A new look at homogeneous freezing of water

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[1] Despite its atmospheric importance, homogeneous freezing of aqueous drops is poorly understood. Here we provide evidence that at atmospheric pressures the conditions leading to the initiation of freezing in pure water are those for which the liquid compressibility and the corresponding density fluctuations reach maxima. This liquid-only criterion for the onset of freezing contrasts with the traditional view that freezing temperatures depend sensitively on the parameters of ice and the ice-water interface. We generalize the connection between compressibility maxima and freezing to aqueous solutions. Utilizing compressibility data, we predict solution freezing temperatures from those of pure water under pressure. These predictions are almost coincident with the parameterizations of droplet freezing temperatures in terms of water activity [Koop et al., 2000] used to predict ice formation in cirrus clouds. Our work then provides a physical basis for this link between water activity in solution and homogeneous freezing temperatures. INDEX TERMS: 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; 0399 Atmospheric Composition and Structure: General or miscellaneous. Citation: Baker, M. B., and M. Baker (2004), A new look at homogeneous freezing of water, Geophys. Res. Lett., 31, L19102, doi:10.1029/2004GL020483.

1. Introduction

[2] In a thorough reexamination of measured homogeneous freezing temperatures of small aqueous solution drops, Koop et al. [2000] found that for a wide range of solutes and solute concentrations at ambient pressure $p_0 = 1$ bar, the freezing temperatures $T_f$ depend only on the water activity $a_w$ of the solution. (For a solution of $N$ solute molecules at temperature $T$ and pressure $p$, $a_w = \exp[\mu_w(N, p, T) / kT]$, where $\mu_w$ is the chemical potential of the water.) This finding provides a very practical way to predict droplet freezing temperatures in the atmosphere, and, since water activity is an equilibrium property of the liquid solution, it suggests that the temperature of onset of homogeneous freezing of aqueous solutions is a property of the liquid phase alone. This poses the question of what determines $T_f(a_w)$, the solution freezing curve at ambient pressure.

[3] Earlier experiments on alkali halide solutions [Kanno and Angell, 1977] had shown that the addition of solutes and applied pressure have similar impacts on homogeneous freezing temperatures of water. Thus, to understand the solution freezing curve, we take a new look at homogeneous freezing of pure water. The dependence of solution freezing temperatures on an equilibrium liquid property suggests that the freezing curve $T_f(p)$ of pure water under applied pressure $\Delta p = p - p_0$ is also a property of the liquid phase alone.

[4] An isolated drop of pure water can remain liquid while cooled (‘supercooled’) below its melting temperature $T_m$ to its homogeneous freezing temperature $T_f$, where the freezing rate increases sharply. For pressures $p \geq 2.1$ kbar the achievable supercooling $T_m - T_f$ is about 70°C [Kanno et al., 1975], comparable with that in other liquids [Angell, 1982], whereas for $p \leq 1$ kbar, the achievable supercooling in water is substantially smaller than that in most simple liquids. These anomalously high freezing temperatures were initially explained [Speedy and Angell, 1976; Kanno and Angell, 1979] by proximity of the freezing curve $T_f(p)$ to a postulated curve limiting the region of mechanical stability of water, in which the isothermal compressibility is positive. This limit was introduced to explain observed rapid increases, with decreasing temperature, in the magnitudes of the thermodynamic response functions (the isothermal compressibility $\kappa = -\partial \ln V / \partial p |_T$, the isobaric expansivity $\alpha = \partial \ln V / \partial T |_p$, and the isobaric specific heat $C_p$). These response functions determine the magnitudes of the associated equilibrium (thermal) fluctuations in volume and entropy about their equilibrium values, $\langle (\Delta V)^2 \rangle = kT\kappa(V)$; $\langle (\Delta S)^2 \rangle = C_p k$, and their correlation $\langle \Delta S \Delta V \rangle = kT \alpha(V)$.

Later theoretical studies [Poole et al., 1992; Sciortino et al., 1997; Mishima and Stanley, 1998] cast doubt on the stability limit hypothesis, however, leaving open the question of what determines the freezing curve $T_f(p)$ in pure water.

[5] In view of the above observations we seek a unified explanation of both freezing curves ($T_f(p)$ and $T_f(a_w)$) in terms of liquid only phenomena with no reference to the parameters of the ice/water interface or of bulk ice. We ask what is special about supercooled water itself in the vicinity of these freezing curves.

2. Homogeneous Freezing of Pressurized Pure Water

[6] In order to gain insight into the special features of supercooled water and solutions near the freezing curve we first consider a simple microphysical model representation of pure water [Truskett et al., 1999] (hereafter, the TDST model). The model includes hard-sphere and background attractive interactions, as well as an orientation-dependent...
energy is contributed by the weak bonds. The strong H-bonds begin to compete with the weak bonds as the temperature and/or pressure is lowered toward the loci of extrema. The loci of extrema thus reflect changes in the character of the H-bonding.

