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# Nucleation rates of water and heavy water using equations of state

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The original formula of Gibbs for the reversible work of critical nucleus formation is evaluated in three approximate ways for ordinary and heavy water. The least approximate way employs an equation of state to evaluate the pressure difference between the new and old phases. This form of the theory yields a temperature dependence for the nucleation rate close to that observed experimentally. This is a substantial improvement over the most commonly used (and most approximate) form of classical theory. © 2004 American Institute of Physics.

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## I. INTRODUCTION

Nucleation refers to the kinetic processes that initiate first-order phase transitions in nonequilibrium systems. It plays a key role in many fields ranging from atmospheric applications to materials science, and its study is currently being stimulated by the development of new experimental and theoretical techniques to measure and predict homogeneous nucleation rates.

In the 1870s Gibbs<sup>1</sup> showed that the reversible work  $W$  required to form a nucleus of the new phase consists of two terms: a bulk or volumetric term that stabilizes the fragmentary new phase and a surface term that destabilizes it. In 1926, Volmer and Weber<sup>2</sup> developed the first nucleation rate expression based on kinetic assumptions. Subsequent refinements and improvements by Farkas,<sup>3</sup> Becker and Döring,<sup>4</sup> Frenkel,<sup>5</sup> and Zeldovich<sup>6</sup> led to what we now call the classical nucleation theory (CNT). In CNT (e.g., Ref. 7) the critical nucleus is treated as a drop with a sharp interface (a dividing surface) that separates the new and old phases. Matter within the dividing surface is treated as a part of a bulk phase whose chemical potential is the same as that of the old phase. In the absence of knowledge of the microscopic cluster properties, particularly the surface tension, bulk thermodynamic properties, and several approximations, discussed below, are used to evaluate  $W$ .

The inputs to CNT are experimental quantities which makes the theory easy and popular to use. For many years, CNT was also regarded as relatively successful since it predicted reasonable critical supersaturations for a wide variety of substances. This view has been tempered by the development of improved experimental techniques that have allowed the accurate measurement of nucleation rates for many substances.<sup>8–20</sup> Comparison of these results with the predictions of CNT has shown that the theory is usually in error, giving rates that are too low at low temperatures and too high at high temperatures,<sup>10,17,18</sup> although the predicted depen-

dence on supersaturation is generally quite satisfactory.

The most fundamental approach to improving CNT is through the development of microscopic theories or simulation methods.<sup>21,22</sup> Although some remarkable progress has been made, a microscopic treatment that is widely applicable to many substances is not yet available. More empirical efforts<sup>22,23</sup> to improve CNT are more widely applicable, but they generally meet with limited success. One of the most successful and general treatments of the temperature dependence of nucleation rates is provided by the so-called scaled model of Hale,<sup>24,25</sup> which will be used below.

The principal goal of this paper is to test a form of classical nucleation theory closest in spirit to the original ideas of Gibbs. It is curious that, despite the long history of this subject, this seems not to have been attempted previously. Three different versions of CNT are used to calculate nucleation rates of water and heavy water. Two of these versions require an accurate equation of state to calculate the work of formation of a critical droplet, which is then used to evaluate the nucleation rate. The theoretical rate predictions are compared with the experimental rates of water and heavy water<sup>18,20</sup> and with the predictions of the scaled model.<sup>24</sup> Significant improvement in the predicted temperature dependence of the nucleation rate was realized. The number of molecules in a critical cluster is also compared with the experimental data using the nucleation theorem.<sup>26</sup>

## II. EQUATION OF STATE APPROACH FOR CLASSICAL NUCLEATION THEORY

### A. Work of formation

Gibbs' result for  $W$ , the reversible work required to form a critical nucleus of the new phase, is

$$W = A\gamma - V(P_l - P_v), \quad (1)$$

where  $A$  and  $\gamma$  are the area and surface tension, respectively, of the nucleus,  $V$  is its volume,  $P_l$  is the pressure of the new bulk reference phase at the same chemical potential as the metastable mother phase, and  $P_v$  is the pressure of the mother phase far from the nucleus. The result strictly applies to droplets of critical size, but its value is independent of any

