, here we will study nucleation of a liquid on small particles.

These small particles are called aerosol particles and in the atmosphere have sizes predominantly in the nano range. Particles with radii of tens of nanometres are typically present at concentrations of 1000s per  $\text{cm}^3$  [1, 5]. The nucleation of a new phase starts with a microscopic droplet. It begins with only a handful of water molecules,

and grows. As the nucleus grows the free energy of the nucleus at first increases, until a maximum is reached, and then the free energy monotonically decreases, allowing rapid growth of the water droplet to a macroscopic size. The maximum in the free energy means that nucleation is an activated process [3, 4]. We will find that the nucleation barrier first becomes small enough to allow rapid nucleation when the radius of the nucleus at the top of the barrier is comparable to the radius of the aerosol particle.

The aerosol particles can be partially or completely soluble in liquid water. For example, they may be composed of salt (NaCl) or sulphuric acid. Both are present in the atmosphere and both are highly soluble in water [1]. Motivated by this we will study nucleation on both soluble and insoluble particles. We will do this using classical nucleation theory and computer simulation. We will start with the theory, before testing it by comparison with simulation results.

**The Kelvin radius.** – Earlier theoretical and experimental work has shown that the nucleation rate is very sensitive to the radius of the particle [1, 2, 5–8]. It also found that the critical nucleus has a radius comparable to that of the particle on which it is nucleating. Thus we start by considering the radius of the critical nucleus, the nucleus at the top of the nucleation barrier. This radius is

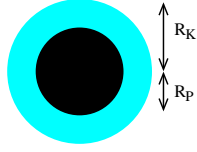


Fig. 1: A schematic of the critical nucleus on an insoluble particle of radius  $R_P$ . The radius of the critical nucleus  $R_K$ , is given by eq. (1). The water is shown as blue and the particle as black.

set by the condition of unstable equilibrium between the nucleus and the surrounding vapour. It is often called the Kelvin radius. For homogeneous nucleation, or for nucleation on a insoluble particle the nucleus is of pure water, and the Kelvin radius  $R_K$  is given by

$$R_K = 2\gamma/(\rho_l S). \quad (1)$$

for  $\gamma$  the liquid/vapour interfacial tension of the pure liquid,  $\rho_l$  the number density in the liquid phase, and  $S$  the supersaturation. Water droplets with radii greater than  $R_K$  will tend to grow, smaller droplets tend to shrink. At a typical atmospheric supersaturation of  $S = 0.02$ ,  $R_K \simeq 50$  nm, or  $\approx 200$  times the diameter of a water molecule. The critical nucleus is very large here.

**Nucleation on insoluble particles.** – We will start by considering nucleation on insoluble particles, and we will consider only particles whose surface is completely wet by the liquid. Then the particle will be covered by a layer of water. This is illustrated schematically in fig. 1, which shows the critical nucleus. A critical nucleus of pure water has a radius  $R_K$ , and so if the particle has a radius  $R_P < R_K$ , then the critical nucleus consists of a spherical shell of thickness  $R_K - R_P$ . However, if the aerosol particle has a radius  $R_P > R_K$ , then a layer of any thickness will result in a droplet (with a particle at the centre) with a radius  $> R_K$ . It will therefore grow. Thus the liquid nucleus is already over the maximum in the free energy, and so there is no nucleation barrier if  $R_P > R_K$ .

However, on particles with radii much less than  $R_K$ , the nucleation barrier will be similar to the, huge, barrier to homogeneous nucleation. Thus the nucleation rate increases sharply with the particle radius as this radius approaches  $R_K$  from below. The explicit form of the nucleation barrier on an insoluble particle was derived by Fletcher [1,6]. For a particle of radius  $R_P$ , it is (assuming complete wetting)

$$\Delta G_{IP}^* = -(4\pi/3) [R_K^3 - R_P^3] \rho_l S + 4\pi [R_K^2 - R_P^2] \gamma \quad (2)$$

for  $R_P < R_K$ . Here,  $S$  is the supersaturation, the difference in chemical potential between the vapour and liquid phases.

