A Study of Heterogeneous Nucleation in Aqueous Solutions

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Single, microscopic, aqueous solution droplets of NaCl, CaCl2, KF, and NaN03 are levitated in a quadrupole trap filled with water vapor at room temperature. The solutions become supersaturated as the pressure of the vapor is slowly reduced until solidification occurs. Both homogeneous droplets and those consisting of a solution jacket surrounding a solid core of a similar salt, KCl for the first three, Na2SO4 for the last, are studied. Except for KF, the solid catalyzes the nucleation, reducing the maximum supersaturation to 48, 78, and 64% of its value in the absence of the solid for the other three, respectively. Classical nucleation theory yields the critical size of the nucleus, its surface energy density, and, assuming it is a spherical cap on the surface of the solid core, the wetting angle.

I. Introduction

Solids in contact with metastable liquids may catalyze the liquid to solid transition.1 It is generally believed that the transition is opposed by the free energy increase which accompanies the formation of the surface of the embryo solid within the liquid.2 Contact between that surface and a catalyst reduces the energy and the limit of metastability.

To obtain valid results when studying the transitions, it is necessary that the liquid be pure and the surface clean. Cleaving a solid may produce a surface8 In this paper we report the results of experiments in which the metastable liquid is a supersaturated solution and the clean surface is produced by precipitation of a solute. A second solute remains completely dissolved in a solution which is slowly made more supersaturated until nucleation occurs.

The sample is a microscopic droplet, charged and then levitated in a quadrupole trap at room temperature. The droplet is in thermodynamic equilibrium with water vapor which fills the trap and whose pressure is varied to control metastability.4

In section II we describe the technique, and in section III we present the classical nucleation theory of Volmer5 and of Turnbull and Vonnegut.6 In section IV we present our results, and in section V we conclude the paper.

II. The Experiment

The solutions to be studied are prepared by mixing measured volumes of saturated solutions of two salts and then diluting the mixture about 50-fold. Reagent grade salts without further purification and HPLC grade water are used. Charged droplets of the mixed solution, roughly 10 μm in diameter, are injected into a quadrupole trap, whose design and operation have been described previously.7 A single particle is trapped. The system housing the trap is evacuated, drying the particle which becomes a solid. The system is then sealed and held at 25 ± 0.05 °C. Water vapor is admitted by opening a valve to a nearby pool of water. The temperature of the pool is slowly cycled, first dissolving one salt and then the second, then precipitating the second, and finally nucleating the solidification of the first.

Though the particle is microscopic with a high surface-to-volume ratio and thus is quick to respond to changing pressure of the water vapor, the system has a surface area about 12 orders of magnitude greater and thus is slow to respond. To maintain equilibrium, the cycle time is typically 1 h or more. To reduce the labor of data collection, the experiment is partially automated.8 A feedback loop using a CCD camera to view the particle is used to continuously match its changing weight with a vertical electric force. The value of the potential needed to produce this force and the temperature of the water source comprise the data.

The levitation technique is an example of "containerless processing" which is advantageous for nucleation studies. Since the sample is microscopic, undissolved impurities are eliminated from most particles. They are untouched except by vapor and thus physically unperturbed, and chemically uncontaminated above the levels achieved by high-vacuum practice.

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III. Heterogeneous Nucleation Theory

Since our experiment is macroscopic and thermodynamic, we will discuss only classical nucleation theory here, which is similarly limited. In this theory bulk matter properties such as density, surface tension, and free energy of condensation are assumed for the embryo solid, which, as we shall see, contains fewer than 200 molecules.

Volmer5 considered a model in which the embryo sits on a flat surface of a solid, the potential catalyst. The top surface of the embryo, in contact with the solution, is spherical, with radius r. See Figure 1. We denote the catalyst, solid, and liquid as C, S, and L. The contact angle θ which minimizes free energy is given by

\[
\cos \theta = \frac{\sigma_{CL} - \sigma_{CS}}{2 \sigma_{SL}} = m
\]

where the \( \sigma \)'s are the interface energy densities. The change in free energy with the production of the embryo

Figure 1. Spherical cap model of the nucleus: C = catalyst, S = solid, L = liquid.
A Study of the Nucleation of the Solution-to-Solid Phase Transition Using Levitated Microscopic Particles

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The solution-to-solid phase transition is studied for eight systems at \( T = 25^\circ\text{C} \), including sodium bromide and potassium chloride solutes with pure and mixed water solvents and methyl alcohol. The samples are microdroplets levitated in a quadrupole trap which is filled with solvent vapor from a cooled liquid source. Within experimental error the supersaturation of the solutions at the transition is the same for all systems: \( s = 3.6 \pm 0.2 \). With a nucleation rate estimated to be \( 10^3 \text{cm}^{-3} \text{s}^{-1} \) classical nucleation theory yields 83 for the number of molecules in the critical nucleus for both salts, and surface energy densities of 51 and 46 erg cm\(^{-2} \) for NaBr and KCl, respectively, independent of solution.

I. Introduction

The nucleation phenomenon by which matter changes phase occurs on a scale of length and time which places it beyond the realm of direct measurement. Clusters of ten to hundreds of molecules existing for \( 10^{-12} - 10^{-8} \) s comprise the new phase in coexistence with the old. Experiments detect the new phase following a growth stage of duration \( 10^{-3} \) s or more in which its volume increases 10 orders of magnitude or more.

These experiments use a variety of techniques to study the vapor-liquid, liquid-solid, and solid-solid transitions. From them and various nucleation theories a general understanding of the phenomenon has emerged. At present though there have been relatively few studies of the nucleation of solid phases, and for those from solutions Adamson suggests "Supersaturation phenomena in solutions, are, of course, very important, but, unfortunately, data in this field tend to be not too reliable". In this paper we report the results of measurements of the solution-to-solid phase transition for the salts KCl and NaBr. In these the samples are single, micrometer-sized particles levitated electro-dynamically. This technique has advantages and disadvantages when compared to the classic cloud chamber technique or the matrix isolation using emulsions. These techniques produce ensembles of non-interacting or essentially closed systems and thus yield ensemble averages for comparison with theory. The single particle, though it may be cycled many times, yields far less information in practical times. The supersaturation obtained in the expansion cloud chamber is transient, complicating the analysis somewhat. That achieved in the diffusion cloud chamber has a gradient, and knowledge of heat and mass transfer is required. Here the microscopic solution droplet is in thermodynamic equilibrium with the solvent vapor as the droplet passes slowly through metastable states of increasing supersaturation. In the emulsions the solutions are in contact with an inert matrix, for example, silicone oil, while here the solution is surrounded by its vapor with the partial pressure of other vapors, principally argon, reduced 6 orders of magnitude or more. The particles are small and thus less likely to contain impurities which can catalyze nucleation. The small particles require a high nucleation rate for practical induction times, and thus the measurements cannot be made over a range of supersaturations.

In section II we present a brief review of nucleation theory, and in section III we describe the levitation technique. In section IV we present our results, and in section V we discuss and compare them with those from related studies, and conclude the paper.

II. Nucleation Theory

What is commonly called classical nucleation theory, which we will call the standard model, yields a nucleation rate

\[
J/(\text{cm}^{-3} \text{s}^{-1}) = J_0 \exp(-\Delta G^*/kT)
\]

(1)

where \( \Delta G^* \) is the maximum free energy barrier to transition to the more stable phase. The system makes the transition by fluctuations in composition. In the standard model the stable phase consists of spherical clusters of uniform density equal to the bulk density, and

\[
\Delta G = \Delta G(\text{surface}) + \Delta G(\text{volume})
\]

\[
= 4\pi r^2 \sigma - (4\pi/3) \rho kT \ln s
\]

(2)

Here \( r \) is the cluster radius, \( \sigma \) the surface free energy density, \( \rho \) the number density of the cluster, and \( s \) the measure of the departure of the system from equilibrium coexistence, the supersaturation. If the cluster grows by fluctuation until

\[
r = r^* = 2\sigma/\rho kT \ln s^*
\]

(3)

then the barrier reaches a maximum

\[
\Delta G^* = \Delta G(\text{surface})/2 = \Delta G^*(\text{volume})/2
\]

\[
= (16\pi/3) \rho^3 (kT \ln s^*)^2
\]

\[
= (4\pi kT \ln s^*)/2
\]

(4)

where \( s^* \) is the number of molecules in the cluster, the critical nucleus.

The "kinetic prefactor" for the vapor-to-liquid transition is

\[
J_0 = q(2\pi m^3/n^2)\rho
\]

(5)

where \( m \) is the mass of the molecule, \( n \) is the number density in the vapor phase, and \( q \) is the sticking coefficient.

A stabilizer for single microscopic particles in a quadrupole trap

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Light scattered from a single particle suspended in a quadrupole trap is focused on the detector array in a charged coupled diode (CCD) camera. The video signals obtained from two successive rows of sensors framing the center of the image are compared and the difference used to control a superposed vertical field, holding the particle at trap center. The system is effective for liquid and solid particles in the size range from 1 to 10 μm trapped in vacuum or vapor.