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particular choice of thermodynamic dividing surface needed to define  $A$  and  $V$ . Gibbs found it convenient to introduce the “surface of tension” dividing surface at which the classical Laplace equation is valid. The Laplace equation governs the pressure drop across a curved interface, and for a spherical droplet of radius  $r^*$  it reads

$$P_l - P_v = 2\gamma/r^*. \quad (2)$$

Specializing to spherical critical nuclei, Gibbs showed that with Eq. (2), Eq. (1) became

$$W = \frac{16\pi}{3} \frac{\gamma^3}{(P_l - P_v)^2}. \quad (3)$$

To apply this famous formula of Gibbs, one has to know the exact surface tension at that radius and the droplet reference pressure. Lacking knowledge of the exact surface tension, the first approximation is to use the experimental surface tension of a flat interface, i.e., set  $\gamma = \gamma_\infty$  to obtain

$$W = \frac{16\pi}{3} \frac{\gamma_\infty^3}{(P_l - P_v)^2}. \quad (4)$$

We call this equation the  $P$  form.

Gibbs’ method for calculating the pressure  $P_l$  will be described below. As far as we know, calculations using this method have never been made for a specific substance. Instead, with only a few exceptions,<sup>27,28</sup>  $P_l$  is approximated by assuming that the droplet is incompressible. In this case, we have

$$P_l - P_v = \Delta\mu/v_l, \quad (5)$$

where  $\Delta\mu = \mu_v(P_v) - \mu_l(P_v)$  and  $v_l$  is the molecular volume of the new phase. The quantity  $\Delta\mu$  is the difference between the chemical potential of the metastable vapor  $\mu_v$  and the chemical potential of matter in the new phase at the pressure  $P_v$ ,  $\mu_l(P_v)$ . This definition is identical to Kashchiev’s.<sup>29</sup> Equation (5) follows from the thermodynamic identity

$$\mu_l(P_l) - \mu_l(P_v) = \int_{P_v}^{P_l} v_l dP, \quad (6)$$

when  $v_l$  is assumed to be constant and the condition of unstable equilibrium between the critical droplet and the metastable vapor,  $\mu_v(P_v) = \mu_l(P_l)$ , is used. With Eq. (5), Eq. (4) becomes

$$W = \frac{16\pi}{3} \frac{\gamma_\infty^3 v_l^2}{(\Delta\mu)^2}. \quad (7)$$

We call this equation the  $\mu$  form. This form is most useful when the chemical potential difference can be found from an equation of state. Generally, this is not the case, and  $\Delta\mu$  is more commonly evaluated using a simpler, but approximate thermodynamic relation that holds when the supersaturated and saturated vapors are ideal gases and the droplet is an incompressible liquid. This relation follows from Eq. (6) after replacing  $P_l$  with  $P_{ve}$ , the equilibrium vapor pressure, and using the condition of bulk two-phase equilibrium,  $\mu_l(P_{ve}) = \mu_v(P_{ve})$ . We then use the definition of  $\Delta\mu$  to eliminate  $\mu_l(P_v)$  and arrive at

$$\Delta\mu = \mu_v(P_v) - \mu_v(P_{ve}) - v_l(P_v - P_{ve}). \quad (8)$$

In the ideal gas limit  $\mu_v(P_v) - \mu_v(P_{ve}) = kT \ln S$ , and  $\Delta\mu$  reduces to

$$\Delta\mu = kT \ln S - v_l(P_v - P_{ve}), \quad (9)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $S$  is the supersaturation. The value of  $S$  is defined as the ratio of the actual and equilibrium monomer partial pressures,<sup>27</sup> but a good approximation is  $S = P_v/P_{ve}$ . It is customary to neglect the term  $v_l(P_v - P_{ve})$ , which is almost always extremely small. For example, for water at 230 K, at  $S = 2000$ , an essentially unattainable value,  $v_l(P_v - P_{ve})/kT \ln S = 3.4 \times 10^{-5}$ . Equation (7) then reduces to the most familiar form used in CNT,

$$W = \frac{16\pi}{3} \frac{\gamma_\infty^3 v_l^2}{(kT \ln S)^2}. \quad (10)$$

For simplicity we call this equation the  $S$  form.

