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# **Quantitative characterization of critical nanoclusters nucleated on large single molecules**

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**First order phase transitions involve nucleation, formation of nanoscale regions of a new phase within a metastable parent phase. Using the heterogeneous nucleation theorem we show how clusters formed by nucleation on single molecules evolve from the gas phase and determine the critical size beyond which condensation starts to form aerosol particles. Our experiments reveal the activation of molecules into droplets to happen via formation of critical clusters substantially larger than the seed molecule. The nano-sized critical clusters were found to be well predicted by the Kelvin-Thomson relation pointing directly to the key step in the phase transition.**

Gas-to-particle conversion in air is known to be an important process in atmospheric aerosol formation and cloud microphysics. Particle/droplet formation is always initiated by nucleation occurring either directly in the gas phase (homogeneous nucleation) or on the surface of pre-existing seed particles (heterogeneous nucleation). The latter is energetically much more favourable resulting in comparatively low vapour supersaturations required for droplet formation. Physico-chemical properties of the nucleation sites such as size, solubility and charging state significantly influence the nucleation process. Nucleation occurs if spontaneously formed clusters reach a critical size allowing the cluster to grow further by condensation. Critical clusters can thus be viewed as the starting point initiating the transition from nanometer sized clusters into macroscopically relevant objects like cloud condensation nuclei and cloud droplets. The importance of quantifying critical nuclei in size and chemical composition was highlighted recently in the context of atmospheric particle formation [1].

Modelling nucleation suffers from the fact that on the one hand cluster dimensions often exceed the applicability range of quantum mechanical approaches and on the other hand they are too small to be modelled accurately by macroscopic theories. This unsatisfying situation is underlined by recent experimental studies reporting nanoparticle activation at sizes much smaller than expected from thermodynamically derived vapour-droplet equilibrium conditions [2,3]. It is notable that we can now analyse experimental nucleation data independent of any theoretical model by applying the nucleation theorems for homogeneous [4,5] and heterogeneous [6] nucleation to obtain the number of molecules in a critical cluster. In this paper, we present precision heterogeneous nucleation experiments which have been analysed with the recently developed heterogeneous nucleation theorem to determine the size of critical clusters formed on pre-existing nucleation sites. We investigated the activation behaviour of single ion molecules in supersaturated *n*-propanol vapour and determined the number of molecules in the critical clusters from heterogeneous nucleation probability vs. saturation ratio curves. The challenging aspects as well as the novelty of this work are related to the experimental precautions undertaken to allow for the direct application of the heterogeneous nucleation theorem to experimental data. Any extra factors influencing the slope of heterogeneous nucleation probability curves need to be eliminated in order to achieve meaningful results. This requires precise settings of the thermodynamic state and strictly monodisperse seed particles as was pointed out recently [7].

Heterogeneous nucleation on single ion molecules was investigated at two different temperatures using an expansion chamber in combination with an optical particle

detection system (constant angle Mie scattering, CAMS-method [8]). Details of the experimental system can be found elsewhere [9,10]. *n*-Propanol vapour was added to the system by controlled injection from a syringe pump and mixed with a well-defined flow of size selected positive or negative ion molecules with diameters between 1.47 nm and 1.78 nm. Ion molecules were generated by electrospray ionization [11] in combination with a high resolution electrostatic size classifier [12]. Further experimental details can be found in [13]. The size of the ion molecules was determined from electrical mobilities according to Ude & de la Mora [14]. Vapour supersaturation was achieved by adiabatic expansion and number concentration of droplets nucleated on ion molecules was measured by the CAMS detector. For each *n*-propanol vapour saturation ratio, the fraction of activated particles relative to total particle number concentration was determined at different temperatures, resulting in temperature dependent nucleation probability curves for each of the investigated ion molecules (see Figure 2).

