Unraveling the "Pressure Effect" in Nucleation

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The influence of the pressure of a chemically inert carrier gas on the nucleation rate is one of the biggest puzzles in the research of gas-liquid nucleation. Experiments can show a positive effect, a negative effect, or no effect at all. The same experiment may show both trends for the same substance depending on temperature, or for different substances at the same temperature. We show how this ambiguous effect naturally arises from the competition of two contributions: nonisothermal effects and pressure-volume work. Our model clarifies seemingly contradictory experimental results and quantifies the variation of the nucleation ability of a substance in the presence of an ambient gas. Our findings are corroborated by molecular dynamics simulations and might have important implications since nucleation in experiments, technical applications, and nature practically always occurs in the presence of an ambient gas.

A gas phase can be supersaturated considerably beyond its equilibrium condensation point before liquid drops form spontaneously. The pathway of the phase transition is blocked because microscopic droplets are thermodynamically less favorable than the bulk vapor. Therefore, the transition can only be initiated by rare fluctuations exceeding a critical size, called the *critical nucleus*. The formation of such a critical nucleus is the limiting step in the transition and its frequency of occurrence is called the *nucleation rate*. Nucleation is behind most phase transition and plays a crucial role in atmospheric processes such as the formation of aerosols or the condensation of water vapor into clouds [1,2]. An accurate experimental evaluation of the nucleation of atmospherically relevant substances and its correct theoretical prediction are essential for a better understanding of climate change and are the subject of intense investigations [3].

Nucleation is highly sensitive to small changes in the state variables describing the system, most notably to temperature. However, condensation is inevitably connected with the release of latent heat. In experiments this latent heat is removed by the presence of a large background of carrier gas. This carrier gas should be noncondensing and chemically inert and should have no influence on the nucleation except serving as the desired heat bath. Nevertheless, many experimental results suggest that there can be an influence on the nucleation rate that can span some orders of magnitude, depending on the pressure and type of the carrier gas (see Refs. [4,5] and references therein). Unfortunately, the overall picture is far from clear. Comparisons of experimental findings cover all possibilities: no effect, increase, or decrease of the nucleation rate with carrier gas pressure. There were some concerns of whether the pressure effect (PE) is not just an experimental artifact, which cannot be completely ruled out in all cases.

However, continuous improvements in the experimental setups confirmed rather than remedied this undesirable and elusive effect.

Following the experimental evidence, theoretical works have tried to explain the pressure effect with varying success. These approaches include changes to classical nucleation theory (CNT) accounting for nonideal behavior of the vapor and/or carrier gas [6], treating the carrier gas as not fully inert or the problem as binary nucleation [7–9], or analyzing its influence on cluster stability and the impingement rate [10], and many more. There remain many contradictions and differences both in the direction and in the magnitude of the effect. These are complicated by the discrepancies between experimental results themselves and in the comparison of experiment and theory.

Here we present a simple yet physically very appealing model that resolves many of the apparent contradictions of the pressure effect. We take a deliberate step back and incorporate the presence of a carrier gas into classical theory in a most natural manner that accounts for the two primal contributions of the carrier gas: the efficiency of thermalization and the additional work that a cluster has to spend for growing in its presence. These contributions have opposite trends and we show how this may be responsible for the existence of apparently contradictory results.

Nucleation theory [11] usually aims at calculating isothermal nucleation rates, taking the constant value of the temperature and the idea of a noninfluential carrier gas for granted. In CNT, the work of formation of a droplet of size n at constant pressure p and temperature T is [11]

$$\Delta G(n) = -n\Delta\mu + s_1\gamma n^{2/3}, \qquad (1)$$

which is the combination of a volume term related to the difference in chemical potential $\Delta\mu$ between the vapor and

the liquid and a surface term needed to build the liquid interface with area $A = s_1 n^{2/3}$ and surface tension γ [$s_1 = (36\pi v_l^2)^{1/3}$ is the surface area per monomer and v_l is the volume per molecule in the bulk liquid]. The vapor pressure p is assumed as ideal and the liquid cluster is considered as an incompressible spherical drop with a sharp interface and bulk liquid properties. The free energy has a maximum at the critical size n^* and its height ΔG^* is