Applying the first two forms of  $W$  requires knowledge of the droplet reference pressure or chemical potential. Usually this information is unavailable, and experimental results are, instead, compared with rates predicted using the  $S$  form because the supersaturation ratio is readily determined from the experimental data.

A less approximate way to evaluate the  $P$  form of  $W$  involves calculating the internal pressure  $P_l$  using the equation

$$kT \ln S = \int_{P_{ve}}^{P_l} v_l dP, \quad (11)$$

which follows from Eq. (6) when the conditions for stable and unstable equilibrium are applied and the ideal gas limit for  $\Delta\mu$  is used. The integral on the right-hand side of Eq. (11) can be evaluated quite accurately if the liquid density or, equivalently, the molecular volume is known as a function of pressure. If the pressure dependence of the density is not available from direct measurements, it may be calculated using the measured liquid isothermal compressibility, preferably as a function of pressure.

## B. Gibbs’ reference state

The calculation of the internal reference pressure  $P_l$  from an equation of state (EOS) follows Gibbs’<sup>1</sup> original reasoning.<sup>29–31</sup> Upon forming a droplet within a homogeneous fluid with uniform chemical potential and temperature, the droplet may be so small that its internal state may not be homogeneous even at the center of the drop. The meaning of the internal pressure and density of the droplet is then obscured, and these values are difficult to determine. To overcome this difficulty, Gibbs introduced the concept of the reference state as the thermodynamic state of a bulk phase whose internal pressure  $P_{ref}$  and density  $\rho_{ref}$  are determined by the same conditions that exist for the new phase and the mother phase, i.e., by assuming that the temperature and the chemical potential are the same everywhere in the nonuniform system. In mathematical terms, the pressure inside the

droplet is calculated such that the chemical potentials are equal in both the metastable vapor and reference liquid phases

$$\mu_v(\rho_v) = \mu_l(\rho_{\text{ref}}), \quad (12)$$

where  $\rho_v$  is the density of the supersaturated vapor and  $\rho_{\text{ref}}$  is the density of the reference liquid state. As a practical matter, one always calculates differences in chemical potential, and because Eq. (12) involves phase densities that generally differ by many orders of magnitude it is convenient to rewrite this equation as an equality of chemical potential differences measured from the common equilibrium state, for which

$$P(\rho_{\text{ve}}) = P(\rho_{\text{le}}), \quad (13)$$

$$\mu_v(\rho_{\text{ve}}) = \mu_l(\rho_{\text{le}}), \quad (14)$$

where  $\rho_{\text{ve}}$  and  $\rho_{\text{le}}$  are the equilibrium vapor and liquid densities, respectively. After subtracting the equilibrium value of  $\mu$  from both sides of Eq. (12), we obtain

$$\mu_v(\rho_v) - \mu_v(\rho_{\text{ve}}) = \mu_l(\rho_{\text{ref}}) - \mu_l(\rho_{\text{le}}). \quad (15)$$

The chemical potentials are calculated from  $\mu = (\partial f / \partial \rho)_T$ , where  $f$  is the appropriate Helmholtz free energy density for the EOS. Once  $\rho_{\text{ref}}$  has been found by solving Eq. (15), the reference pressure  $P_{\text{ref}}$  is straightforward to calculate from the EOS. To implement this approach, we need a satisfactory EOS. There are many possible candidates in the literature, but most are not sufficiently accurate. Three EOS's for water and one for heavy water were used in this work. They are described later.

### C. Nucleation rate expressions

The conventional Becker-Döring expression<sup>7</sup> for the classical nucleation rate is

$$J_{CL} = J_0 \exp\left(-\frac{W}{kT}\right), \quad (16)$$

with the pre-exponential factor

$$J_0 = \sqrt{\frac{2\gamma_\infty}{\pi m}} v_l \left(\frac{P_v}{kT}\right)^2, \quad (17)$$

where  $m$  is the mass of a condensable vapor molecule, and the other symbols have been defined already.