The key issue in this study was to identify and use seed particles of strictly monodisperse size since any finite distribution of particle sizes leads to a flattening of heterogeneous nucleation probability curves and hence underestimation of critical cluster sizes. We chose ion molecules of particular species, which can be regarded as perfectly monodisperse seed particles. In the present study, positive tetraheptylammoniumbromide (monomer  $\text{THA}^+$  and dimer  $\text{THA}_2^+\text{Br}$ ) and tetradodecylammoniumbromide (monomer  $\text{TDDA}^+$ ) ions as well as the negative dimer cluster  $\text{THABr}_2^-$  were used. In Figure 1 size distributions of the corresponding ions are illustrated. The remaining measured widths of the peaks are below a relative full width at half maximum (FWHM) of 3% and can be

attributed to the non-ideal transfer function of the electrostatic classifier. The mobility classified sizes of these ions were found to be 1.47 nm, 1.78 nm, 1.70 nm and 1.54 nm for  $\text{THA}^+$ ,  $\text{THA}_2^+\text{Br}$ ,  $\text{TDDA}^+$  and  $\text{THABr}_2^-$ , respectively (see also Table 1). These substances were described in detail earlier as mass and mobility standards [14]. In Figure 2 the temperature dependence of heterogeneous nucleation probability curves is shown for selected ions. As can be seen, with decreasing temperature as well as decreasing ion molecule size the saturation ratio required to activate the ion molecules is increased.

Quantitative information on critical cluster size is obtained from the heterogeneous nucleation theorem for charged particles [15],

$$\left. \frac{\partial \ln \left( \ln \frac{1}{1-P} \right)}{\partial \ln S} \right|_T = \Delta N_2^* - \Delta N_1^*, \quad (1)$$

where  $P$  and  $S$  denote heterogeneous nucleation probability and vapour saturation ratio,  $T$  is temperature, while  $\Delta N_1^*$  and  $\Delta N_2^*$  are the excess numbers of molecules in a stable pre-nucleation cluster and the critical cluster, respectively. Excess number is the number of molecules in the cluster minus the number that would occupy the cluster volume if filled with vapour phase. Liquid being much denser than the vapour,  $\Delta N_2^*$  is fairly accurately equal to the number of molecules in the cluster.  $\Delta N_1^*$  needs to be considered in eq. (1) only if stable pre-nucleation clusters will actually be formed in the considered system. To illustrate this issue, Figure 3 shows the formation free energy curves as a function of number of *n*-propanol molecules in the cluster. Classical nucleation theory for homogeneous and ion-induced nucleation (with zero contact angle) has been used to create these curves. The formation free energies have been made self-consistent [16] so

that the formation free energy of the monomer (number of molecules  $N = 1$ ) in the case of homogeneous nucleation and a bare ion ( $N = 0$ ) in the case of ion-induced nucleation have been set to zero. The resulting form for the homogeneous formation free energy is

$$\Delta G(N) = -(N-1)kT \ln S + (A(N) - A(1))\sigma \quad (2)$$

and for the ion-induced free energy

$$\Delta G(N) = -NkT \ln S + (A(N) - A(0))\sigma + \frac{q^2}{8\pi\epsilon_0} \left(1 - \frac{1}{\epsilon_r}\right) \left(\frac{1}{r(N)} - \frac{1}{r(0)}\right). \quad (3)$$

In these equations  $\sigma$  is the “bulk” surface tension (for flat surfaces),  $r(N)$  and  $A(N)$  are the radius and surface area of a  $N$  cluster,  $q$  is the charge of the ion,  $\epsilon_r$  is the (bulk liquid) dielectric constant of the formed  $n$ -propanol cluster and  $\epsilon_0$  permittivity of vacuum. The homogeneous formation free energy curve (Fig. 3) does not contain a minimum, and thus the process does not involve stable pre-nucleation clusters. The ion induced formation free energy with an ion radius 0.1 nm has a minimum followed by a maximum, corresponding to the occurrence of a pre-nucleation cluster and critical clusters, respectively. The curve with an ion radius 0.9 nm has no minimum, and thus no stable pre-nucleation clusters are formed on an ion of this size (assuming a zero contact angle).

For practical reasons we applied the heterogeneous nucleation theorem to physically consistent fit functions determined from the experimental data [13]. In Table 1,  $\Delta N_2^* - \Delta N_1^*$  including uncertainty ranges are given for the different seed ion molecules and two temperatures at the onset saturation ratio, i.e. the saturation ratio where  $P = 0.5$ .