According to classical nucleation theory, when the nucleation barrier is  $\Delta G^*$ , the rate per particle,  $J$ , is given by  $J = \nu \exp(-\Delta G^*/kT)$ , where  $\nu$  is a kinetic prefactor

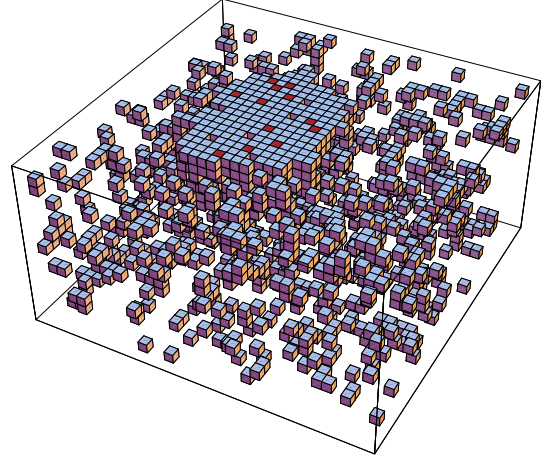


Fig. 2: A simulation snapshot of a liquid droplet containing  $n_{SOL} = 123$  soluble non-volatile molecules. The droplet is at vapour/liquid coexistence,  $S = 0$ . Molecules of the nucleating liquid phase are shown as pale blue cubes. The non-volatile molecules are shown as dark red cubes. The simulation is for a cubic simulation box 36 lattice sites across, but we only show the bottom half of the simulation box in order to make it easier to see the droplet. As the droplet is approximately at the centre of the simulation box, we see a cut through not only the simulation box but also the droplet.

which will be of order one over the characteristic molecular timescale [3,4]. See refs. [4,9–11] for recent theoretical work on nucleation on solid particles. This includes work on particles whose surface is only partially wet by the liquid. We do not consider particles that are partially wet here as these are less effective at inducing nucleation.

Now, the nucleation barrier for homogeneous nucleation is  $\Delta G_{HOMO}^* = (16\pi/3)\gamma^3/(\rho_l S)^2$ , and we can use this expression to rewrite eq. (2) as

$$\Delta G_{IP}^* = \Delta G_{HOMO}^* [1 - 3(R_P/R_K)^2 + 2(R_K/R_P)^3] \quad (3)$$

for  $R_P < R_K$ . For water  $\gamma \simeq 70$  mJ/m<sup>2</sup>, and  $\rho_l = 3 \times 10^{28}$ /m<sup>3</sup> [12]. Thus at a supersaturation  $S = 0.02kT$ , the barrier  $\Delta G_{HOMO}^* \simeq 10^5 kT$ . This is enormous and means that the rate of homogeneous nucleation is completely negligible, however, it also implies that nucleation on solid particles even if they have a radius that is say 90% of  $R_K$ , is also negligible. For  $R_P = 0.9R_K$ ,  $\Delta G_{IP}^* \simeq 10^4 kT$ . This is still far too large to allow nucleation.

**Nucleation on soluble particles.** – It has been appreciated since the work of Köhler [13] in the 1930s that impurities that dissolve in the nucleating phase can dramatically lower the barrier to nucleation. He studied the effect of salt particles on the nucleation of water. Note that salt is highly non-volatile, the ions do not evaporate from water. Motivated by this, our model particle will be composed of molecules of a single component of completely soluble and completely non-volatile molecules. By