The scaled model is based on CNT, and it yields a universal dependence of nucleation rate on  $T_c/T - 1$ . The two parameters of this model are the nearly universal constant  $\Omega$ , which is interpreted as the excess surface entropy per molecule, and the constant rate prefactor  $J_0$  ( $\approx 10^{26} \text{ cm}^{-3} \text{ s}^{-1}$ ). The value of  $\Omega$  for nonpolar substances is around 2.2, whereas for polar materials it is about 1.5. For later use, and as an example,  $\Omega$  is 1.476 for heavy water and 1.470 for water. The model works well for many substances for which the CNT fails. In the scaled model, the nucleation rate is given by the expression

$$J = J_0 \exp\left[-\frac{16\pi}{3} \Omega^3 \left(\frac{T_c}{T} - 1\right)^3 / (\ln S)^2\right]. \quad (18)$$

### D. Number of molecules in the critical nucleus

In addition to the nucleation rate, another physical quantity of interest is the size of the critical nucleus, which is experimentally determinable from measured nucleation rates using the nucleation theorem in the approximate form,<sup>26,32</sup>

$$n^* \approx \frac{\partial \ln J}{\partial \ln S}. \quad (19)$$

The experimentally determined values of  $n^*$  can be compared with the theoretical values based on the different forms of  $W$  using the rigorous form of the nucleation theorem:<sup>29</sup>

$$\frac{\partial W}{\partial \Delta \mu} = -\Delta n^* / (1 - \rho_v / \rho_l). \quad (20)$$

For the formation of liquid droplets in a dilute vapor, Eq. (20) reduces to

$$\frac{\partial W}{\partial \Delta \mu} = -n^*. \quad (21)$$

The critical number  $n^*$  can also be computed from classical considerations. Since the volume of a spherical critical nucleus is  $V^* = 4\pi r^{*3}/3$ , one can calculate the number of molecules in the nucleus from the relation  $n^* v_l = V^*$ . Applying the Gibbs-Thomson or Kelvin equation,<sup>33,34</sup>  $\Delta \mu = kT \ln S = 2\gamma v_l / r$ , one finds

$$n^* = \frac{32\pi v_l^2 \gamma_\infty^3}{3(kT \ln S)^3}. \quad (22)$$

## III. EQUATIONS OF STATE FOR WATER AND HEAVY WATER

### A. IAPWS-95

This EOS was published by the International Association for the Properties of Water and Steam (IAPWS-95).<sup>35,36</sup> It is an analytical equation based on a multiparameter fit of all the experimental data available at temperatures above 234 K. It is very accurate and, therefore, highly suitable for use in the EOS approach, but only for  $T \geq 234$  K. This EOS fails to provide a continuous representation of single phase fluid states in the metastable and unstable regions of the phase diagram, but this is not a limitation for the present application.

### B. Crossover equation of state (CREOS)

Kiselev and Ely<sup>37</sup> have developed an EOS that describes classical mean-field behavior far from the critical region and smoothly crosses over to the singular behavior near the critical point. Their EOS for ordinary water<sup>37</sup> at low temperatures has been termed CREOS-01, while the heavy water version<sup>38</sup> is referred to as CREOS-02. To make these equations work at low temperatures, the scenario of a second critical point at low temperature<sup>39</sup> was exploited by Kiselev and Ely.<sup>37</sup> The CREOS equations describes only the liquid states of the system.

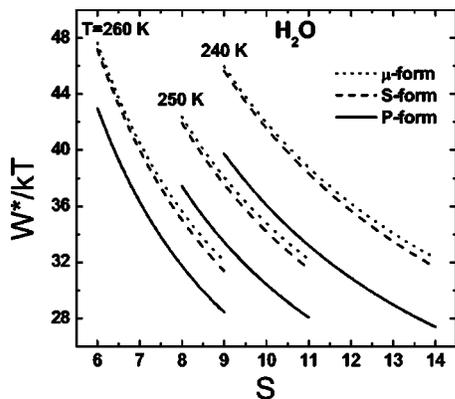


FIG. 1. The work of formation for water droplets using the IAPWS-95 EOS with the three forms of CNT at  $T=240, 250,$  and  $260$  K.

