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UNIFYING PERSPECTIVES FROM NUCLEATION THEORY***

McGraw, R. and Lewis, E.

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Brookhaven National Laboratory

P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

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Deliquescence and Efflorescence of Small Particles: Unifying Perspectives From Nucleation Theory

Robert McGraw and Ernie Lewis

*Atmospheric Sciences Division, Environmental Sciences Department
Brookhaven National Laboratory, Upton, NY 11973*

Abstract. We examine size dependent deliquescence/efflorescence phase transformation for particles down to several nanometers in size. A thin layer criterion (TLC) is introduced to define a deliquescence relative humidity (DRH) for small particles. The usual bulk deliquescence conditions are recovered in the limit of large dry particle size. Nano-size particles are shown to deliquesce to metastable states via a nucleation process at relative humidity just below the DRH. The nucleation barrier is located at a critical solution layer thickness and vanishes at the DRH defined by the TLC. Methods from nucleation theory form the basis for the analysis and yield new insights into the theory, facilitate the interpretation of measurements, and point to unification of deliquescence and efflorescence processes for particles in the nano regime. Methods include thermodynamic area constructions, Legendre transforms relating the binary free-energy surfaces for deliquescence and efflorescence processes, and application of nucleation theorems.

Key Words: Nucleation theory, Small particle deliquescence and efflorescence, Nucleation theorem, Kinetic potential

INTRODUCTION

Following the uptake of water by deliquescence, atmospheric particles can easily grow to several times their dry diameter. The larger particles are more efficient scatterers for visible light, condensation sinks for condensable vapors, and active sites onto which cloud droplets can form. Heterogeneous chemical transformations are also affected by the water uptake. Through such effects, hygroscopic particle growth has important consequences for aerosol radiative forcing of climate both directly, through short wavelength scattering, and indirectly, through cloud modification.

Several theoretical studies over the past decade have focused on particle size effects during deliquescence [1-3], and on the nucleation of efflorescence [4-5]. In the large particle limit where the theory is well established, deliquescence is known to occur sharply with increasing relative humidity as the free energies of the initial state (salt particle plus vapor) and final state (solution drop plus vapor) become equal [6]. For small systems the theories tend to diverge - as do the criteria for predicting when deliquescence occurs. Some authors simply retain the criterion of free-energy equality [1, 3]. On the other hand Djikaev et al. [2] note the presence of a nucleation-like barrier to the deliquescence of small particles that can prevent the process, and introduce the

criterion that deliquescence occurs under conditions that the barrier vanishes - in analogy with Kohler-type activation [7]. There appears to be no general agreement as to which criterion to use and subsequent authors have either extended free energy equality [8] or used the vanishing barrier criterion [9] to define the deliquescence point in the small particle regime.

The present analysis supports the vanishing barrier criterion. We find barrierless deliquescence initiated at the (unstable) equilibrium conditions that (1) the chemical potential of salt in the core equals that in a surrounding thin solution layer and (2) the chemical potential of water in the thin solution layer equals that in the vapor. These are clear generalizations to arbitrary size of the corresponding bulk criteria given above. But only in the bulk limit is the thin layer criteria (TLC) equivalent to free energy equality.

Thermodynamic properties of coated particles are developed for layers of arbitrary thickness. Analysis is carried out using the classical capillary drop model and extended using the Gibbs dividing surface model so as to obtain a self-consistent theory for small particles that includes surface enrichment effects and interfacial tension composition dependence

MAXWELL-LIKE AREA CONSTRUCTIONS

We present several useful and very general area constructions. These are based on Eq. 1 below, which can be derived several ways, but in very general form using the so-called “kinetic potential” of nucleation theory [10]. In outline, the ratio of pressures P_1 / P_{1eq} (or relative humidities RH / RH_{eq}) in Eq. 1 equals the ratio of condensation rate (proportional to applied external vapor pressure, P_1) to evaporation rate (proportional to equilibrium vapor pressure of the drop, P_{1eq}). Now the integral of the logarithm appearing in Eq. 1 is just the logarithm of the extended product of condensation to evaporation rates, or kinetic potential (KP) [10, 11]. For the thermodynamic systems discussed here the KP is equivalent to a reduced free-energy difference - in nucleation theory, for example, the reduced barrier height. But the KP is more general in that it can be defined for purely kinetic problems where one has available *only* a sequence of forward and reverse rates [11].

$$\frac{G_f - G_i}{kT} = - \int_{n_1(i)}^{n_1(f)} \ln \left(\frac{P_1}{P_{1eq}} \right) dn_1 = -n_{dry} \int_{n_1(i)}^{n_1(f)} \ln \left(\frac{RH}{RH_{eq}} \right) d(n_1 / n_{dry}) \quad (1)$$

Figure 1 shows $\ln(RH_{eq})$ plotted versus the molecular ratio of water in the solution layer, n_1 , to total salt originating from the dry particle, n_{dry} . Calculations are for an ideal solution of NaCl and water, dry particle diameter of 7.2nm, and $T = 300K$ [12]. Horizontal lines in the figure are lines of constant $\ln RH$ corresponding to the external vapor pressure of water over the drop. The TLC deliquescence relative humidity DRH , computed at 84.5%, is given by line a-f. (The bulk DRH for this system is 75% [8].) The critical RH for salt nucleation (efflorescence), ERH , fluctuates as expected of a nucleation process [13], but is approximately located at 50% RH (line c'-c).