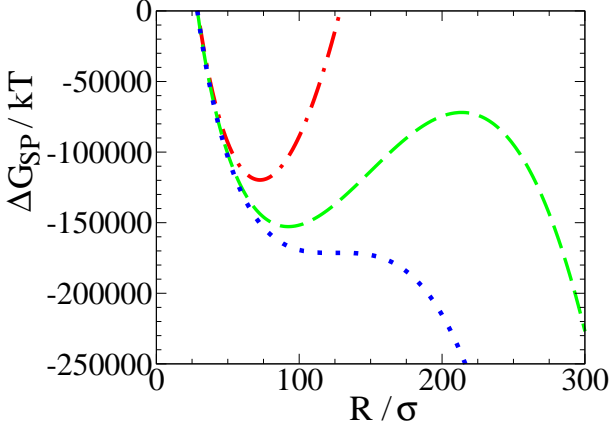


Fig. 3: Plots of the free energy  $\Delta G_{SP}/kT$ , of water droplets containing  $n_{SOL} = 8 \times 10^4$  non-volatile molecules that form an ideal solution. The free energy is plotted as a function of the radius of the droplet  $R$ , and the  $R$ -independent  $\Delta G_{SOL}$  is subtracted from the free energy in each case, just leaving the  $R$ -dependent terms. As  $\Delta G_{SOL}$  will depend on  $S$ , not only are the absolute values of  $\Delta G$  not meaningful, also the values of  $\Delta G$  on curves at different  $S$  cannot be compared. The dot-dashed red, dashed green, and dotted blue curves are at supersaturations  $S/kT = 0, 0.01$  and  $0.0192$ , respectively.

completely non-volatile we mean that the molecules never leave the droplet. The importance of both salt and sulphuric acid to nucleation in the atmosphere is well appreciated [1] but there have been no simulation studies, and most theoretical studies have employed the highly approximate classical nucleation theory [4,7,14–18]. However, Talanquer and Oxtoby [19] have applied density functional theory to the problem. The focus of much of the work has been on complexities not present in our simple model, such as partial solubility [19], or many components [17], or on features specific to particular systems [16]. See ref. [14] for a modern application of classical nucleation theory to the nucleation of water on salt. Work on the fundamentals has been held back by the lack of exact simulation results, which has left uncertainty as to whether the theoretical predictions are accurate.

Here we will first consider the nucleation of water on soluble particles, and then test the theories we use via a comparison with essentially exact results from simulation. See fig. 2 for a simulation snapshot of a droplet. The simulation is of a simple lattice gas model that we will describe below.

The classical nucleation theory expression for the free energy of a nucleus of radius  $R$ ,  $\Delta G_{SP}$ , is

$$\begin{aligned} \Delta G_{SP}(R) &= -v(R)\rho_l S + 4\pi R^2\gamma \\ &+ n_{SOL}kT \ln[n_{SOL}/v(R)] + \Delta G_{SOL} \end{aligned} \quad (4)$$

where  $v(R) = (4\pi/3)R^3$  is the volume of the droplet, and  $n_{SOL}$  is the number of molecules in the soluble particle.

$\Delta G_{SOL}$  is the one-body term in the free energy change in transferring the non-volatile molecules into the liquid phase. We expect this to be large and negative, but as it is  $R$  independent it does not affect the nucleation rate, and so we will not consider it further. The  $R$ -dependent term is the ideal solution term in the free energy (the third term). Note that in the simple free energy expression of eq. (4) we neglect any change in the interfacial tension due to the non-volatile molecules. Also, the soluble molecules enter the free energy only via an ideal solution term. This is an approximation valid only when  $n_{SOL}/v(R)$  is small.

*The size of soluble particles at coexistence.* To make further progress we focus on the nucleation rate as a function of particle size. Dusek *et al.* [5] have experimental evidence that this is the most important parameter for determining how effective an aerosol particle is at inducing nucleation and we wish to better understand this observation. Now, while the size of a solid particle is trivially known, it is fixed and given by the particle’s radius, this is not the case for soluble particles. These dissolve to form a droplet of solution whose radius is a function of  $S$ . To give ourselves a fixed lengthscale we focus on the equilibrium radius of the droplet of solution at coexistence,  $R(S=0)$ . The radius  $R(S=0)$  is highly relevant to studies of the atmosphere as we expect it to closely equal the Stokes radius of the particle, which will determine how rapidly the particle sediments out of the atmosphere.