The quadrupole trap, introduced by Straube in 1956, is widely used in condensed matter studies on microscopic samples. Because of the relatively small specific charge of the particle, its motion is significantly affected by gravity. In order to maintain particle position at, or orbiting about, trap center it is necessary to superpose a static, vertical, dipole field. Since particle specific charge commonly changes over the course of a study, it is necessary to vary the field and desirable to do this continuously by some servomechanism.

Two systems for achieving balance have been described. In the first particle image is formed and split, with the two parts illuminating two detectors. Their outputs are compared to produce an error signal to control the vertical field. In the second the particle, a liquid droplet of radius greater than 70 μm, is back lit and the shadow image falls on a vidicon tube. From the video signal the top edge of the image is located to control the vertical field and the left and right edges to determine particle size. Relative and absolute masses are measured with uncertainties of 0.1 and 5%, respectively.

We have constructed a system using a charge coupled diode (CCD) video camera to stabilize liquid droplets of radius down to 1 μm and solid particles of comparable volume. The system works well for particles whose motion is damped by a surrounding gas and for those trapped in vacuum.

The scheme is as follows. A particle is trapped and illuminated by an unfocused beam from a helium-neon laser. Light scattered roughly 90° is received by a zoom lens system and focused on the CCD array in the camera. Observing the image on the monitor, the operator manually adjusts the dipole field to balance gravity and center the particle. The camera is moved vertically to center the image between two rows of sensors chosen to define the null point. The video signal from these two rows is gated into a control circuit. This gated signal consists of two pulses of width about 0.5 μs, height up to 1 V, and separation 64.5 μs, received 60 times per s. The two are sent to two peak detectors whose outputs pass to a comparator. The comparator controls the count direction of a 10-bit, up-down counter which is incremented or decremented with the video synch pulse. The counter state is read by a digital-to-analog converter whose output is summed with the manually controlled dipole field potential, completing the feedback loop.
Another Reading of 'In breeding'

Jeffrey H. Bar"s letter on "inbreeding." January 1989, page 18, appears to be a fine example of "inbreeding" whatever he means by the term. He suggests that two possible interpretations of the high percentage of faculty that the "elite" physics departments draw from among themselves — whether these are the best PhD programs or that these departments are simply trying to maintain their desirable rankings — the data support the latter. It's clear that these raw data are consistent with either possibilities and therefore support neither above the other.

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Bar"s comments: The data suggest that a rather small group of programs in this case tend to maintain and enhance their reputations by hiring one another's graduates. Although highly ranked PhD programs might find that many of the best candidates for positions come from their own and other PhD programs, such advocacy would not account for the marked degree of "inbreeding" that these data demonstrate. It's difficult to believe that of the faculty members in these 12 programs, graduated from one of these nine 12 programs. Surely, the notable programs produce a sufficient number of graduates who are as well qualified as those from the elite programs that the notable-program graduates could be more strongly represented on the elite faculties.

Reference

EVAPORATION OF AMMONIUM NITRATE PARTICLES CONTAINING AMMONIUM SULFATE

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(First received 28 December 1987 and in final form 21 April 1988)

Abstract—Single solid particles with initial composition about 80% NH₄NO₃ by number, 20% (NH₄)₂SO₄, are levitated in an electric quadrupole trap at T = 25°C. Particle mass is measured continuously over periods of up to 8 h as NH₄ and HNO₃ evaporate and are removed. For particles in vacuum the HNO₃ effective pressure p(Torr) = a(1 - x), where a is the sticking coefficient, is measured to be log (p/Torr) = -7.46 ± 0.06, where x is the NH₄NO₃ mole fraction and a = 2.00 ± 0.06 with an estimated uncertainty in a of 5% of this value. At x = 1, in good agreement with that calculated from thermodynamics, p = 9.46 x 10⁻⁶ Torr. For particles in water vapor, at humidities below the lowest deliquescence point at 62%, the evaporation rate increases. No mass increase is detected when the water vapor is introduced. For r.h. > 40% (the evaporation rate is independent of NH₄NO₃ mole fraction until that falls below about 0.2. The results suggest that NH₄ and NO₃⁻ losses are solvated in an absorbed water layer with the solvation controlling evaporation. In a warm atmosphere without NH₄ and HNO₃ solvated mixed NO₃⁻-SO₄²⁻ particles would lose most of their NO₃⁻ in 1-h, according to our results.

Key word index: Nitric acid, solid solution, water coating effect.

INTRODUCTION

Major components of the fine fraction of atmospheric aerosols are SO₄²⁻, NO₃⁻ and NH₄⁺ ions. In urban areas the fraction ranges up to 60% of the total suspended particulate matter. Together aerosol NH₄⁺ and NO₃⁻ are volatile, yielding gaseous NH₃ and HNO₃. The lifetime of aerosol NO₃⁻ is estimated to be a few days (Seinfeld, 1986). With known free energies and mixing rules, thermodynamics yields values of equilibrium partial pressures of H₂O, NH₃ and HNO₃ in the presence of aqueous NH₄NO₃ solution droplets, with and without SO₄²⁻ (Stelson et al., 1984; Tang, 1980). Solid dynamics is not known. In the atmosphere equilibrium does not occur and the dynamics of exchange between vapor and aerosol depends not only on energetics but also on the physics of transport in both phases (Schwartz and Freiberg, 1981) and on the accommodation or sticking coefficient. Laboratory studies of these systems are needed.

Few such studies have been reported. Appel et al. (1980) detected aerosol NH₄NO₃ volatility by trapping particles in Teflon filters and passing clean air over them. They found that about half the NO₃⁻ was lost by evaporation. Larson and Taylor (1983) measured the size change of NH₄NO₃ solution droplets in a flowing moist air column from which NH₃ and HNO₃ were stripped. They analyzed their results using gas phase transport theory and solution thermodynamics and concluded that sticking coefficient was unity. Richardson and Hightower (1987) measured the rate of evaporation of a single solid (crystalline) NH₄NO₃ particles levitated in vacuum. A small sticking coefficient was required to explain their results. Tang et al. (1981) have reported deliquescence of a mixed NO₃⁻-SO₄²⁻ particle but did not measure evaporation. We know of no study of mixed NO₃⁻-SO₄²⁻ particle evaporation.

We have levitated solid mixed particles in vacuum and in water vapor at pressures below the deliquescence point and have measured loss of mass by the gravity-balance method (Davis and Ray, 1980) as NH₃ and HNO₃ evaporate. Subsequent light scattering measurements and simple kinetic theory yield vapor pressures for the dry and water-coated particles for NH₄NO₃ mole fraction ranging from zero to about 0.8. Interesting surface and bulk effects are revealed. The dynamics of these particles in the atmosphere is discussed.

METHOD

The single-particle levitation scheme used here is the same as that used in the NH₄NO₃ study (Richardson and Hightower, 1987). The experimental procedure is as follows. Saturated solutions of NH₄NO₃ and (NH₄)₂SO₄ (ACS grade) are prepared. Equal volumes of each are mixed then diluted about 10-fold with distilled water. This sample is loaded into our particle gun and charged droplets are shot into the powered quadrupole trap. Dry air in the trap causes rapid evaporation of the water. All but one particle are dropped, the system is sealed and evacuated to a pressure below 10⁻² Torr in about 5 min. The particle, illuminated by laser light, is centered by manual adjustment of the gravity-balancing electric field. As
On the stability limit of charged droplets

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Single, highly charged droplets of dioctylphthalate and sulphuric acid of radius between 1 and 10 µm are suspended in vacuum in a quadrupole trap. As the droplets evaporate their radius is monitored continuously by light scattering and their charge is determined periodically by weighing balancing. The droplets break when the electric stress exceeds that of surface tension. The largest fragment remains trapped allowing a determination of the change in volume and charge. The fraction of volume and charge lost is found to be independent of particle size and sign of charge and is variable. The oil drops lose (15.0 ± 3.9) % of their charge on breakup and (2.25 ± 0.06) % of their mass. The acid droplets lose (49.4 ± 8.3) % of their charge and less than 0.1 % of their mass. The acid results are compared with those from a model of field emission based upon prolate spheroid deformation and the formation of Taylor cones. For both oil and acid droplets the stability limits are in agreement with those predicted by Lord Rayleigh.

INTRODUCTION

The stability of a charged conducting drop was considered by Lord Rayleigh (1882). He analysed the cylindrically symmetric normal modes of oscillation of the drop. With charge less than a critical value, dependent on droplet size and surface tension, the spherical shape is very stable. With charge at the critical value, the Rayleigh limit, small quadrupole distortions are unsupported. Well above this limit, octupole and higher distortions are unsupported. For the latter case Rayleigh concluded, without relation to his analysis, that "the liquid is thrown out in fine jets."

Taylor (1964) reconsidered the system by examining the stresses at the drop surface, which he analysed for large quadrupole deformation. With Lord Rayleigh's comment about jets and evidence provided by Zeleny (1917) in a related experiment on the formation of a jet at the tip of a glycerine column in a charged capillary, Taylor went beyond the spheroidal approximation to consider a local deformation which might lead to a jet. This is in the form of a cone of semivertex angle 49°29', the Taylor cone, which produces enhanced stress.

Brezier-Smith et al. (1971) simulated a drop at the Rayleigh limit, treating the liquid as inviscid and incompressible. Initially in their simulation the droplet is spherical but becoming a prolate spheroid. This shape is largely maintained until the axial ratio reaches ca. 2.5, when Taylor cones suddenly form at the ends.