The condition for critical cluster (pre nucleation cluster) in unstable (stable) equilibrium with the surrounding vapour is found by locating the maximum (or minimum) of the formation free energies (2) and (3). The conditions are given by Kelvin equation

$$kT \ln S = \frac{2\sigma M}{N_A \rho r} \quad (4)$$

for neutral particles and Kelvin-Thomson (K-T) equation [17]

$$kT \ln S = \frac{2\sigma M}{N_A \rho r} - \frac{q^2 M}{8\pi\epsilon_0 N_A \rho r^4} \left(1 - \frac{1}{\epsilon_r}\right) \quad (5)$$

for charged particles. Here  $M$  and  $\rho$  denote molecular weight and (liquid) density of the condensate and  $N_A$  is Avogadro's number. For thermodynamic data used see Table S1 in [13]. The vapour saturation ratio determines the curvature of the equilibrium cluster surface, and thus the cluster radius. In the case of heterogeneous nucleation, the critical cluster is located upon the seed particle, and the number of molecules is related to the radius through a geometric relation involving contact angle. The contact angle describes the interaction between the cluster molecules and the seed particle (wetting ability) and it can depend on the radius of the cluster [18]. Under the assumption of complete wetting (contact angle  $0^\circ$ ) the volume of the seed particle fully contributes to the critical cluster volume and correspondingly the curvature of the surface of a cluster containing a certain number of molecules can be directly determined. Thereby, the volume of the critical cluster  $V_{crit}$  can be calculated according to

$$V_{crit} = V_{seed} + \Delta N_2^* \cdot V_{n-prop}^l, \quad (6)$$



where  $V_{seed}$  is the volume of the seed particle and  $V_{n-prop}^l$  the volume of one  $n$ -propanol molecule in bulk liquid. For spherical critical clusters the diameter  $d_{crit}$  is calculated from

$$d_{crit} = \sqrt[3]{\frac{6V_{crit}}{\pi}}. \quad (7)$$

In Figure 4, the initial seed ion molecule size and the size of the critical cluster together with corresponding values according to the classical K-T equation are shown for 263K and 273K. For simplicity, we show the critical cluster diameters assuming that there are no pre-nucleation clusters ( $\Delta N_1^* = 0$ ) as suggested by the classical theory for ions of studied size. The purely experimentally determined error bars indicate remarkably good agreement of our data with K-T equation spanning entirely the range of uncertainty given by a possible adsorbed monomolecular layer. The sizes of the critical clusters as plotted in Figure 4 can thus be viewed as the minimum sizes possible under complete wetting. On the other hand, by considering only  $V_{seed} / 2$  in Equation 6 it can be quantitatively shown that a significant effect of a non-zero contact angle on the critical cluster size can be ruled out. This is a consequence of the fact that the final critical cluster is substantially larger than the initial seed molecule. Accordingly, the bulk values used for surface tension and dielectric constant to compute K-T equation represent reasonable approximations in our study where the bare ion is covered by substantially more condensate than just a monolayer. Similarly, a recent theoretical nucleation study [19] has

found little effects of a Tolman-type corrected surface tension compared to the surface tension of a plane surface.

It is important to note that activation behaviours of different seed molecules ( $\text{TDDA}^+\text{Br}$ ) and molecules with different polarity ( $\text{THABr}_2^-$ ) do not follow the size dependence of the  $\text{THA}^+\text{Br}$  molecules indicating different nucleation behaviour. However, the critical clusters (full symbols) are approximately in line as expected from the K-T prediction. One of the major shortcomings attributed to the classical K-T equation is related to the fact that this equation does not allow to differentiate between positive and negative polarities [20]. Here we show, however, that K-T provides a rather precise tool to determine critical cluster sizes regardless of the properties of the individual seed particles. Notably the experimentally observed temperature dependence is within error exactly in accordance with K-T equation. From Figure 4 it becomes clear that the nucleating molecules forming a critical cluster are shifting the size of the initial seed particle towards the Kelvin-Thomson diameter providing the curvature for which the vapour is in equilibrium. This formation of critical clusters with diameters given by the Kelvin-Thomson equation is observed regardless of the actual properties of the particular seed particles. Further addition of a single vapour molecule by statistical fluctuation causes the critical cluster to grow immediately by condensation. Thereby the initial seed molecule becomes visible and hence detectable by optical methods. We would like to emphasize that all our evaluations are independent of classical / macroscopic assumptions with the only exception that we assume macroscopic liquid density in the critical cluster. Departure of cluster density from the macroscopic value towards smaller densities would even improve agreement between experimental data and K-T. Figure 4 also illustrates

homogeneous nucleation data in comparison to Kelvin equation at 265K [21]. The agreement of critical cluster size in homogeneous nucleation with Kelvin was also found with other compounds [22,23].