The radius  $R(S=0)$  is just that at the minimum of the free energy of eq. (4) at  $S=0$ . It is given by

$$R(S=0) = \left(\frac{3}{8\pi}\right)^{1/2} \left(\frac{n_{SOL}kT}{\gamma}\right)^{1/2}. \quad (5)$$

Note that this implies that the concentration of the non-volatile molecules scales as  $n_{SOL}^{-1/2}$ , and so our assumption that the solution is dilute is justified for large soluble particles. We have plotted  $\Delta G_{SP}(R)$  at  $S=0$  in fig. 3 (the red dot-dashed curve). The curve has a global minimum at a radius of  $72.6\sigma = 23$  nm. This plot is for a particle of  $n_{SOL} = 8 \times 10^4$  soluble molecules, which produces rapid nucleation at a supersaturation that lies in the range over which rapid nucleation occurs in the atmosphere. Particles of this size reduce the nucleation barrier to zero at  $S = 0.0192kT$  (see the dotted blue curve).

*Activation of the soluble particles.* As  $S$  is increased and the vapour becomes supersaturated the droplet at the minimum in the free energy swells and becomes metastable. This is seen in the green dashed curve in fig. 3, where we see that the minimum in  $\Delta G_{SP}$  has moved to a larger value of  $R$  and is now only a local minimum. The global minimum is now of course the bulk liquid. However, we see that there is still a nucleation barrier that separates the metastable droplet and the bulk liquid. Indeed for the green dashed curve which is at  $S = 0.015kT$  this barrier is  $81,000kT$  and so the metastable droplet is actually very stable. But increasing the supersaturation to  $S = 0.0192kT$  abolishes the barrier: the maxima and

minima coalesce to form an inflection point, see the blue dotted curve, and nucleation is now rapid. Note that at  $S = 0.0192kT$  the barrier to homogeneous nucleation is  $270,000kT$  so homogeneous nucleation is irrelevant here.

The nucleation barrier disappears when the minima and maxima in  $\Delta G_{SP}$  come together, see the blue dotted curve in fig. 3. This disappearance of the barrier corresponds to what Köhler called activation of the aerosol particles. It occurs when the first and second derivatives of  $\Delta G_{SP}$  are both equal to zero. This gives us two simultaneous equations which we can solve to obtain the value of  $S$  at which the barrier disappears. We denote this value by  $S^{(a)}$ , and it is given by

$$S^{(a)} = \frac{8\sqrt{2\pi}}{9} \frac{\gamma^{3/2}}{\rho_l(n_{SOL}kT)^{1/2}} = \frac{4}{3\sqrt{3}} \frac{\gamma}{\rho_l R(S=0)}, \quad (6)$$

where we used eq. (5) to obtain the second equality. This shows that nucleation becomes rapid at a supersaturation that varies as one over the radius of the droplet at coexistence. The Kelvin radius when the nucleation barrier drops to zero is  $R_K^{(a)} = 2\gamma/(\rho_l S^{(a)})$ , or  $R_K^{(a)} = (9/4\sqrt{\pi})(n_{SOL}kT/\gamma)^{1/2}$ . As the scaling of both  $R(S=0)$  and  $R_K^{(a)}$  are the same, nucleation is predicted to occur at the universal ratio

$$\frac{R(S=0)}{R_K^{(a)}} = \frac{2}{3\sqrt{3}} = 0.38. \quad (7)$$

In words: at coexistence the droplet has a radius  $R(S=0)$ , and both the nucleation barrier and Kelvin radius of a droplet of pure water in the vapour are infinite. Then as the supersaturation is increased both the nucleation barrier and the Kelvin radius of the vapour decrease, until when this Kelvin radius  $R_K$  has dropped to approximately  $1/0.38 \simeq 2.6$  times  $R(S=0)$ , the nucleation barrier becomes zero. Note that here we are using  $R_K$  to measure the supersaturation. This is always possible in an experimental system, provided  $\gamma$  and  $\rho_l$  are known. We are also using  $R(S=0)$  to measure the size of the soluble particle.

Equation (7) is the most important finding of the present work. It is consistent with the experimental finding of Dusek *et al.* [5] that the supersaturation at which nucleation occurs is very sensitive to the size of the aerosol particles, but much less sensitive to the chemistry of the particles. Essentially, they found that the size of the largest aerosol particle present determines the supersaturation at which nucleation occurs. It also shows that soluble particles are much more effective at inducing nucleation than insoluble particles. Above, we found that even for an insoluble particle with radius  $R_P = 0.9R_K$  the nucleation barrier for water was very large. Here we have found that a soluble particle eliminates the barrier completely when its radius  $R(S=0)$  is less than  $0.4R_K$ .