Several experimental studies of the Rayleigh limit have been reported.

[319]
Measurements of scattering of light from layered microspheres

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Experimental elastic-scattering characteristics of layered microspheres are reported. Single particles consisting of glass cores coated with glycerine are suspended in an evacuated quadrupole trap, and scattered light intensity is measured at a fixed angle as the glycerine evaporates. The results are compared with those calculated for concentric spheres using the Mie theory. Excellent agreement is obtained for glycerine layers of thickness less than 700 nm. For thicker layers, differences occur that are attributed to the effect of gravity on particle structure.

Aden and Kerker1 solved the problem of scattering from a layered sphere, using the Mie–Debye theory. This system, which includes coated particles, immiscible liquid droplets, and vesicles, presents an interesting departure from the much-studied homogeneous sphere. Although the solution was given in 1951, to our knowledge no precision experiment to verify it has been reported. In this Letter we present the results of such an experiment.

In this experiment light was scattered from single glycerine-coated glass microspheres levitated in a quadrupole trap.2 Because of the glycerine volatility the coating thickness decreases from as much as 2.5 μm to zero over the period of a measurement, yielding a rich variation in scattered intensity for comparison with theory. Also, because the size of the glass microsphere varies from particle to particle, each gives a unique spectrum.

Hightower and Richardson3 recently illustrated the response of a layered sphere to an incident plane wave with computations of scattered light intensity and energy density within and near the particle. They used the program of Wiscombe4 to evaluate the solution of Aden and Kerker for the special case of resonant response. Here their results are extended to the general case of the present experiment. Excellent agreement between theory and experiment is obtained when the glass sphere volume is less than ~20% or more than ~60% of the particle volume.

The glass microspheres were obtained from Duke Scientific. They have a mean radius of 4.0 μm, with a standard deviation of 0.9 μm. The glass has a density of 2.4–2.5 g/cm³ and an index of refraction of 1.51. Pure glycerine has a density of 1.260 g/cm³ at room temperature and an index of refraction of 1.473. The glass spheres are supplied dry and are suspended without cleaning in a glycerine–alcohol solution. Particles of this suspension are shot into the trap and charged by friction. The chamber is slowly evacuated to a pressure of a few hundred pascals so that glycerine evaporation is not diffusion limited.

Polarized light from a He–Ne laser is incident upon the trapped particle. Scattered light is detected by a photomultiplier tube behind an aperture subtending 0.001 sr, fixed at 90.5° from the exit beam. The photomultiplier tube output is recorded continuously until glycerine evaporation is complete.

Fig. 1. Record of intensity of light scattered 90.5° from a glycerine-coated glass microsphere. Upper trace: early in the evaporation period (1 min/maj/div). Middle trace: midway in the evaporation period (30 sec/maj/div). Lower trace: late in the evaporation period (30 sec/maj/div). Letters identify features for comparison with Fig. 2.
Resonant Mie scattering from a layered sphere

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The theory of Aden and Kerker is used to compute the resonant response of large layered spheres to an incident linearly polarized plane wave. Cases considered include hollow spheres and those with transparent and absorbing cores whose diameters range from zero up to that of the particle. Both core and layer resonances are studied. The results are presented as partial wave amplitudes, energy densities, and scattered light intensities for a typical resonant mode, TE_{39}.

I. Introduction

The scattering of light from large spheres has been studied by many researchers. Several reviews of this work are contained in monographs.1-3 Of recent and special interest are resonances in the sphere–light interaction, discovered by Ashkin and Dziedzic in the radiation pressure on optically levitated particles4 and detected in a variety of high-resolution experiments stimulated by this work.5-7 Following this discovery the theory of the interaction has been carefully reexamined and found to be in excellent agreement with experiment.

An interesting variation of the homogeneous-sphere scattering is that of the layered sphere. This problem was solved by Aden and Kerker for two concentric spheres.9 Wait10 has generalized this solution to a sphere with continuous radial variation of composition, and Bhattacharya11 has considered a similar problem. Fenn and Oser12 and Kattawar and Hood13 applied the Aden-Kerker results to water-coated carbon particles. Toon and Ackerman14 have presented new algorithms for computing the scattering by reformulating the Aden-Kerker results to avoid numerical instabilities. Various perturbation approaches have also been published.15-17 Pluchino18 has computed the effect of resonance on the emissivity of an aluminum oxide sphere coated with a thin carbon layer.

None of these studies presents a comprehensive treatment of the resonance of a layered sphere, however. In this paper we consider the Aden-Kerker theory of scattering from concentric spheres at and near resonance for a variety of particles, including a hollow sphere and spheres with transparent and absorbing cores. We investigate both the core resonance and the shell resonance. We present graphically the solution to the transcendental resonance equation for a representative layered particle and illustrate our results with plots of partial wave amplitudes, energy densities, and scattered light intensities vs frequency of the incident wave. Possible applications of these results in aerosol science are discussed. In a companion paper, we compare equivalent results with those obtained experimentally.19

II. Theory

A wave polarized in the x direction and of amplitude $E_0$, wavenumber $k$, is incident in the z direction on a layered sphere with the center at the origin. The core of the sphere has radius $r_1$ and refractive index $m_1$. The shell has outer radius $r_2$ and index $m_2$. The sphere is surrounded by vacuum. We must determine the fields in the core, layer, and near zone to determine energy distribution at resonance, and in the far zone to determine scattering. Expressions for the former are given in the Appendix.

The components of the outgoing wave far from the particle are written in spherical coordinates as

$$E_r = (i/kr) E_0 \exp(i(kr - \omega t)) \cos \phi S_1(\theta), \quad (1a)$$

$$E_\phi = (i/kr) E_0 \exp(i(kr - \omega t)) \sin \phi S_2(\theta). \quad (1b)$$

The scattering functions $S_1(\theta)$ and $S_2(\theta)$ are expanded as

$$S_1(\theta) = \sum_{n=1}^{\infty} (2n + 1)/n(n+1)[a_n \pi_n(\theta) + b_n \tau_n(\theta)], \quad (2a)$$

$$S_2(\theta) = \sum_{n=1}^{\infty} (2n + 1)/n(n+1)[a_n \tau_n(\theta) + b_n \pi_n(\theta)], \quad (2b)$$

where $\pi_n(\theta)$ and $\tau_n(\theta)$ are simply related to the associated Legendre polynomials (see Ref. 1, p. 124). The partial wave coefficients are given by
EVAPORATION OF AMMONIUM NITRATE PARTICLES

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Abstract—Microscopic anhydrous ammonium nitrate particles are levitated in a vacuum in an electric quadrupole trap at 25°C. Size and mass changes of the evaporating particles are monitored continuously in situ using light scattering and gravity balancing. Both supersaturated liquid droplets at the zero-solvent limit and crystalline solids are studied. The measured vapor pressure of the liquid is $p = (3.18 \pm 0.45) \times 10^{-6}$ torr.

Fresh solid particles evaporate at a rate $\frac{dr}{dt} = -0.23 \ \text{Å s}^{-1}$ where $r$ is an equivalent radius. Beyond 4 h the rate is a constant $-0.06 \ \text{Å s}^{-1}$. These rates are consistent with that predicted from thermodynamics if the mass accommodation coefficient is $\alpha = 0.02$ initially and 0.004 after 4 h. Aerosol sampling by several groups indicates the presence of solid ammonium nitrate particles in the atmosphere. Long lifetime and long-range transport of these particles are predicted regardless of ammonia and nitric acid vapor concentrations.

Key word index: Ammonium nitrate, light scattering, sticking coefficient.

INTRODUCTION

Ammonium nitrate is a common atmospheric aerosol occurring in both solid and solution form. In contrast with ammonium sulfate, the nitrate is volatile at normal temperatures. For solution droplets a complex exchange of $\text{H}_2\text{O}$, NH$_3$ and HNO$_3$ between the vapor and condensed phases occurs. Thermodynamic analysis (Tang, 1980) predicts the occurrence of acid particles as a result. A recent review by Stelson et al. (1984) contains many references to related studies.

Larson and Taylor (1983) have measured the evaporation of ammonium nitrate solution droplets passing through a chamber in which NH$_3$ and HNO$_3$ are removed from the ambient vapor. They find good agreement between their results and thermodynamic and kinetic theory predictions.

Stelson et al. (1979) have discussed the dynamics when the particle is solid ammonium nitrate. They use thermodynamic data and the high-temperature measurements of dissociation pressure by Brandner et al. (1962) to conclude that much of the ammonium nitrate in a volume of air is in the vapor phase as dissociation product.

We have measured the rate of evaporation of anhydrous ammonium nitrate particles at 25°C using the technique of single-particle levitation in an evacuated quadrupole trap (Richardson et al., 1986). The particles occur in both solid and liquid phases, the latter unexpected. The results are compared with thermodynamics and used to discuss particle dynamics in the atmosphere.

METHOD

The levitation technique has been described elsewhere (Richardson and Kurtz, 1985). A properly shaped oscillatory electric field may yield forces which confine μm-size charged particles to very small volumes for unlimited times. Particle mass-to-charge ratio may be measured in situ with a precision of 0.1%.