While the Kelvin-Thomson prediction is within the uncertainty limits of our experiments, it tends to slightly overestimate the experimental critical cluster sizes by roughly 15-20 molecules. This can probably be interpreted by a recently derived modification of the classical Kelvin-Thomson equation. Taking into account effects of the central electric field and the disjoining pressure on condensing thin liquid films [24] leads to a reduction of the nucleation barrier and correspondingly to lower saturation ratios required to achieve critical cluster formation. Our results clearly support the macroscopic Kelvin / Kelvin-Thomson theory being able to describe vapour equilibrium conditions for critical clusters with diameters as small as a few nanometers. However, the classical nucleation theory often fails to explain experimental heterogeneous nucleation data quantitatively. Our data thus support the recent theoretical study [25] which has demonstrated that the Kelvin equation is more fundamental than classical nucleation theory.

The results of our experiments indicate that the size of the critical cluster agrees quite well with the Kelvin / Kelvin-Thomson prediction, although the initial seed is substantially smaller (see schematic illustration in Figure S1 [13]). Until recently it has been widely accepted that seed particles need to be larger than the Kelvin or Kelvin-Thomson radius in order to be activated. This would be the case if particles only activated for growth when the nucleation barrier vanishes and (barrierless) condensation occurs. However, this ignores the fact that a nucleation barrier can be crossed by kinetic processes, and hence also smaller particles can activate for growth via heterogeneous or

ion induced nucleation. As a consequence, our data quantitatively indicate a considerable extension of the fundamental detection range of condensation particle counters (CPCs) down to nano- / subnano-particles or even single molecules which is of great practical importance [26,27,28].

The clustering of initially gas-phase molecules transitioning into bulk liquid phase material takes place within a narrow range of molecule numbers. In their pioneering work on gas-phase clusters more than two decades ago, Castleman and Keesee [29] raised the question how large a cluster needs to be until it displays properties of the macroscopic bulk phase. We now have obtained clear experimental evidence that critical clusters with radii down to about 2 nm are satisfactorily described by the (macroscopic) Kelvin / Kelvin-Thomson relation. This will give new firm insight to nucleation and initial growth processes in atmospheric conditions as well improve our understanding of nanomaterials.

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Figure 1. Size distributions of  $\text{THA}^+\text{Br}$  (solid) and  $\text{TDDA}^+\text{Br}$  (dashed) ions as well as  $\text{THABr}_2^-$  (dotted) as determined with the nano-DMPS.

Figure 2: Heterogeneous nucleation probability  $P$  vs. vapour saturation ratio for nucleation of  $n$ -propanol on  $\text{THA}^+\text{Br}$  ions at 273K (red) and 263K (blue). Open squares refer to the dimer with mobility diameter 1.78 nm and full squares to the monomer with 1.47 nm. Lines are fitted to the data according to physically consistent heterogeneous nucleation probability functions. Corresponding onset saturation ratios ( $P = 0.5$ ) are indicated by vertical dotted lines.

Figure 3: Formation free energies for homogeneous nucleation (solid line) and ion induced nucleation of  $n$ -propanol ( $S = 3.0$ ,  $T = 273.15$  K) at two different ion sizes (dashed line is calculated for ion radius 0.9 nm, dotted line for ion radius 0.1 nm). Pre-nucleation clusters are expected to form only when the energy curves go through a minimum as is the case for an ion with radius 0.1 nm.

Figure 4: Experimental onset saturation ratios measured at 273K (red) and 263K (blue) as function of seed particle mobility diameter for ions (open symbols) together with the diameter of the corresponding critical cluster (full symbols). Circles refer to  $\text{THA}^+$  monomer, squares to  $\text{THA}_2^+\text{Br}^-$  dimer, triangles to  $\text{TDDA}^+$  and stars to  $\text{THA}^+\text{Br}_2^-$  dimer. Solid lines indicate the prediction of the Kelvin-Thomson equation at 273K (red) and

263K (blue). Horizontal error bars were obtained by means of variation analysis and indicate the possible range of critical clusters. Vertical error bars show experimental uncertainty in saturation ratio (typically below 2% of absolute value). For comparison the agreement of homogeneous nucleation data and Kelvin equation is shown for 265K (cyan).