We should be clear about the assumptions that underlie our finding of a universal ratio at the onset of nucleation. They are: 1) that the particle is composed of non-

volatile and highly soluble molecules; 2) that the nucleating droplets are dilute (true if the particles are large, see eq. (5)); 3) that the dissolved particles do not strongly modify the surface tension  $\gamma$ ; and 4) that our simple classical nucleation theory provides a good approximation to the free energy of the droplet. Throughout this work we only consider particles which satisfy 1), and this clearly applies to salt and sulphuric acid particles. However, we will now test assumptions 2) to 4), using the results of computer simulation of a simple model. We will now introduce this model.

**Model.** – Water is very difficult to model [20], so here we will study a simple lattice gas model. As our prediction is universal, we predict that  $R(S=0)/R_K^{(a)}$  should always be approximately 0.4, we can test it on any model. So we choose a simple one. The model we choose is a three-dimensional lattice gas on a simple cubic lattice with nearest-neighbour interactions. We will study the model at fixed chemical potential  $\mu$ , volume  $V$  and temperature  $T$ , as in our earlier work [21, 22]. The simple model will enable us to obtain exact simulation results for nucleation on soluble particles for the first time. It also allows us to carefully test theory, because the input quantities required by theory, such as the surface tension, are accurately known [25, 26].

The model is specified by two parameters. The first is the ratio  $kT/\epsilon$ , where  $-\epsilon$  is the interaction energy of a pair of molecules on adjacent lattice sites. We will work at  $\epsilon/kT = 1.4$  and  $1.2$ . These temperatures are chosen for convenience for simulations. The critical point of the model is at  $\epsilon/kT_{cp} = 0.887$  [23], so we are working at 63 and 74% of the critical temperature. At these two temperatures,  $\gamma/kT = 0.495$  and  $0.310$ , respectively [25, 26]. Our unit of length is the lattice spacing. As  $\rho_l \simeq 1$  at both temperatures the Kelvin radii vary with supersaturation as  $0.99/S$  and  $0.62/S$ , at  $\epsilon/kT = 1.4$  and  $1.2$ , respectively. The second parameter is the chemical potential  $\mu$ . At coexistence the chemical potential  $\mu_{CO} = -3\epsilon$  [24]. Thus the supersaturation  $S = \mu - \mu_{CO}$ . Note that the equilibrium behaviour of our model is identical to that of the Ising model and that in Ising model notation  $\epsilon = 4J$ , and  $S = 2h$  [24].

Impurities that are soluble in the nucleating phase but are highly non-volatile are easily modelled within a lattice-gas model. We simply let them be another species of molecule that interact both with each other and with the molecules of the liquid with an energy  $-5\epsilon$ . This then means that the energy cost of moving them from the liquid to the vapour is approximately  $6 \times 5 \times 1.2kT = 36kT$ , which is prohibitive so they are effectively non-volatile. As the interaction between two non-volatile molecules is the same as that between a non-volatile molecule and a liquid molecule, the non-volatile molecules form an ideal solution in the liquid. They are highly soluble.

Combining all these interactions, we have that the appropriate weight of a state is  $\exp(-H/kT)$ , with

$H(\mu, V, T, n_{SOL})$  given by

$$\begin{aligned}
H = & -\epsilon \sum'_{i,j} \delta(n_i, 1) \delta(n_j, 1) - 5\epsilon \sum'_{i,j} \delta(n_i, 2) \delta(n_j, 2) \\
& -5\epsilon \sum'_{i,j} [\delta(n_i, 1) \delta(n_j, 2) + \delta(n_i, 2) \delta(n_j, 1)] \\
& -\mu \sum_i \delta(n_i, 1)
\end{aligned} \tag{8}$$

where  $n_i = 0, 1$  or  $2$ , if site  $i$  is empty, filled with a liquid molecule, and filled with a non-volatile molecule, respectively.  $\delta(m, l)$  is the Kronecker delta, which equals one for  $m = l$  and is zero otherwise. The primes over the first 3 sums indicate that they are over all nearest-neighbour pairs of sites.