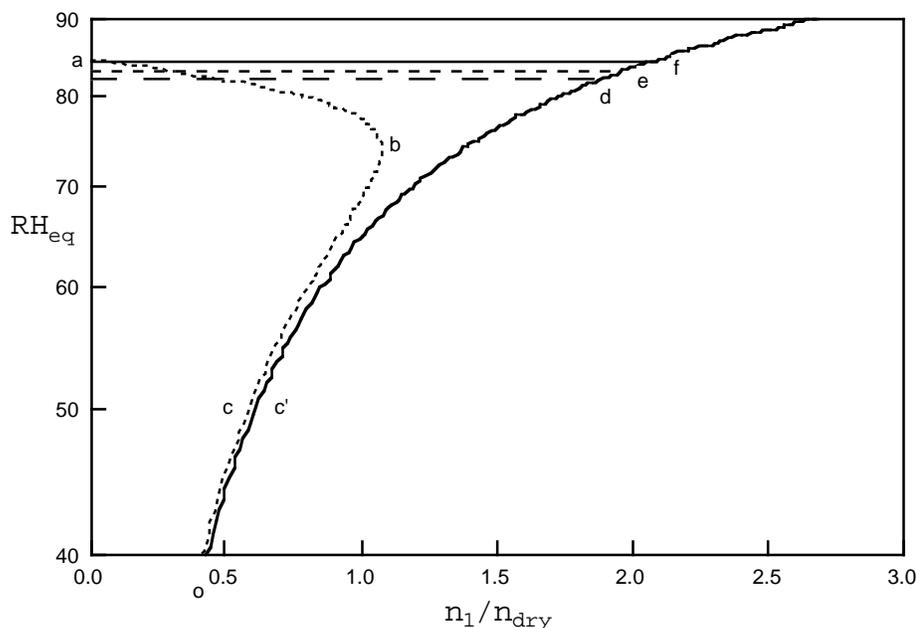


Figure 1. Phase diagram for particle-droplet transformation in the NaCl-H₂O system. Dry particle diameter is 7.2 nm. Dotted curve, equilibrium states of the mixed-phase particle beginning with thinly coated salt (a) and following increasing dissolution of the salt core through states (b), (c), and finally (o) (complete dissolution). Solid curve, equilibrium states of the fully dissolved solution droplet.

Free-energy differences from Eq. 1 are readily interpreted in terms of areas using Fig. 1. The (large negative) change in free energy upon deliquescence at the *DRH* (transition a→f) is proportional to the total crescent-shaped area bounded by curves a-b-c-o, o-c'-d-e-f, and line a-f, with proportionality constant $-n_{dry}$. Below the *DRH*, e.g. at the relative humidities indicated by the dashed horizontal lines, there is a nucleation barrier to the process located at the point of crossing with the mixed-phase branch. The barrier height is, to within this same proportion, equal to the area between these curves up to the crossing point. Uncertainty in measurement of *RH* (1-2%) will prevent observation of nucleation deliquescence for particles in this (7.2 nm diameter) size range. Nucleation requires that the barrier be small (of order $10kT$), which for dry particles this size requires relative humidities well within 1% of the *DRH*. Finally, there is a small positive change in free energy associated with the efflorescence transition (c'→c) proportional to the small cusp area c'-o-c (also order $10kT$) This is the barrier height that must be overcome to form the critical salt nucleus (state c) from the metastable solution drop (state c').

UNIFYING PERSPECTIVES

We have seen for particles small enough that deliquescence can occur as a nucleation process, with transition below the *DRH* to metastable states such as d and e along the fully-dissolved branch of Fig. 1. This nucleation will be very difficult to observe at current lower limits of dry particle diameter for which measurements have

been reported (in the 5-10nm range [8]) due to uncertainty in measurement of RH . Nevertheless, even within the size range of current measurements the theory predicts strong similarities between deliquescence and efflorescence that are not evident in the bulk, including the common area constructions for the free energy changes associated with these processes described above. This unification opens the door for powerful methods, developed historically within the context of nucleation theory, to be brought to bear for analysis of deliquescence and efflorescence. Methods covered in this talk (see also [12]) will include: (1) extension of nucleation theorems to relate change in deliquescence (efflorescence) barrier heights to changes in RH and number of water molecules (positive or negative) in the particle/drop; (2) demonstration that binary free energy surfaces for deliquescence/efflorescence processes are linear in $\ln RH$ and connected with each other through Legendre transformation; and (3) applications of capillarity, self-consistent nucleation theory [14], and the Gibbs dividing surface.

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