### C. JA-EOS

Jeffery and Austin<sup>40</sup> (JA) have developed an analytical equation of state to describe water. It has several interesting properties, but also an important drawback. Similar to the CREOS equation, it predicts a low temperature critical point associated with two metastable phases of supercooled water. It also provides a continuous description of single-phase states in the two-phase region, similar to the van der Waals and other cubic EOSs. We found that it could not accurately predict the low temperature vapor-liquid binodal line, although it is capable of accurate predictions of the equilibrium vapor pressure if either the correct equilibrium vapor or liquid density is supplied independently. Consequently, we use it only to calculate properties of vapor states, as described below, to complement the CREOS equations.

## IV. RESULTS OF EOS APPROACH

### A. Water

Before applying the different equations of state to calculate nucleation rates, differences in the critical work of formation  $W$  for the various forms of CNT were examined. Figure 1 shows  $W$  of water droplets using the IAPWS-95 (Ref. 35) at  $T=240, 250,$  and  $260$  K. As can be seen from the graph, the results for the  $\mu$  form and for the  $S$  form are close to each other at low  $S$  and start to deviate slightly at high  $S$ . The maximum deviation is of order  $kT$ , which will give a difference in nucleation rates of only a factor of 3 and is, thus, inconsequential. It is clear from this figure that the  $P$  form gives significantly different results. The  $W$  for the  $P$  form is much lower than for the other forms. Since the nucleation rate depends exponentially on  $(-W)$ , higher nucleation rates will result for the  $P$  form. An important point to note is that the gap between the  $P$  form and other versions grows as  $T$  decreases, so the predicted temperature dependence should also be greatly improved.

The other EOS used to describe water at low temperature is the CREOS-01. A similar calculation was made for the CREOS-01 as described below. For  $T \geq 240$  K, where the results can be compared, we found essentially no difference between the  $W(P\text{-form})$  predictions of these two EOSs.

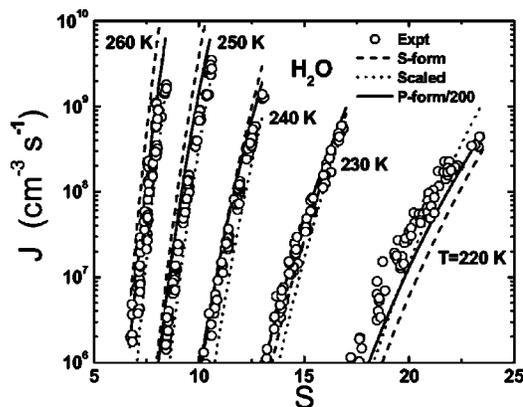


FIG. 2. Comparison of the experimental rates of Wölk and Strey (Ref. 18) (open circles) for water down to  $T=220$  K with two versions of CNT based on the CREOS-01 and with the scaled model.

Because it fails to describe the vapor states of the fluid, the CREOS-01 was used only for the liquid states, while the JA-EOS was used for the vapor, in the following way. To calculate the equilibrium vapor density  $\rho_{ve}$  and liquid density  $\rho_{le}$  one solves, respectively, the two equations,

$$P_{ve}^{\text{expt}}(T) = P_{JA}(\rho_{ve}), \quad (23)$$

$$P_{ve}^{\text{expt}}(T) = P_{CRI}(\rho_{le}), \quad (24)$$

where  $P_{ve}$  is the experimental equilibrium vapor pressure.<sup>18</sup> Then, to find  $\rho_{ref}$  the JA-EOS and the CREOS-01 were combined in the following equation

$$\mu_{JA}(\rho_v) - \mu_{JA}(\rho_{ve}) = \mu_{CRI}(\rho_{ref}) - \mu_{CRI}(\rho_{le}). \quad (25)$$

The rationale for this procedure is that the JA-EOS is accurate for densities and chemical potential differences of vapor states, while the same is true of the CREOS-01 for the liquid states.