**Computer simulation technique.** – In the absence of non-volatile molecules our simulations are simply Glauber dynamics Monte Carlo simulations of a lattice gas. We pick a lattice site at random, and attempt to change its state, from empty to containing a molecule if it is empty, and from containing a molecule to empty if it contains a molecule. If the change in  $H$ ,  $\Delta H$ , due to this attempted change is negative we always accept; if  $\Delta H$  is positive we accept it with a probability  $\exp(-\Delta H/kT)$ . These dynamics do not conserve the number of liquid molecules.

We want to work at a fixed number of the non-volatile molecules, so when our system has these molecules we modify the dynamics as follows. We again pick a lattice site at random, and if it is either empty or contains a molecule of the liquid phase, our dynamics are as before. However, if the lattice site contains a non-volatile molecule then we employ Kawasaki dynamics. We pick one of the 6 adjacent lattice sites and attempt to swap the contents of the pair of sites. If  $\Delta H$  is negative we always accept the swap, whereas if it is positive we only swap with a probability  $\exp(-\Delta H/kT)$ . These dynamics allow the number of molecules of the nucleating liquid phase to vary, which is necessary to allow nucleation, but they fix the number of non-volatile molecules, which is required to model nucleation on a particle composed of a fixed number of the non-volatile molecules.

Now, a critical nucleus may consist of 1000s of molecules and its rate of formation can be extremely low, meaning that enormously long simulations would need to be performed before it will appear. To get round this problem, a number of computer simulation techniques have been developed that allow the calculation of very low rates. They are computationally demanding, but with our simple model accurate calculations are feasible. One such technique is the Forward Flux Sampling (FFS) algorithm of Allen, ten Wolde, Warren and Frenkel [27–29]. This is the technique that we will use. We follow the original algorithm [27, 28] closely, and our procedure is identical to that in our earlier work [22]. See this reference for further

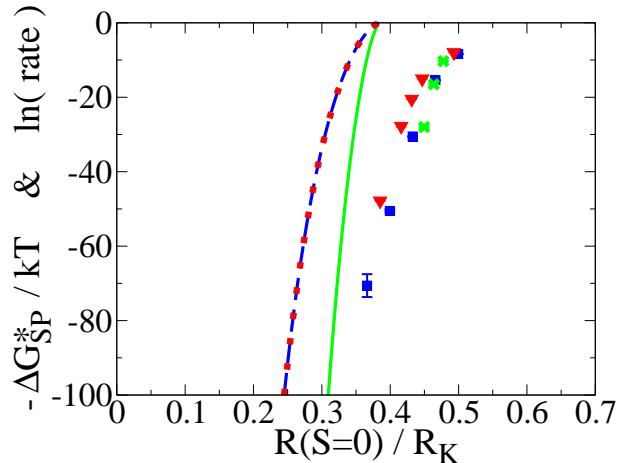


Fig. 4: Plots of minus the classical nucleation theory barrier,  $-\Delta G^*/kT$ , and the log of the simulation rate, as functions of the ratio between the radius of the metastable droplet at coexistence,  $R(S=0)$ , and the Kelvin radius,  $R_K$ . All data are for nucleation on soluble particles. The Kelvin radius varies as  $1/S$  so the  $x$  axis is proportional to the supersaturation  $S$ . The curves are from theory and the points are from simulation. There are statistical error bars for all points but in most cases they are smaller than the point size. The green solid curve and green crosses are for  $\epsilon/kT = 1.4$  and a particle of  $n_{SOL} = 123$  molecules. The blue dashed curve and blue squares are for the same temperature but  $n_{SOL} = 33$  molecules. The red dotted curve and red triangles are for the higher temperature  $\epsilon/kT = 1.2$  and  $n_{SOL} = 33$  molecules.

details.