If the particle is liquid and light is scattered from it, index of refraction, dependent on composition, may be measured to about 0.1% and radius to 10 ppm.

A schematic drawing of the apparatus is shown in Fig. 1. A quadrupole is housed in a massive temperature-controlled vacuum chamber. The chamber is connected to a 1700 s$^{-1}$ turbomolecular pump through high-conductance and precision leak valves in parallel. It is vented through particulate filters and Drierite, zeolite and liquid-nitrogen-cooled traps in series. An air pump capable of flushing 250 ml s$^{-1}$ of filtered air through the chamber is attached. This provides a barrier to room air when the top port is open.

![Schematic diagram of the apparatus](image-url)
Growth Rate Measurements for Single Suspended Droplets Using the Optical Resonance Method

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An experimental technique described with which the growth rate of a single solution droplet by water vapor condensation can be repeatedly measured with high precision. The technique involves the use of an electrodynamic cell to suspend a NaCl solution droplet in water vapor and a CO₂ laser to momentarily perturb the droplet-vapor equilibrium. The droplet size change during condensational growth is monitored with a tunable dye laser for a particular optical resonance due to Mie scattering. A consideration of the coupled heat and mass transfer processes during droplet growth indicates that the best agreement between theory and the experimental results is obtained with a condensation coefficient close to unity.

INTRODUCTION

The application of single particle levitation techniques has made it possible to study many interesting and important processes associated with aerosols. A recent review by Davis (1983) on transport phenomena with single aerosol particles serves as an excellent reference to both experimental techniques and aerosol transport theories. More recently, Tang and Munkelwitz (1984) have studied crystal nucleation from aqueous electrolyte solutions by determining the critical supersaturation at which a suspended solution droplet transforms into a salt crystal. Richardson and Spann (1984) have measured the water cycle in ammonium sulfate. Kurtz and Richardson (1984) have detected solid-solid, solid-liquid, and liquid-liquid phase transitions in the lithium iodide-water system. Richardson and Kurtz (1984) have described a novel isopiestic measurement of water activity in lithium halide solutions.

Spann and Richardson (1985) have studied ammonium acid sulfate systems.

We report here an experimental technique with which the growth rate of a salt solution droplet by water vapor condensation can be repeatedly measured with high precision. The technique utilizes a tunable dye laser to generate a set of time-resolved optical resonances for solution droplet undergoing condensational growth. Since for a given resonance the ratio of the particle radius, r, to the resonant wavelength, λ, remains constant, the experimental particle size resolution, Δr/r, is determined by the dye-laser linewidth, Δλ/λ (Ashkin and Dziedzic, 1977). Consequently, a size resolution of 1 part in ~6000 is easily achievable with a commercial dye laser having a bandwidth of 1 Å in the visible region. Such size resolutions allow detection of "monolayer deposition" on a micrometer-size particle.

In the present study, the technique is illustrated with an NaCl solution droplet initially in equilibrium with water vapor at ambient temperature. The equilibrium is slightly perturbed by momentarily irradiat-
Optical measurement of the evaporation of sulfuric acid droplets

C. B. Richardson, R. L. Hightower, and A. L. Pigg

Single micron-size sulfuric acid droplets are levitated in vacuum in a quadrupole trap through which passes the beam from a He-Ne laser. Scattered light is monitored by a fixed detector as cavity resonances are excited in the evaporating droplet. Mie-Debye theory is used to determine particle size, which, with kinetic theory, yields vapor pressure. Over the temperature range studied, -10 to +30°C, the vapor pressure of pure sulfuric acid is

\[ \ln p (\text{Torr}) = (20.70 \pm 1.74) - (9360 \pm 499)/T (K) \]

I. Introduction

The scattering of light from microscopic spheres can yield their size when the results are analyzed using Mie-Debye theory.\(^1\)\(^-\)\(^8\) High precision is possible if the light excites cavity resonances in the spheres. These resonances were discovered by Ashkin and Dziedzic in optical levitation.\(^4\) They have been detected in fluorescence\(^6\) and elastic\(^6\) and Raman scattering.\(^7\)

Ashkin and Dziedzic\(^5\) have discussed the utility of resonant light scattering for the measurement of particle evaporation. A fixed frequency source may be used to determine the radius with a precision of 10 ppm as a micron size evaporating droplet passes through resonances.

We have levitated single, charged droplets of sulfuric acid in vacuum in a quadrupole trap\(^3\) and measured their rate of evaporation by monitoring the intensity of light scattered 90°. The vapor pressure of the pure liquid is thus determined for temperatures between -10 and +30°C.

Sulfuric acid is a significant part of the particulate matter in the earth's atmosphere. The rate of formation of liquid droplets by vapor phase condensation and the lifetime of the droplets are dependent on the liquid vapor pressure. Although the literature on sulfuric acid thermodynamics is extensive, vapor pressure measurements are few and in general are made on aqueous solutions for which acid pressures are low.\(^5\) Gmitro and Vermeulen\(^10\) have calculated the partial pressures of H\(_2\)O, SO\(_3\), and H\(_2\)SO\(_4\) above the solutions for compositions between 10 and 100% acid and for temperatures between -50 and 400°C using the thermodynamic data of Giaque et al.\(^11\) Verhoff and Banko\(^8\) noted the sensitivity of the results to changes in input values. For example, a 0.3% change in the heat of formation of the acid leads to an 81% change in vapor pressure.

Two recent measurements have been made on concentrated solutions. Roedel\(^12\) monitored the transfer of radioactive \(^35\)S atoms between acid pools at 95-97% concentration and room temperature. His best value for "pure (99%)" acid at 23°C is

\[ p (\text{Torr}) = (2.5 - 0.8^{+1.3}) \times 10^{-5}, \text{~10 times less than that calculated by Gmitro and Vermeulen.} \]

Ayers et al.\(^13\) transferred the vapor over a pool of 98% acid to an alkali detector. Between \(T = 338\) and 445 K they find

\[ \ln p (\text{atm}) = 16.259 - 10,156/T (K) \]

for 99% acid, giving by extrapolation

\[ p (\text{Torr}) = 0.99 \times 10^{-5} \text{ at } 23^\circ C, \text{ in fair agreement with the Roedel value.} \]

The results reported here are the first for supercooled acid and the first over a wide range of temperatures around normal.

II. Experiment

A. Apparatus

A schematic drawing of the experimental arrangement is shown in Fig. 1. The major parts of the apparatus are a quadrupole trap of Wuerker design\(^8\),\(^14\) for particle levitation, a massive temperature-controlled vacuum chamber housing the trap, a turbomolecular pump for production of high vacuum, a 5-mW He-Ne laser light source, and a photomultiplier detector. The design and operating parameters of the trap have been presented elsewhere.\(^15\)
A charged micron-size particle of lithium iodide is suspended in a specimen. The study of liquids in microgravity conditions appears as a very promising field among the number of applications in space technology. The expensive and difficult in situ experiments are performed in space. One of the reasons to develop systems for ground support is the search for inexpensive, small scale facilities. The use of neutral buoyancy technique offers to Scientists a cheap, short time preparation of samples for experimentation with interference in simulated microgravity. Concerning anisometric interfaces, this technique has been used for a long time for static processes and recently small scale experiments have been considered in connection with the dynamics of liquid bridges. In this paper the main effects on the dynamics of a liquid bridge due to the presence of an opposite fluid flow are considered. In addition, the influence of experimental boundary conditions is discussed.

MEASUREMENT OF PHYSICAL PROPERTIES OF MATERIALS USING ACOUSTIC ELEVATION: E. F. Travis, Jet Propulsion Laboratory, Pasadena, CA. Microgravity conditions allow the processing of melts in a containerless manner through acoustic (or other) positioning and manipulation techniques. The interaction of the acoustic radiation pressure with the liquid and solid samples also allows the measurement of certain properties of the materials under microgravity conditions. Surface tension, viscosity, index of refraction, and compressibility can be measured using samples up to cm in size. One significant application lies in the determination of the properties of supercooled liquids. Work supported by NASA

THE EFFECTS OF GRAVITY LEVEL DURING DIRECTIONAL SOLIDIFICATION OF ALUMINUM ALLOYS: K. N. Armitage, W. M. H. Johnstone, and M. S. Collins, University of Alabama at Birmingham, Birmingham, AL 35294. Variations in critical morphology and volume fraction are often observed in microgravity melts. These phenomena are thought to have a significant influence on the service life of components. Recent research has indicated that directional solidification under microgravity conditions can affect the shape and volume fraction of the critical phase in these alloys. This work was done in the reduction of gravity induced flows such as convection. In this study, a magnetic field was utilized to develop flow during growth based on the melt direction solidification experiments. A comparison has been made between the critical phase morphology of the alloys grown with and without magnetic fields. The alloys were directionally solidified under a magnetic field and under microgravity conditions.

MEASUREMENT OF ACCELERATION THROUGH THE MARKSHALL SPACE FLIGHT CENTER MATERIALS AND PROCESS CENTER LABORATORY

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MEASUREMENT OF THE WATER CYCLE IN MIXED AMMONIUM ACID SULFATE PARTICLES

J. F. SPANN* and C. B. RICHARDSON

Physics Department, University of Arkansas, Fayetteville, AR 72701, U.S.A.