Nucleation rates of water using the CREOS-01 (Ref. 37) results were calculated for temperatures from 260 to 220 K, as shown in Fig. 2. Rates using the IAPWS-95 EOS were also calculated for  $T \geq 240$  K, but since they are nearly identical to the CREOS-01 results, we show only the CREOS results. The  $P$ -form results are divided by a factor of 200. Because the predictions of the  $S$  form and  $\mu$  form are so close to each other, only the results of the  $S$  form are plotted. The figure also shows the predictions of the scaled model.<sup>25</sup> Both the  $P$ -form and the scaled model results describe the data well in terms of both the temperature dependence and the supersaturation dependence. The classical Becker-Döring result, based on the  $S$  form gives a clearly inferior account of the temperature dependence.

From the experimental rates and the nucleation theorem, the number of molecules in the critical droplet  $n^*$  can be determined. Figure 3 shows the experimental values<sup>18</sup> and the values derived from the  $P$  form of  $W$  versus the predictions of the Gibbs-Thomson formula, Eq. (22), at the different temperatures. Only the CREOS-01 EOS was used to calculate  $n^*$  using the formula

$$n^* = \frac{32\pi\gamma_\infty^3}{3(P_{ref} - P_{ve})^3} \rho_{ref}, \quad (26)$$

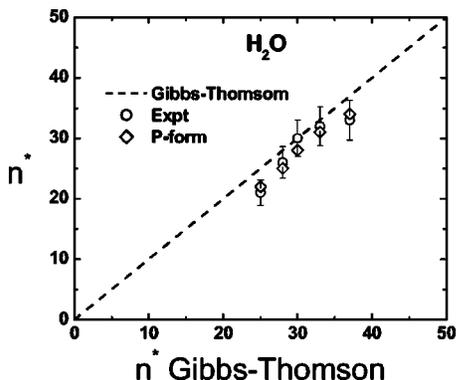


FIG. 3. The number of water molecules in the critical cluster found experimentally (Ref. 18) using the nucleation theorem and the  $P$ -form calculations. The dashed-line shows the full agreement with the Gibbs-Thomson equation.

which is readily found from Eqs. (4) and (20). The experimental data were found by Wölk and Strey<sup>18</sup> using the equation

$$n^* = \frac{\partial \ln J}{\partial \ln S} - 2. \quad (27)$$

The calculated  $n^*$  values using the  $P$  form of the CNT show excellent agreement with the measured ones. This result is not unexpected since the  $P$  form of the CNT gives the right  $T$  and  $S$  dependence, and since  $n^*$  is essentially equal to the derivative of  $\ln J$  with  $\ln S$ .

## B. Heavy water

The only EOS valid at low  $T$  to describe  $D_2O$  is the CREOS-02.<sup>38</sup> As for CREOS-01, this equation also describes only liquid states, and there is no other EOS to describe the vapor states. Consequently, to evaluate the chemical potential of the metastable vapor, the assumption that the vapor is ideal has been used, i.e.,  $\mu(\rho_v) - \mu(\rho_{ve}) = kT \ln S$ . To calculate the equilibrium liquid density  $\rho_{le}$  the experimental equilibrium vapor pressure<sup>18</sup>  $P_{ve}(T)$  has been equated with the CREOS-02 pressure at the equilibrium liquid density,

$$P_{ve}(T) = P_{CR2}(\rho_{le}). \quad (28)$$

To find  $\rho_{ref}$  the ideal vapor assumption was used to obtain

$$kT \ln S = \mu_{CR2}(\rho_{ref}) - \mu_{CR2}(\rho_{le}). \quad (29)$$

The reference pressure is then obtained as  $P_{ref} = P_{CR2}(\rho_{ref})$  after the solution to Eq. (29) is found.

Figure 4 shows the rates, divided by a factor of 100, predicted by the  $P$  form using the CREOS-02 (Ref. 38) equation. The results show good agreement with the experimental  $T$  and  $S$  dependence.