[8] Figure 2 shows that the calculated positions of the extrema in $\kappa$ lie very close to the observed freezing curve for pressures $p_0 \leq p \leq 1.1$ kbar; the extrema of $\alpha$ and $C_p$ lie a few degrees lower. At ambient pressure the compressibility maximum occurs at $T = 235K$, and at $p = 1$ kbar the maximum occurs at $T = 218K$. Both values are equal, within 1°C, to the measured freezing temperatures at those pressures.

[9] The line of compressibility maxima reproduces that found in molecular dynamics simulations [Sciortino et al., 1997] of supercooled water, where it marks a change in local structure of the liquid. The near coincidence of compressibility maxima with the observed freezing curve for moderate pressures $p \leq 1$ kbar in both the analytic model and in the simulations suggests that water at these pressures is a substance for which homogeneous freezing temperatures can be approximately determined without calculating the freezing rate; the criterion for the onset of freezing is that the liquid compressibility reach a maximum.

[10] This criterion complements determinations of freezing temperatures based on the freezing rate. According to classical nucleation theory [Pruppacher and Klett, 1997], the rate is proportional to the probability of forming an ice embryo of a temperature dependent critical size. This probability depends sensitively on the properties of bulk ice and the ice-water interface. The liquid-only criterion for the initiation of freezing could then represent a reduction in the barrier to nucleation near the compressibility maximum, where there is a change in the H-bond structure of the metastable liquid. Here we present a simple heuristic picture showing how this reduction might come about.

[11] As the temperature decreases toward $T_f(p)$ water density fluctuations rise, so that it is increasingly likely to find regions in which the density of the metastable water approaches that of ice. At $p = p_0$, $T = 235K$ the volume of a critical nucleus $V_c \approx 4 \times 10^{-27}$ [m$^3$] [Pruppacher and Klett, 1997]. Using the value $\kappa \approx (1 - 2) \times 10^{-4}$ [bar$^{-1}$] (obtained from the TDST model or the simulations) gives $((\Delta V)_{a}^{1/3}/V_c \approx 0.03$, comparable to the relative difference in ice and water molecular volumes, $(v_i - v_w)/v_w \approx 0.05$.

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**Figure 1.** Response functions of pure water calculated from TDST model [Truskett et al., 1999]. (a) Isothermal compressibility $\kappa$ [10$^{-5}$/bar], (b) isobaric specific heat $C_p$ [kJ/mol-K], and (c) isobaric expansivity $\alpha$[10$^{-3}$/K].

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**Figure 2.** Measured freezing temperatures and loci of extrema in the calculated response functions for pure water. Dots: measured homogeneous freezing temperatures [Kanno et al., 1975]. Positions of extrema in $\kappa$ shown by thick solid line: extrema in $C_p$, thin line: and extrema in $\alpha$, dashed line.
works. Applied pressure can have similar impacts on H-bonding in aqueous solutions, guided by the fact that solutes and D2O occupy a sufficiently large volume of low density, solute-free water. 

3. Homogeneous Freezing of Aqueous Solutions

[12] We now apply these ideas to the initiation of freezing in aqueous solutions, guided by the fact that solutes and applied pressure can have similar impacts on H-bond networks [Leberman and Soper, 1995] and on compressibility [Tammann, 1923] in water.

[13] At fixed temperature the compressibility of pure water, \( \kappa_w \), increases as pressure is reduced toward the freezing curve (Figure 1a). Analogously, at fixed temperature the solution compressibility \( \kappa_{solute} \) should increase as solute concentration is lowered, reaching a maximum where there is a change in the character of the H-bonding. The value of the concentration at which this maximum occurs depends on the response of the water to the particular solute. We assume that the solution freezes at that temperature that maximizes \( \kappa_{solute} \).

[14] To predict the freezing temperatures of solutions, we compare the dependence of \( \kappa_{solute} \) on solute content to the dependence of \( \kappa_w \) on pressure. We express the solute content in terms of a pressure scale \( \Pi \), the approximate osmotic pressure. For a solution of activity \( a_w \) at temperature \( T \) and ambient pressure, \( \Pi(a_w, T) = -(1/v_w(T))kT \ln(a_w) \), where \( v_w(T) \) is the molar volume of water. In Figure 3a we show measured room temperature compressibilities of NaCl solutions and of pure water under applied pressure up to 1 kbar at \( T = 25^\circ C \) [Rogers and Pitzer, 1982]. (A 2 M solution corresponds to \( \Pi \approx 100 \) bar.) Figure 3a shows that in the parameter ranges where the data overlap \( \kappa_{solute}(\Pi) \approx 10 \kappa_{solute}(\Pi) \). That is, adding solute to pure water to increase the osmotic pressure from 0 to \( \Pi \) produces the same change in the water compressibility as does the application of pressure \( \Delta \Pi \approx 10 \Delta \Pi \).