**Testing theory with computer simulation.** – To test our prediction that  $R(S=0)/R_K^{(a)}$  is universal we have plotted nucleation rates as a function of  $R(S=0)/R_K$  in fig. 4. The simulation rates are in units of  $\text{cycle}^{-1}$ , where 1 cycle is 1 attempted Monte Carlo move per lattice site. The theoretical predictions are just  $-\Delta G_{SP}^*/kT$ , which is equal to the log of the rate if  $\nu = 1 \text{ cycle}^{-1}$ . We see that all 3 curves from theory are close together and that the 2 curves with the same value of  $n_{SOL}$  but different  $\gamma$ s are actually identical. Plotted in this way the theory rates are independent of  $\gamma$ . The simulation rates also are close to falling on one common curve. However, this curve is shifted to values of  $R(S=0)/R_K$  that are around 0.1 higher than the theoretical predictions. Thus, the nucleation barriers as predicted by theory become negligible just below 0.4, in accordance with our analytic predictions, but the barriers in simulation become negligible at a slightly higher value  $\simeq 0.5$ .

Plotting the simulation data in fig. 4 requires that we obtain the radius of the droplets at coexistence,  $R(S=0)$ , within simulation. We do this by running a simulation at  $S=0$ , to obtain the excess number of molecules,  $n_{EX}$ , i.e., the number in the simulation box when a droplet is present minus the number when there is no droplet. This is then converted into a radius via  $R(S=0) = [(3(n_{EX} +$

$n_{SOL}/4\pi)^{1/3}$ . For example, for  $n_{SOL} = 123$  at  $\epsilon/kT = 1.4$ , we find that  $n_{EX} \simeq 1287$  and so  $R(S = 0) = 6.95$ . Theory predicts a smaller radius of 5.69. The theoretical predictions are systematically too low. For  $n_{SOL} = 33$ , simulations yield  $R(S = 0) = 4.13$  and 4.78, at  $\epsilon/kT = 1.4$  and 1.2, respectively. The theoretical predictions for the  $n_{SOL} = 33$ , are  $R(S = 0) = 3.05$  and 3.71, at  $\epsilon/kT = 1.4$  and 1.2, respectively.

The discrepancy between theoretical and simulation values for  $R(S = 0)$  is not surprising. We should bear in mind that both the shape and size of the nucleus fluctuate and that the figure of 1287 is an average over these fluctuations, which are neglected in the simple theory. See fig. 2 for a snapshot of a droplet at  $S = 0$ . Also, the theoretical estimate relies on the use of the interfacial tension of a flat (not curved) interface of a pure liquid. Our interface is not only curved, it is between the vapour and a solution of non-volatile molecules. These are repelled by the interface, and so according to the Gibbs' adsorption equation [12], they act to increase the interfacial tension and hence the radius of the droplet.

**Conclusion.** – We have two main results. The first result applies to nucleation on soluble particles. It is that the nucleation barrier should become zero at a supersaturation  $S$  such that the ratio of the droplet diameter at coexistence,  $R(S = 0)$ , to the Kelvin radius at  $S$ , equals a universal value of 0.38. This prediction may be at least part of the reason for the finding of Dusek *et al* [5] that at constant size, the chemistry of an aerosol particle has only a weak effect on the nucleation. We predict that so long as the particle is non-volatile and highly soluble in water, its chemistry should not matter at all. The second result is that when comparing particles of the same size, nucleation will occur on soluble particles at lower supersaturations than on insoluble particles. Nucleation occurs on soluble particles at supersaturations where  $R_K$  has dropped to around  $1/0.38 \simeq 2.6$  times the diameter of the droplet formed by the soluble particle. It must drop to almost the radius of the particle itself for rapid nucleation to occur on an insoluble particle.

As the prediction of this universal value of the ratio  $R(S = 0)/R_K^{(a)}$  came from an approximate theory, we introduced a simple lattice-gas model and used exact computer simulations of this model to test the theory. We found that simulation rates obtained at different temperatures and particles did indeed collapse onto approximately the same curve. This curve was however shifted by approximately 0.1 in relation to the theoretical curve. The fact that our theory and simulation rates are both approximately universal functions of  $R(S = 0)/R_K$  encourages us to believe that this dimensionless variable is the best variable for plots of the nucleation rate on soluble particles. It may therefore be instructive to plot experimental nucleation data as functions of this variable.

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