(First received 9 July 1984 and in final form 10 October 1984)

Abstract—A single ammonium-hydrogen-sulfate particle is levitated in an evacuated quadrupole trap at room temperature and the temperature of an attached tube containing bulk water is slowly cycled introducing then removing water vapor. With increasing pressure the particle dissolves in stages, then grows as a solution droplet by water absorption. With decreasing pressure the droplet supersaturates, crystallizes, then dehydrates completely to return to its initial state. Particle mass, and thus composition, is measured continuously with an electrostatic balance. Twenty-six cycles were studied as solution composition ranged from ammonium bisulfate through letoviceite to ammonium sulfate in roughly equal steps. Composition was changed in situ by reaction with ammonia at low partial pressure. With solution composition characterized by \[ x = \frac{\text{[NH}_4\text{]}}{\text{[SO}_4\text{]}} \text{,} \] deliquescence was found to occur at water activity \[ a_w = 0.394 - 0.029(1 - x) \] for \( 1 \leq x \leq 1.5 \) and \[ a_w = 0.710 - 0.023(1 - x) \] for \( 1.5 \leq x < 2 \). Particle growth occurs at deliquescence and subsequently is in excellent agreement with that predicted in a model proposed by Tang for dissolution of a two-component mixed solute. Water activities of the solution droplets are measured up to \( a_w = 0.9 \). The results are compared with those predicted by the Zdanovskii-Stokes-Robinson method of interpolation from binary data and with those obtained using the mixing rule of Meissner and Kusik. Particle crystallization from supersaturated solution is analyzed thermodynamically using measured water activities, the Gibbs-Duhem equation, and classical nucleation theory. The specific free energy barrier to crystallization, \( \Delta G/m \), is found to increase from near zero to 0.04 eV as composition ranges from \( x = 1 \) to 2, where \( n \) is the number of formula units in the critical nucleus. New phase diagrams are presented and used to discuss the dynamics of mixed sulfate particles in the atmosphere.

Key word index: Acid sulfate particles.

INTRODUCTION

Sub-\( \mu \)m atmospheric particles are composed primarily of sulfate and ammonium ions. Christian Junge (1953) using chemical spot testing of particles collected by a fractionating impactor concluded, "The measurement at Round Hill (Mass.) thus confirmed once more that the natural aerosol particles below about 0.8 \( \mu \)m radius consist almost entirely of \( \text{SO}_4^{2-} \) and \( \text{NH}_4^+ \), a fact which is probably valid the world over". Brosset (1978) identified ammonium sulfate, letovicite and ammonium bisulfate in the water-soluble fraction of particles collected on the Swedish west coast. Ono (1978) analyzed fine particles collected on the summit of Mt. Fuji and with the detection of sulfuric acid and ammonium sulfate further confirmed Junge's conclusion. Weiss et al. (1982) have measured with 5-min time resolution the composition of submicron particles collected near the Shenandoah National Park (Virginia). On average, fifty-eight per cent of the mass was in the two ions with the molar ratio \( [\text{NH}_4]/[\text{SO}_4] \) ranging between 0.5 and 2.0 with some regularity.

Several theoretical and laboratory studies of the ammonium-hydrogen-sulfate-water system have been made. Wishaw and Stokes (1954) have measured the water activity of ammonium sulfate solution. Tang et al. (1978) have measured the deliquescence and growth in moist atmospheres of particles of the mixed salts \( \text{NH}_4_x\text{H}_2-x\text{SO}_4 \) with \( x = 1.00, 1.57, 1.69 \) and 2.00. These authors have constructed a room temperature phase diagram of the mixed sulfate-water system using the solubility data tabulated by Scidell and Linke (1963), sulfuric acid solution water activity (Robinson and Stokes, 1959) and thermodynamic reasoning. This diagram has proven very valuable in analyzing field measurements.

Ammonia concentrations in the atmosphere and gas-to-particle conversion rates determine the mixed sulfate particle compositions. Scott and Cattel (1979) have measured the ammonia vapor pressure over anhydrous ammonium sulfate. Their analysis of results predicts a rapid decrease in ammonia pressure with decrease in \( x \). Brosset (1983) has calculated NH\(_3\) pressure over the mixed salt solutions. Much higher values are found than those over the solids. Brosset (1978) has noted that to predict the dynamics of ammonium-hydrogen-sulfate-water particles in the atmosphere requires a more complete phase diagram than that now available, including relative humidities at which liquid-to-solid phase transitions occur.

We have measured the water cycle in 26 mixed ammonium-hydrogen-sulfate salts ranging in composition from pure ammonium bisulfate to pure ammonium sulfate. Single \( \mu \)m-size particles are levitated in vacuum. Water vapor is introduced from a chilled pool, following the example of Stokes (1947).

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161. MEASUREMENT OF THE DELIQUESCENCE, ACTIVITY, AND CRYSTAL NUCLEATION OF THE MIXED AMMONIUM SULFATE-AMMONIUM BISULFATE-WATER SYSTEM AT ROOM TEMPERATURE. J. F. Spann, C. B. Richardson, Physics Department, University of Arkansas, Fayetteville, Arkansas 72701

Large amounts of sulfate compounds in atmospheric aerosols are thought to result from SO₂ gas emissions of industries which burn coal as a source of energy. These aerosols often consist of concentrated solutions of (NH₄)₂SO₄-NH₄HSO₄. We have made thermodynamic measurements of the (NH₄)₂SO₄-NH₄HSO₄-H₂O system at room temperature using single electrodynamically suspended particles. A particle, initially NH₄HSO₄, is suspended in vacuum and then dissolved as the pressure of water vapor admitted increases through the deliquescence point. The particle is recrystallized and subsequently absorbs ammonia to become a mixed (NH₄)₂SO₄-NH₄HSO₄ crystal. The cycle is repeated until pure ammonium sulfate is obtained. A phase diagram showing constant water activity for the mixed solution, both dilute and supersaturated, will be presented along with a model of dissolution of the mixed crystals consistent with our measurements. Free energies of dissolution and crystal nucleation barriers are calculated from our measured activities.

THURSDAY MORNING - SECTION E - GENERAL - S. E. Friberg, Presiding

162. AGGREGATION OF HEXADECYLAMMONIUM-4,4,4-TRIFLUOROBUTYRATE IN BENZENE. Barbara J. Konieczko, Department of Chemistry, Purdue University, Lafayette, IN 47907

Solutions of hexadecylammonium-4,4,4-trifluorobutyrate in benzene were studied as a function of concentration at several temperatures by means of ¹H nuclear magnetic resonance spectroscopy. The association of the surfactant was described in terms of a multiple equilibrium model, as well as a single equilibrium model. The distribution of micellar size was obtained as a function of surfactant concentration. It was found that an increase in temperature was accompanied by an increase in the free energy change for aggregation and a decrease in the apparent aggregation number. The system was also studied with added amounts of water.

163. MICELLAR SOLUBILIZATION OF CHOLESTERYL ESTERS BY A NONIONIC SURFACANT. Hans Schott, School of Pharmacy, Temple University, Philadelphia, PA 19140 and F. A. A. Sayeed, Abbott Laboratories, North Chicago, IL 60064

Micellar solubilization of cholesteryl stearate, olate, linoleate, and linolenate by the nonionic surfactant nonoxynol 10 (Igepal CO-710 of GAF Corp.) was investigated as a function of temperature. Below the melting points of the esters, solubilization limits increased gradually with temperature. Successive transitions to smectic, cholesteric, and isotropic liquids resulted in sharp increases in solubilization limits and heats of solubilization. Only small differences in solubilization were observed at reduced temperatures of 4°C above the crystalline melting points (°K), where solubilization decreased by only 12% from cholesteryl linoleate to the olate. Therefore, the solubilization limits of the esters at any temperature depend mainly on their physical state at that temperature. At 37°C, stearate and olate are crystalline solids and were solubilized considerably less than linoleate and linolenate, which are smectic and cholesteric liquid crystals, respectively. This may explain the lesser tendency of polyunsaturated cholesteryl esters to form atherosclerotic plaque.

164. MICELLAR SOLUBILIZATION OF MIXTURES OF CHOLESTEROL WITH CHOLESTERYL ESTERS AND WITH LECITHIN. Hans Schott, School of Pharmacy, Temple University, Philadelphia, PA 19140 and F. A. A. Sayeed, Abbott Laboratories, North Chicago, IL 60064

The solid phase in equilibrium with cholesterol solubilized in aqueous micellar nonoxynol 10 (Igepal CO-710) solutions was the monohydrate (CHMo). Its limit of micellar solubilization increased linearly with temperature and nearly tripled between 27°C and 51°C. Binary mixtures of CHMo and cholesteryl stearate, olate, linoleate, or linolenate were solubilized by nonoxynol solutions. The micellar solubilization limit of CHMo was not reduced by the esters. The solubilization limits of the esters were reduced by CHMo to about 7% at 27°C and 37% at 44°C. Similar reductions resulted when the surfactant
MEASUREMENT OF THE WATER CYCLE IN A LEVITATED AMMONIUM SULFATE PARTICLE

C. B. RICHARDSON and J. F. SPANN

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(First received 15 December 1983; and in revised form 26 January 1984)

Abstract—Single micron-size ammonium sulfate particles are suspended electrodynamically in a vacuum. Water vapor is slowly admitted until deliquescence occurs, then slowly removed until the solution droplet crystallizes. Deliquescence is shown to occur through three-phase equilibrium states. During dehydration the vapor pressure of the supersaturated solution is measured. The results are compared with a recent theory of aqueous electrolytes extrapolated to the very high concentrations encountered and used with simple nucleation theory to estimate the magnitude of the free-energy barrier to crystallization.