[15] We assume that the approximate relationship between \( \kappa_{solute} \) on pressure and \( \Delta \Pi \) is maintained as the samples are cooled, so that if \( \kappa(\Delta \Pi, T) \) is maximized at \( T = T_p \), then \( \kappa_{solute}(\Pi) \approx 1 \Delta \Pi, T \) also reaches a maximum at \( T = T_p \), where both samples will freeze. Hence

\[
T_f(a_w) \approx T_f(\Delta \Pi = 10 \Pi(a_w, T_f)) \tag{1}
\]

[16] Thus we can determine the freezing temperature \( T_f \) at ambient pressure of an NaCl solution of water activity \( a_w \) (having osmotic pressure \( \Pi(a_w, T_f) \)) by setting it equal to the measured freezing temperature of pure water under applied pressure \( \Delta \Pi = 10 \Pi(a_w, T_f) \). To the extent that the response of \( \kappa_{solute} \) to an increase of \( \Pi \) is similar for other solutions, we can use equation (1) to predict their freezing temperatures as well. These predictions are presented in Figure 3b and compared with the measured solution droplet freezing temperatures discussed by [Koop et al., 2000]. The resulting freezing curve is almost indistinguishable from the empirical fit of these droplet freezing temperatures to measured water activities presented in that paper. The link between compressibility maxima and the onset of freezing appears to hold for all these solution droplets as well as for pure water under pressure, so that we have a unified explanation of both freezing curves \( T_f(p) \) and \( T_f(a_w) \) in terms of bulk liquid properties.

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4. Discussion

[17] The parameterization of droplet freezing temperatures in terms of water activity [Koop et al., 2000] is used to predict homogeneous nucleation of ice in the atmosphere [e.g., Haag et al., 2003; Kärcher and Lohmann, 2002], a process of importance to climate and radiative balance [Baker, 1997; Intergovernmental Panel on Climate Change, 2001]. Our work suggests the physical basis for this water activity criterion is that the value of the water activity at the freezing temperature identifies the position of the compressibility maximum in supercooled solutions. The compressibility reflects features of the H-bond networks that control the nucleation barrier.
[18] Figure 3b shows there is some spread in $T_f(a_n)$ values for the data set used by [Koop et al., 2000]. Moreover, recent laboratory measurements [e.g., Cziczo et al., 2004, and references therein] of $T_f$ for aerosol droplets show some larger variations, particularly at low activities and for some solute species. While these variations may in part be due to differences in laboratory technique and in kinetic factors, they may also be useful as tests and extension of our ideas. The scale factor 10 in equation (1) was obtained from NaCl solution data at room temperature. Small variations in this factor with temperature and/or composition would, according to our ideas, correspond to some variation in freezing temperatures for different solutes at a given water activity. Extension of our analysis to a range of solutions and temperatures would allow further tests of the link between compressibility maxima and freezing temperatures.

[19] The ideas presented here can also be tested by and applied to other issues of current interest related to supercooled water and droplet freezing, as follows.

4.1. Phase Diagram of Water

[20] One of the obstacles to further theoretical exploration of the homogeneous freezing criterion is uncertainty in the underlying phase diagram of low temperature liquid water. Several molecular dynamics simulations yield first order phase transitions between liquid phases of different densities in supercooled water [e.g., Poole et al., 1992; Tanaka, 1996; Sciortino et al., 1997; Brovchenko et al., 2003]. Each liquid-liquid coexistence curve ends at a critical point, where the compressibility and density fluctuations become infinite and above which the two metastable phases of liquid water become indistinguishable. The simulations differ significantly in the predicted locations and numbers of these liquid-liquid critical points. We suggest that an additional constraint be placed on input parameters for the simulations; namely, that the calculated locus of maxima in $\kappa$ be coincident with the observed homogeneous freezing curve $T_f(p)$.

4.2. Size Effects on Freezing

[21] Homogeneous freezing temperatures depend on sample size, even if the sample surface has no impact on individual ice nucleation events within it. Moreover, it has recently been suggested [Tabazadeh et al., 2002] that freezing of small aqueous droplets might initiate near the droplet surface. If so, this could partially explain the spread in measured $T_f$ values for aerosol particles. According to our picture, enhanced density fluctuations near the surface might contribute to reduction of the nucleation barrier there relative to that in the bulk. Examination of the spatial distribution of density fluctuations inside small droplets could then shed light on the possible role of the droplet surface in the onset of freezing and hence on freezing rates in atmospheric clouds.

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