#### Physico-chemical properties of seed ion molecules and critical clusters

Seed ion molecule	Chemical formula	Atomic mass (Da)	Mobility diameter (nm)	$\Delta N_2^* - \Delta N_1^*$ (273K)	$\Delta N_2^* - \Delta N_1^*$ (263K)
THA <sup>+</sup> monomer	(C <sub>7</sub> H <sub>15</sub> ) <sub>4</sub> N <sup>+</sup>	410.78	1.47	<b>47</b> $\frac{+19}{-8}$	<b>42</b> $\frac{+21}{-11}$
THA <sub>2</sub> <sup>+</sup> Br dimer	((C <sub>7</sub> H <sub>15</sub> ) <sub>4</sub> N) <sub>2</sub> <sup>+</sup> Br	901.46	1.78	<b>48</b> $\frac{+26}{-7}$	<b>44</b> $\frac{+26}{-13}$
THABr <sub>2</sub> <sup>-</sup> dimer	(C <sub>7</sub> H <sub>15</sub> ) <sub>4</sub> NBr <sub>2</sub> <sup>-</sup>	584.60	1.54	<b>50</b> $\frac{+10}{-6}$	<b>37</b> $\frac{+7}{-4}$
TDDA <sup>+</sup>	(C <sub>12</sub> H <sub>25</sub> ) <sub>4</sub> N <sup>+</sup>	691.31	1.70	<b>56</b> $\frac{+29}{-13}$	<b>53</b> $\frac{+28}{-12}$

Table 1:  $\Delta N_1^*$  and  $\Delta N_2^*$  are the excess numbers of molecules in a stable pre-nucleation cluster and the critical cluster, respectively.