INTRODUCTION

A charged particle in an inhomogeneous electric field which oscillates symmetrically in time seeks a point of zero field and may therefore be trapped with electric forces alone. A great variety of traps based on this principle (Paul and Raether, 1955) have been reported. Most use electrodes with cylindrical symmetry to produce a field with the null-point centered. The simplest of these was that of Straubel (1956) consisting only of a wire ring driven at high voltage. Charged microscopic particles are trapped in the center. Other noteworthy traps include the parallel flat discs of Straubel (1959), and the sphere-tube arrangement of Berg and Gaukler (1969). Interesting non-cylindrical traps are the cube of Wuerker er al. (1959) and the 'racetrack' of Church (1969).

An even greater variety of experiments have been carried out on trapped particles. Those in atomic physics (see, for example, Richardson et al., 1968) have been reviewed by Dehmelt (1969) and by Wineland et al. (1983). Those on microscopic particles include measurement of light scattering by Straubel (1973) and by Blau et al. (1970), of laser heating by Waniek and Jarmuz (1968), of chemical reactions by Straubel (1982), of vapor pressure and gas transport by Davis and Ray (1980) and of condensation growth by Rubel (1981).

We report here the measurement of the deliquescence and subsequent evaporation and recrystallization of single ammonium sulfate particles in electrodynamic suspension. A charged solution droplet is injected into a gas-filled trap which is then evacuated to a pressure of $10^{-6}$ Torr. Water vapor is slowly admitted to the trap until the (now solid) particle deliquesces, then slowly removed until it recrystallizes. Particle relative mass and vapor pressure are measured over the cycle which is repeated as required to insure reproducibility and determine precision. This is the first use of high vacuum in the measurement of trapped particle thermodynamics.

This work is part of a laboratory investigation of the dynamics of sulfate aerosols significant in the atmosphere. In a closely related study Orr et al. (1958) used an electrostatic mobility chamber to measure the size of submicron aerosols, including ammonium sulfate, as a function of relative humidity. Winkler and Junge (1972) used a delicate quartz fiber microbalance to measure the water absorption of natural and artificial aerosols with the results analyzed by Winkler (1973). Tang et al. (1977) used a flow reactor and light scattering to measure the growth of sodium chloride particles by water absorption. The method was also applied to ammonium bisulfate (Tang and Munkelwitz, 1977) and to mixed salts (Tang et al., 1978). Recently Tang and Munkelwitz (1984) have used electrodynamic suspension of single particles to measure crystal nucleation in sodium chloride and ammonium sulfate solutions.

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synthesized which are capable to and thus mimic biological activity found...

PHYSICAL PROPERTIES OF AEROCOLOIDAL TRANSPORTING PARTICLES...

ISTS AND APPLICATIONS IN TRANSPORT...ing Engineering, University of Maryland, College Park, MD, 20740.

MEASUREMENT OF PHASE CHANGES IN LiI-nH2O, C.C. Richardson, C.A. Kurtz, Physics Department, University of Arkansas, Fayetteville, Arkansas 72701

Solid-solid, solid-liquid, and liquid-solid phase changes are produced in a levitated microscopic lithium iodide particle at room temperature by varying the surrounding water vapor. Five crystalline phases with composition LiI-nH2O, n = 0, 1, 2, 3 are observed at room temperature. Water vapor pressures are measured at the transitions. The hysteresis detected is evidence of nucleation by thermodynamic fluctuations which will be discussed. Water in excess of that in the saturated solution is absorbed in the solid-liquid phase change, suggesting the formation of an intermediate compound. The liquid-solid phase change is from a supersaturated vapor having composition N = [H2O]/[LiI] = 0.81 ± 0.07 and water activity a2 = 8.8 x 10^-4. The results will be compared with theories of electrolytes at high concentration.

INVESTIGATION OF THE REACTION BETWEEN SINGLE AEROSOL ACID DROPLETS AND AMMONIA GAS...y, Chemical Research and Development Center, A.P.E., MD, 21003 and J.W. Centry, University of Maryland, College Park, MD, 20743.

An experimental technique has been developed for the continuous measurement of the reaction dynamics between single liquid droplets and reactive gases. The technique is based on the suspension of electrically charged droplets in an electrodynamic field where droplet masses are determined from weight balancing direct current voltages. From the droplet mass history the extent of reaction is determined as a function of time, particle size and ammonia gas concentration. It is found surface phase reaction, gas phase diffusion and internal particle diffusion sequentially control the particle reaction dynamics. The transport from gas phase diffusion to internal particle diffusion controlled reactions is initiated by particle crystallization. The time of crystallization decreases with increasing ammonia gas pressure and decreasing particle size. Surface saturations of ammonium phosphate are calculated from internal particle diffusion models for times corresponding to particle crystallization as a function of particle size and ammonia gas pressure.

APPLICATION OF AN ELECTRODYNAMIC BALANCE FOR MEASURING HETEROGENEOUS KINETICS...hose single particles at close to ambient temperatures has been modified for use in studying fast reactions at elevated temperatures. A particle typically 10-60 um in diameter is suspended in the quadrupole and heated by a focused CO2-laser to temperatures up to 6000 K. The transient heating rate depends upon the power input and the particle size but is under a millisecond for most practical purposes. The particle temperature is measured above 600 K by use of 3-color pyrometry using liquid-nitrogen-cooled detectors with effective wavelengths of 2 um, 4 um, and 4.8 um. A servo-system with a response time of 10 millisecond has been installed to permit continuous weight measurements. Examples of application of the electrodynamic balance for the measurement of vaporization refractory oxides and decomposition of limestone are provided.
from the most stable Pt₄ cluster by addition of a single Pt atom to the unmodified compact Pt₄ structure. This would imply the formation of an outgrowth which, except for the structure (8,2), cannot generate a structure with large spherical density. A significant reorganization is required to restore the compactness. In a similar way, the low-density surface of a crystal restructures relative to the crystal bulk. The number of MIDs is a good index number of the stability of the clusters of class A. Indeed, all its most stable clusters have the largest number of MIDs at the EHT level. This property is also true at the EHT-SO level except for the structures (11,1) and (12,1), which come after (11,2) and (12,2) while they have one MID less. These exceptions have been explained by the small geometrical constraints existing for bilayer clusters and by the sp populations.

When structures of class C are considered, the MID index number is only a helpful indication of the stability at the EHT level since some structures of class C have the largest cohesive energies without having the maximum number of MIDs. These structures have a large spherical density. Structures (8,24), (10,35), and (12,6) illustrate this point. As their SO contribution is weak, structures with the maximum number of MIDs ((8,21) from class C and (10,1) and (12,2) from class A) reappear as the most stable isomers at the EHT + SO level.

Since structures of class C are not suitable for an extension toward an infinite crystal and their cohesive energies are lower than for those of the fcc or hcp bulk, compounds of class A or B should prevail for the medium or large clusters. With such a growth, the mean number of MID per atom can converge to 6, the value for the bulk. For the small systems, the occurrence of some fragments of fcc or hcp type (Pt₁, Pt₄, Pt₆, Pt₆, Pt₁₉, Pt₁₉, Pt_{12}, and Pt₁₃) in the growth at the EHT + SO level is due more to their own compactness than to their classification as clusters of class A.

The EHT and EHT + SO methods are more selective than the simple Lennard-Jones interactions. For example, one Pt₁₃ structure clearly emerges as the most stable within the EHT + SO framework while 987 structures are quasi-degenerate within a Lennard-Jones analysis.

The present results will be used to study the hydrogenation process of the Pt₄ clusters.

Acknowledgment. This work has been supported by an ATP surface grant from the CNRS. We are pleased to thank Professor Fraissard for many discussions on the existence and the properties of small particles of platinum. We are grateful to Dr. Spanjaard for stimulating discussions on spin-orbit influence.

Registry No. Pt, 7440-06-4.

A Novel Isopiestic Measurement of Water Activity in Concentrated and Supersaturated Lithium Halide Solutions

C. B. Richardson* and C. A. Kurtz

Contribution from the Physics Department, University of Arkansas, Fayetteville, Arkansas 72701. Received May 2, 1984

Abstract: In a variation of the Stokes bithermal isopiestic method, single microscopic drops of lithium bromide and lithium iodide aqueous solutions at room temperature are levitated electrodynamically in a closed chamber from which air is removed and to which is connected a vial of pure water at lower temperature. Water temperature is varied between -74 and +21 °C to measure concentrated and supersaturated solution water activity from 4.5 × 10⁻³ to 0.9. The results are compared with those of regular solution theory and the adsorption and stepped-hydration theories of Robinson and Stokes.