All the aforementioned experimental data has been taken by Wölk and Strey<sup>18</sup> using a pulse chamber. Other experimental data have been taken by Khan *et al.*<sup>19</sup> and Kim *et al.*<sup>20</sup> using a supersonic nozzle technique. This technique yields a very high nucleation rate at high supersaturation values. The results predicted by the  $P$  form with CREOS-02 are compared in Fig. 5 with both the scaled model and an

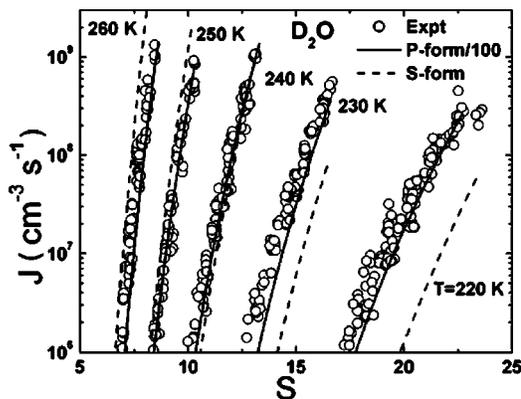


FIG. 4. Comparison of the experimental rates of heavy water by Wölk and Strey (Ref. 18) down to  $T=220$  K with the predictions of the  $P$  form of the CREOS-02.

empirical function by Wölk and Strey.<sup>18,41</sup> The empirical function was developed by fitting all of the low  $S$  nucleation rate data.<sup>18</sup>

From Fig. 5, we notice that the scaled model gives very good results at these high supersaturation values, while the  $P$ -form results based on CREOS-02 lie within an order of magnitude of the measured values, but do not reproduce the  $T$  dependence quite as well as for the low  $S$  pulse chamber data.

Figure 6 shows the number of molecules in the critical droplet calculated from the experimental data<sup>18</sup> and the  $P$  form of  $W$  using the nucleation theorem plotted versus the number of molecules predicted by using the Gibbs-Thomson formula at the different temperatures. As for ordinary water,  $n^*$  calculated from the  $P$  form of the CNT is in excellent agreement with the measured values. Again, since the  $P$  form of the CNT reproduces the experimental  $T$  and  $S$  dependence of  $J$  and since  $n^*$  is essentially the slope of the  $\ln J - \ln S$  curve, this good agreement is not surprising.

## V. DISCUSSION OF WATER RESULTS

The results show a clear advantage of using the  $P$  form over the other versions. Note that the  $\mu$  and  $S$  forms, which

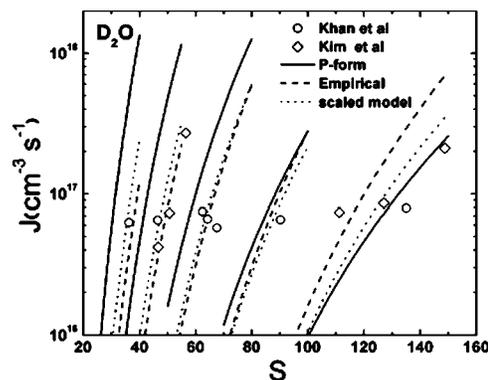


FIG. 5. Comparison of two different sets of supersonic nozzle rates at high  $S$  for heavy water (Refs. 19 and 20) with the  $P$ -form results using CREOS-02 and with the scaled model and the empirical function. Calculated results are shown at  $T=237.5$ , 230, 222, 215, and 208.8 K from left to right. Temperatures for the experimental results are close to these values.

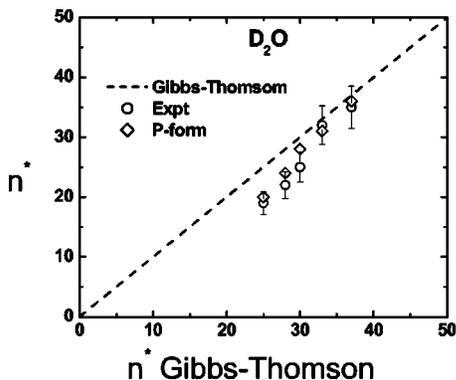


FIG. 6. As in Fig. 3, but for heavy water.