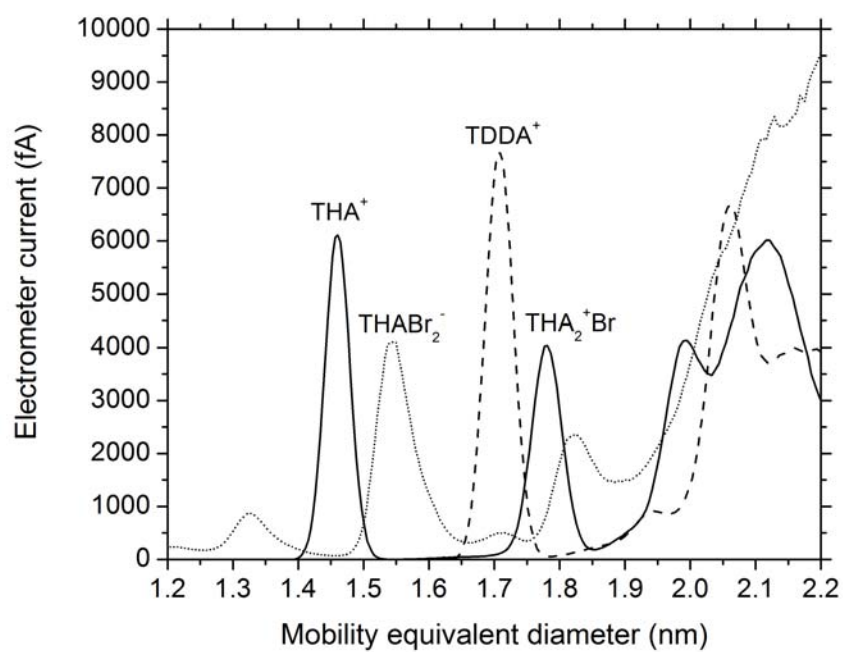


Figure 1

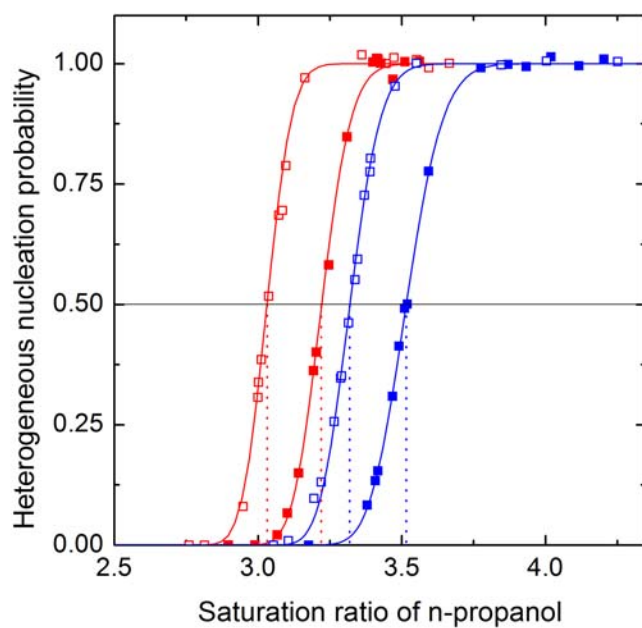


Figure 2

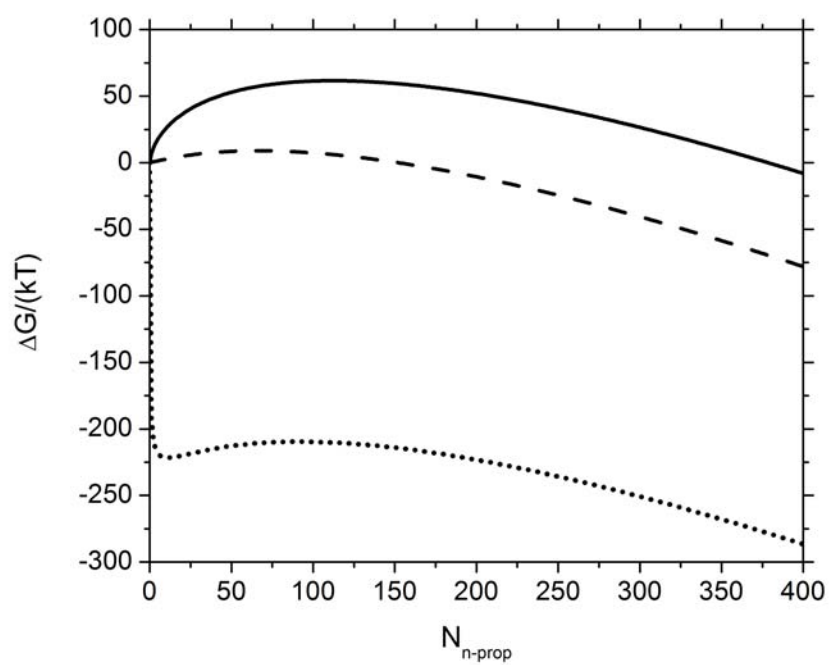


Figure 3

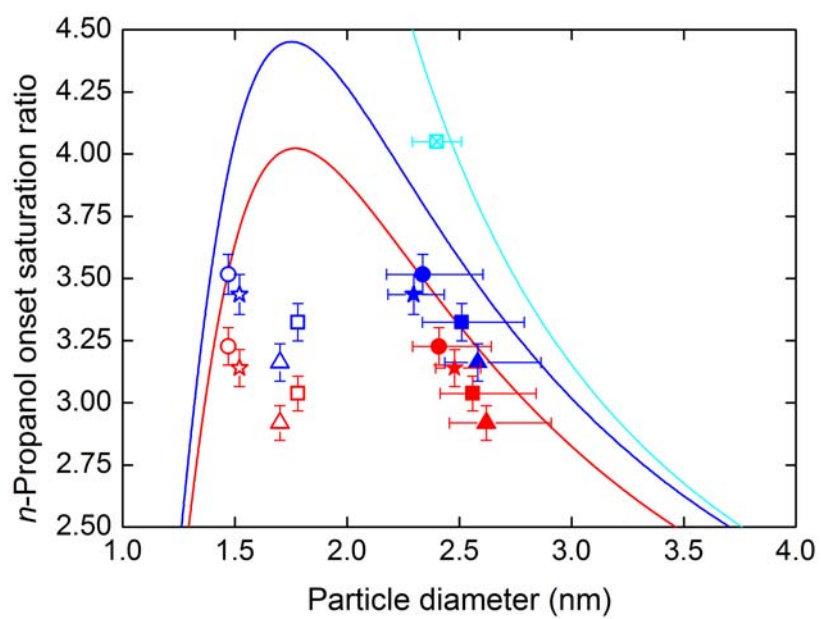


Figure 4