The isopiestic method for the determination of water activities in salt solutions is simple, precise, and general. Known amounts of nonvolatile solutes are placed in open containers in an isothermal enclosure into which water is introduced. At equilibrium the solution water activities are equal and the compositions are determined by weighing. With activities of reference solutions, e.g., NaCl, KCl, H₂SO₄, and CaCl₂, determined by vapor pressure and other measurements, the comparison method has yielded activities, of hundreds of solutions over wide ranges of concentrations and temperatures. With temperatures fixed to ±0.05 K or better, temperature differences between samples less than 10⁻⁴ K, and mass measurements precise to ±0.05%, the method yields composition ratios with a precision greater than 10⁻⁴ and ultimately, osmotic coefficients φ = \( \frac{\mu}{(\mu)_{SO}} \) in water with a precision greater than 10⁻⁵. Here \( N = [\text{H₂O}] / [\text{X}] \) is the solvent-solute molar ratio.

A lower bound on \( \sigma \), placed by the crystallization of the reference, e.g., \( \sigma > 0.753 \) for NaCl at 25 °C. In a variation on the method which avoids the lower bound, Stokes replaced the solution reference with pure water at reduced temperature. He obtained good agreement with other measurements but did not push \( \sigma \), below 0.2889. A second lower bound is placed by crystallization of the unknown of course. Though many of the compounds listed in ref 1 have been measured to saturated solution, we know of no listings there for supersaturated solutions. Ionic solutions at the high concentrations of supersaturation may become ordered liquids for which water activity can serve as a probe.

We report here the results of an isopiestic study of lithium bromide and lithium iodide solutions by the Stokes method in which water activity is measured down to 4 × 10⁻³. Our method differs in the handling of the sample. We have reduced its mass to 10⁻⁴ g, as compared with the 1 g typical of isopiestic samples, have levitated it electrodynamically in a small sealed chamber from which air is removed, and have weighed it in situ and continuously with a noncontacting electrostatic balance.

With a microscopic spherical sample in a small chamber containing only water vapor, equilibrium is established much faster. More importantly, levitation of microscopic droplets allows supersaturation terminated only by homogeneous nucleation of crystallization.

We apply regular solution theory, adsorption model theory, and stepped-hydration model theory to our results.

INVESTIGATION OF AMMONIUM SULFATE AEROSOLS USING ELECTRODYNAMIC SUSPENSION, C. B. Richardson, J. F. Spann, C. A. Kurtz, Physics Department, University of Arkansas, Fayetteville, AR 72701

A laboratory study of sulfate aerosols is in progress. Single, micron-size, ammonium sulfate particles are suspended in a quadrupole ion trap into which are introduced reactive gases. Particle growth is monitored optically, aerodynamically, and by using the trap as a mass spectrometer.

The trap is constructed of stainless steel and nickel mesh. It has a height of 12 mm and a diameter of 20 mm. Voltages between 100 and 1000 are applied at a frequency of 200 Hz. The trap is mounted in a glass and stainless steel chamber connected to a manifold through a precision leak valve. Gases fill the manifold through bakeable stopcocks. The system is evacuated by a turbomolecular pump. With a base pressure of 10^{-6} torr, the solution composition is 44.4% ammonium sulfate and their position is fixed within about 2 microns except at high vacuum when small oscillations occur. Trapping times are unlimited.

Vertically polarized light from a helium-neon laser is scattered from the particle and detected visually and photoelectrically by two photomultiplier tubes, one fixed at 90° in the horizontal plane, the other moveable. Mie theory is fit to the scattered light results to obtain particle radius and refractive index. Gravity is balanced by a vertical field to determine relative mass with a precision of about 2 x 10^{-5}. The particle motion is resonantly driven to measure damping and determine surface area.

The response of the particle to changing pressure of water vapor has been measured. The results include the following.

a) At ambient temperature T = 23.5°C, the transition from anhydrous (NH₄)₂SO₄ occurs at water pressure P = 18.0 ± 0.2 torr. The solution composition is 44.4 ± 0.3% ammonium sulfate. These values are in good agreement with the T = 25°C values of Robinson and Stokes: 18.9 torr, and 44.2%.

b) During the transition, when the particle is layered, Mie scattering at 90° is detected. Regular oscillations in intensity are recorded.

c) Growth is reversed and the vapor pressure of water vapor has been measured. At the point of transition to solid, P = 10.8 ± 0.9 torr when the composition is 72.3 ± 0.7% ammonium sulfate.

d) The trap is evacuated and the anhydrous particle is held at P = 3 x 10^{-6} torr for 48 hours. An upper limit on the evaporation rate yields upper limits on the vapor pressures of 4% and ammonia of 2 x 10^{-6} and 6 x 10^{-6} torr, respectively.

This work is supported by NSF Grant ATM 8202766.
MEASUREMENT OF PHASE CHANGES IN A MICROSCOPIC LITHIUM IODIDE PARTICLE
LEVITATED IN WATER VAPOR

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Single, micron-size lithium iodide particles are suspended electrostatically in vacuo in a quadrupole ion trap at room temperature and measured gravimetrically and by light scattering their response to changes in the pressure of ambient water vapor over the range 1 X 10^{-5} to 5 Torr. Five crystalline phases are detected including one not previously reported. Pressures at the phase changes are measured with the results analyzed thermodynamically to determine nucleation free-energy barriers. The transition from crystal to saturated solution is time resolved with the results suggesting the presence of an intermediate disordered solid, possibly an intercalation compound. The supersaturated solution vapor pressure is measured as composition ranges between 12 an 68 mol kg^{-1} and used with nucleation theory to analyze the crystallization.

Several benefits are derived from reducing the sample to microscopic size and levitating it, as demonstrated by our results. High specific area and low thermal inertia lessen the departure of the system from equilibrium. The elimination of solid contact for support and containment removes a source of physical perturbation of the sample surface and chemical contamination. Finely dividing a purified bulk sample can eliminate foreign nuclei which serve to catalyze phase changes and therefore allow investigation of those produced spontaneously by fluctuation.

The lithium iodide—water system has been the subject of a large number of studies using a variety of techniques. The continuing interest may be due to its relative simplicity in composition with relative complexity in properties. At room temperature the solid is known to exist as anhydrous LiI, LiI·nH_{2}O, n = 1, 2, 3 [1]. The structures of the dihydrate are known [2] and for it X-ray patterns differ between laboratories [3]. Two forms n = 1/2 [1] and n = 3/2 [4] have been, but not confirmed. Lithium iodide monohydrate is a good solid electrolyte [5]. The high ionic conductivity is consistent with the known disorder in the positions in the crystal. Thermogravimetric pressure measurements have been used to determine the phase diagram of the solid system and the entropy changes at the transitions [6, 7], explained disagreements characterize many results. Dilute-solution vapor pressures have been measured [8].

Where possible we compare our results with others, and offer explanations where significant agreement is found.

1. Introduction

We have suspended single microscopic particles of lithium iodide in a quadrupole ion trap at room temperature and measured gravimetrically and by light scattering their response to changes in the pressure of ambient water vapor over the range 1 X 10^{-5} to 5 Torr. Five crystalline phases are detected including one not previously reported. Pressures at the phase changes are measured with the results analyzed thermodynamically to determine nucleation free-energy barriers. The transition from crystal to saturated solution is time resolved with the results suggesting the presence of an intermediate disordered solid, possibly an intercalation compound. The supersaturated solution vapor pressure is measured as composition ranges between 12 and 68 mol kg^{-1} and used with nucleation theory to analyze the crystallization.

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Where possible we compare our results with others, and offer explanations where significant agreement is found.

2. The measurement technique

The quadrupole ion trap by which the sample is levitated is similar to that used by Wuerker and Langmuir in their pioneering work [9], a description of the system is given elsewhere.
HI 3 Photon Excitation of Compound Plasmon Resonances in Aluminum. C. B. RICHARDSON and B. W. MCLENN, University of Arkansas.--Modulated aluminum surfaces were excited by a superposition of pair pulses at 9680 Å spacing, displaced slightly in angle. Surface plasmons are excited by light at 6328 Å wavelength incident in a plane perpendicular or parallel to the angle bisector. Resonant processes up to sixth-order in the photon-plasmon-grating interaction are required to yield the diffraction observed. For a grating with 2θ between the rulings and parallel incidence, the relative intensity of light produced by the sixth-order and second-order processes is 4 × 10⁻⁴. These and similar results will be compared with a quantum theory of intermediate plasmon-photon resonant states.

HI 4 Plasmon Loss in Photoelectron, Auger and KLL Spectra of Al and Mg. *JAN M. BROOGER and PAUL M. VAN ATTERUM, Department of Molecular Spectroscopy, Univ. of Nymegen, Netherlands.--The intensities of plasmon loss satellites of core lines and valence band transitions in the x-ray photoelectron - and Auger spectra of Al and Mg were determined by convoluting the no-loss spectra with asymmetric Lorentzians. In both metals the intrinsic plasmon loss intensity is 25° of the total plasmon loss intensity. Extrinsic plasmon loss intensity was determined independently from photoelectric energy loss spectra. Photoelectron gain satellites were observed in the KLL-Auger spectra, confirming the importance of the intrinsic plasmon losses.

*Submitted by N. Benczer-Koller.