were based on the assumption of liquid incompressibility, give poor results when compared with the experimental data. This is strong evidence against the assumption that liquid water is incompressible. Figure 7 shows the liquid density as a function of temperature at different pressures as calculated from IAPWS-95 and CREOS-01, which are in excellent agreement with each other and with experiment<sup>42,43</sup> over wide ranges of pressure and temperature. A similar figure can be found in the paper by Kiselev and Ely,<sup>37</sup> but we have extended the comparison to higher pressures. From this figure, one can see that at all temperatures the density of liquid water is strongly pressure dependent. Liquid water is unusually compressible, especially at lower temperatures.<sup>44</sup> Also note that at a pressure between 190 and 300 MPa, the densities predicted by CREOS-01 and IAPWS-95 equations start to differ qualitatively. The CREOS-01 equation predicts that at the higher pressures the well-known density maximum of water no longer occurs. This is in accord with the experimental density measurements of Petitot, Tufeu, and Le Neindre<sup>43</sup> that show no density maximum for  $P \geq 200$  MPa down to  $T = 251.15$  K. The disappearance of the density maximum is also consistent with the observation that water's viscosity decreases and its diffusivity increases with increasing pressure up to a pressure of about 200 MPa. At higher pressures, these anomalies in water's transport coefficients vanish, and water behaves more normally with further increases in pressure.<sup>44,45</sup> In contrast, the IAPWS-95 equation continues to predict this feature. This suggests that nucleation rates

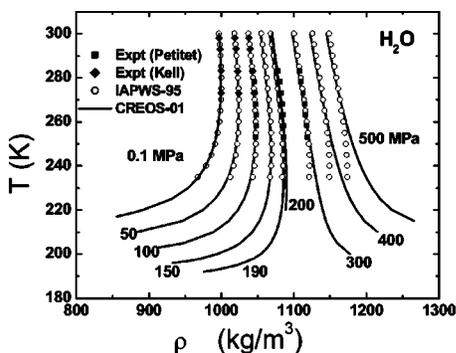


FIG. 7. The temperature-density isobars of water using the IAPWS-95 EOS and the CREOS-01 compared to experimental data of Kell and Whalley (Ref. 41) and Petitot, Tufeu, and Le Neindre (Ref. 43).

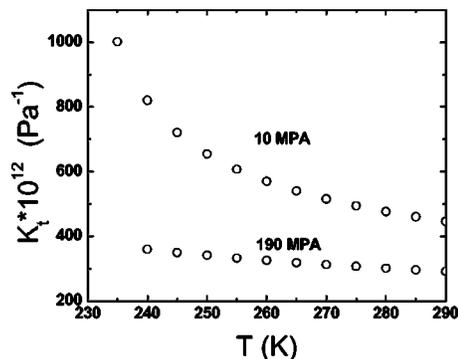


FIG. 8. Isothermal compressibility of liquid water at 10 and 190 MPa calculated from the fit of Kanno and Angell (Ref. 46).

calculated using the IAPWS-95 equation at  $T \leq 240$  K would differ, perhaps substantially, from those found here using CREOS-01. This conjecture awaits a means of using the IAPWS-95 equation at low  $T$  before it can be tested.

Figure 8 shows the isothermal compressibility as a function of temperature at 10 MPa (the differences in the isothermal compressibility between 1 atm and 10 MPa are small) and at 190 MPa, calculated using the fit of Kanno and Angell.<sup>46</sup> From this figure, it is clear that the isothermal compressibility decreases sharply when the pressure is increased to values typical of critical nuclei. It should be kept in mind that the reference pressure for critical droplets can reach very high values, up to 400 MPa or higher, and so the high pressure behavior of the EOS is of considerable importance in calculating nucleation rates using the  $P$  form of CNT.

One last point concerns a purely practical matter. In Sec. II, an alternative to using a full EOS to do the  $P$  form calculations was noted. This method was tested using accurate fits for the liquid density as a function of pressure and employing Eq. (11). Results essentially identical to those shown here were obtained.

In conclusion, we have applied Gibbs' original formula to water and heavy water using accurate equations of state for the fluid properties. Significant improvement in the predicted temperature dependence of the nucleation rate was realized for each substance. This appears to be due to the extraordinary isothermal compressibility of these two substances at the low temperatures where nucleation rates are generally measured. Two different types of EOS were used in our calculations, but each accurately treats the anomalously high compressibility of fluid water in the appropriate temperature range.

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