HI 5 Photoelectron Injection in Gases from Thin Metal Films on Quartz. *K. SIGOMOS and I. C. CHRISTOPHOROU, Oak Ridge National Laboratory.--The photoelectron injection current (PEIC) in gases from thin metal films of Pd, Au, and Au + Pd on quartz was measured in a function of film thickness, film homogeneity, gas pressure, pressure-reduced electric field and photocathode material conditioning. The PEIC varies with film composition and thickness. It increases almost exponentially with decreasing film thickness in the range 300 to 400 Å, but decreases below 30 Å. These results will be discussed, and their relevance to studies of the behavior of excess electrons in fluids, where optimum PEICs are required, will be indicated.

*Research sponsored by the Division of Biomedical and Environmental Research, U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

HI 6 DOUBLE QUANTUM EXTERNAL PHOTOELECTRIC EFFECT (DQEE) IN TETRACNE. S. Arnold (Polytechnic Institute of NY and M. Pope (NTU). In 1965 Pope et al observed a DQEE in crystalline tetraene. This process consists of the emission of photoelectrons under the action of light of energy much below that of the external ionisation threshold of the crystal. The photoemission rate varies as the square of the light intensity I, with the energy of the most energetic electron unaffected by photon energy in this low energy region. They attributed the DQEE to the interaction of two hitherto undetected charge-transfer (CT) excitons. This conclusion was challenged by Haarer and Castro, who failed to observe any DQEE at all in tetracene. The experiment of Pope et al has been repeated using much more sensitive equipment developed by Arnold. New results verify the existence of the DQEE, which is proportional to I²/3 and the process is independent of photon energy or single exciton excitation. An energetic prediction of possible resolution is that the interaction of a free conduction electron with a trapped CT exciton.

3. S. Arnold, to be published.

HI 7 Properties of He Adsorbed on Graphite Derived from Scattering Data. W. M. CARLSON and M. W. COLE, Penn State.--With data for He and He scattering from graphite as input, we derive the atom-surface interaction in terms of a summation of pair potentials (0.1-10 K, Yuk-6, exp-6). The anisotropy of the pair interaction is taken into account to obtain a good fit to the matrix elements. The model potential is then used to calculate the band structure of He on graphite. By including the effects of band structure and adatom-adatom interactions, we find the ground state energy of helium on graphite derived from thermodynamics agrees to within one per cent of that derived from scattering for both He isotopes. We also use the model potential to calculate other thermodynamic properties of He films on graphite at low coverages.


HI 8 Selective Adsorption of He and Ne on the Basal Plane of Graphite. *G. Derry, D. Wensers, and D. R. Frankl, Penn State U.--Atomic beams of He and Ne were reflected from basal surface of graphite single crystals in ultrahigh vacuum. The bound state eigenvalue spectra of both isotopes were inferred from the selective adsorption minima in the reflected intensity. The results are E, = 12.06 ± 0.11 meV, E, = 6.36 ± 0.11 meV, E, = 2.85 ± 0.10 meV, E, = 1.01 ± 0.09 meV, and E, = 0.17 ± 0.06 meV for He on graphite, and E, = 13.59 ± 0.08 meV, E, = 5.36 ± 0.15 meV, and E, = 1.78 ± 0.11 meV for Ne on graphite. These data were obtained on two crystals, and measurements on a third crystal are in progress. The energy level values obtained for He adsorption are close to, but slightly deeper than those obtained by Boato et al. and agree well with analysis of thermodynamic data.*

*Submitted by U. F. FRANKL.

HI 9 Magnetoplasma Polaritons at the Interface Between a Semiconductor and a Metallic Screen. P. HALEVI, JCAHP, Ando.--In a semiconductor interface between a metallic screen and a highly conducting metallic screen supports polaritons which propagate at a right angle to a static magnetic field lying in the plane of the interface (Voigt geometry). In the case of negligible-plasmon-phonon interaction there is a propagation window below the cyclotron frequency and another one above the hybrid cyclotron plasma frequency. For a given orientation of the magnetic field these modes propagate in opposite directions. In case of a polar semiconductor there are three propagation windows whose limiting frequencies depend on the cyclotron, plasma, transverse phonon, and longitudinal phonon frequencies. These modes also exhibit nonreciprocity with respect to their direction of propagation. Effects of damping, of the finite conductivity of the metallic screen and the possibility of experimental detection of the predicted modes are discussed.

HI 10 Build up of Reflected Signal in Time in a Frequency and Spatially Dispersive Medium. *D. N. PATTAN-ATAK and J.L. BIRMAN, CONN-M.I.T. 1001. We consider the problem of a reflected signal from a Spatially Dispersive Dielectric Half-Space. The build up of the reflected signal to its asymptotic steady state coupled to mass motio reflectivity.

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*Supported by NSF-DMR 1234567.

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*Supported by NSF-BHE 1234567.

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SESSION JF Thursday morning

JA 1

JA 2

The present paper presents some historical and international status of the field, and some recent advances in the field of fluid mechanics and continuum mechanics.

JA 3

JA 4

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JA 6

JA 7

JA 8

JA 9
PHOTON EXCITATION OF COMPOUND PLASMON RESONANCES IN ALUMINUM

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Received 25 September 1978

We have studied the diffraction of light from aluminum surfaces ruled in parallelogram patterns. Sharp intensity variations are detected and compared with results of a quantum theory of the excitation of compound processes including as many as three virtual plasmons in resonance.

1. Introduction

In explaining the observed variations in the intensity of light diffracted from aluminum and gold gratings, Ritchie et al. [1] presented a quantum theory of a compound process in which a final photon state develops from an intermediate surface plasmon state resonantly excited. The process is at least second-order in the photon-plasmon-grating interaction to conserve momentum in the creation and annihilation of the virtual plasmon. The probability of excitation may be a Lorentzian function of the photon-plasmon energy difference or, at a fixed photon energy, of the various momenta transferred. The sharply peaked variations in the diffracted light intensity indicate narrow plasmon resonances in the 0.3 to 1.3 \( \mu \text{m} \) wavelength region studied. Ritchie et al. point out the possibility of higher-order processes leading to the same photon final state. In a fourth-order process, for example, the intermediate state could include two virtual plasmons and one virtual photon in resonance. The probability of excitation of such a state would vary as the product of Lorentzian functions having different resonance denominators. The diffraction peaks observed by Ritchie et al. cannot reveal the excitation of these interesting compound resonances.

We have detected surface plasmon resonance effects in the diffraction of light from aluminum gratings which are evidence of photon-plasmon-grating interactions at least of sixth order, confirming the prediction of Ritchie et al. of the existence of these intermediate states.

2. Experiment

The gratings were prepared holographically using photoresist on glass plates and a fringe pattern formed by splitting the beam of an argon-ion laser tuned to 0.4579 \( \mu \text{m} \). They were made in the form of grids by rotating the plates in their planes through an angle \( \beta \) between 90 s exposures to the fringe pattern. After development, the surfaces were coated with aluminum to a depth of roughly 0.1 \( \mu \text{m} \). From diffraction, the grating spacing \( d \) was found to be 0.898 \( \pm 0.005 \mu \text{m} \) and the modulation amplitude \( h \) was found [2] to be between 0.014 \( \mu \text{m} \) and 0.030 \( \mu \text{m} \) for the gratings studied.

The gratings were mounted in a two-axis goniometer and illuminated by unpolarized light at 0.6328 \( \mu \text{m} \) from a helium-neon laser. Diffracted light was detected by a 9502 B photomultiplier. A polarizer and
Measurement of the Speed of Light

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Measurement of the speed of light by the rotating mirror method of Foucault using a laser source and photodiode detector is described. With a path length of 38 m and rotation rates up to 500 Hz, the result \( c = 3.00 \pm 0.08 \times 10^8 \text{ m/sec} \) is obtained.

The measurement of the speed of light by the rotating mirror method of Foucault is at once beautiful in its simplicity, significant in its content, and impressive in its outcome. With a light source and detector, three mirrors, and a lens students can, in effect, measure transit times for light of \( 10^{-7} \text{ sec} \) over a path within a classroom and, with the simple equipment we will describe, to a precision of better than 1%.

The arrangement of these components, identical to the original arrangement of Foucault, is shown in Fig. 1. In 1850 Foucault obtained the result \( c = 298,000 \pm 500 \text{ km/sec} \). He and others, including Michelson, subsequently refined the technique, principally through the introduction of longer paths. Michelson's first result, given in 1879 was \( c = 299,910 \pm 50 \text{ km/sec} \), his last from the measurements from Mt. Wilson in 1926 was \( 299,798 \pm 4 \text{ km/sec} \).

Light from the source \( L \) is reflected from the rotating mirror \( M \) so that the beam is swept through a large arc. Within that arc it strikes normally a plane reflector \( R \), returning from it to the mirror \( M \). Because \( M \) has rotated through an angle \( \theta \) during the light's transit of \( MRM \) the beam returns to the partially reflecting mirror \( S \) along a path deviating \( 2\theta \) from the incident path. At \( S \) it is reflected to the detector \( D \) which is moveable perpendicular to the reflected beam. The lens \( F \) having a focal length one-fourth the distance between \( L \) and \( R \) is placed midway between them producing a sharp image of the source at \( R \) and at \( D \). The procedure is to set the rotational frequency \( f \) of the mirror to various values and for each to locate the position \( p \) of...