$$\Delta G^* = \frac{16\pi}{3} \frac{v_l^2 \gamma^3}{\Delta \mu^2}. \tag{2}$$

The isothermal steady-state nucleation rate then is

$$J_{\text{CNT}} = K \exp(-\Delta G^*/k_B T), \tag{3}$$

where K is a kinetic prefactor. In CNT, the difference in the chemical potential is given by

$$\Delta \mu = k_B T \ln S - v_l(p - p_{\text{eq}}). \tag{4}$$

Here, $S = p/p_{\text{eq}}$ is the supersaturation and p_{eq} is the equilibrium vapor pressure. The second term in Eq. (4) is arising from the pressure-volume work the liquid drop has to perform against the ambient *vapor* pressure [12]. It is typically small and hence commonly neglected but we keep it here for clarity. We now naturally account for the presence of an ideal carrier gas by noting that the cluster must also perform pV work against the ambient *carrier gas* pressure, $W_c = p_c V(n) = n v_l p_c$ [13]. The work of formation including pV work now reads

$$\Delta G_{pV}(n) = -n \Delta \mu_{\text{eff}} + s_1 \gamma n^{2/3}, \tag{5}$$

where we have cast the pV contributions into an "effective chemical potential"

$$\Delta \mu_{\text{eff}} = k_B T \ln S - v_l(p + p_c - p_{\text{eq}}). \tag{6}$$

Physically, this expression for the chemical potential difference between the vapor and liquid phases can easily be derived from the thermodynamics of a system formed by a condensable vapor plus ideal carrier gas. More specifically, the second term on the right-hand side of Eq. (6) arises from the integration of the Gibbs-Duhem equation for the liquid, which has been considered as incompressible, and where it is important to note that the chemical potential of the liquid has to be evaluated at the *total* pressure of the system [13,14].

Replacing $\Delta \mu$ by $\Delta \mu_{\text{eff}}$ in Eq. (2), the barrier becomes $\Delta G_{pV}^* = (16\pi/3)(v_l^2 \gamma^3/\Delta \mu_{\text{eff}}^2)$ and the pV-corrected rate follows directly from Eq. (3) as

$$J_{pV} = K \exp(-\Delta G_{pV}^*/k_B T). \tag{7}$$

The main designated role of a carrier gas is to keep T constant. However, this thermalization might not be perfect and nucleation then happens under nonisothermal conditions. The classical work of Feder et al. offers analytical expressions to quantify this influence on the nucleation rate [15,16]. Physically, it is controlled by the competition

between the energy increase due to latent heat and the energy removal through elastic collisions with vapor and carrier gas molecules. The parameter

$$q = h - \frac{k_B T}{2} - \gamma \frac{\partial A(n)}{\partial n} \tag{8}$$

quantifies the energy released when a monomer is added to a cluster, which is the latent heat h per molecule (corrected by a small amount $k_B T/2$) minus the energy spent on increasing the surface area $A(n)$ against the surface tension. The mean squared energy fluctuation removed by collisions with impinging molecules is

$$b^2 = 2k_B^2 T^2 \left(1 + \frac{N_c}{N} \sqrt{\frac{m}{m_c}}\right) \tag{9}$$

for an ideal monoatomic vapor and carrier gas [16] (m is the molecular mass, N the number of molecules of the condensable). Equation (9) indicates that a large number of carrier gas molecules N_c and a light (small molecular mass m_c) carrier gas are most effective for a good and fast thermalization. Finally, the influence of nonisothermal effects on the steady-state nucleation rate is determined by the combination of q and b:

$$J_{\text{nonisoth}} = \frac{b^2}{b^2 + q^2} J_{\text{isoth}}. \tag{10}$$

We now obtain the full pressure effect of the carrier gas on the nucleation rate by combining Eqs. (10) and (7), taking the latter as the isothermal but pV-corrected rate:

$$J_{\text{PE}} = \frac{b^2}{b^2 + q^2} J_{pV}. \tag{11}$$

Obviously, the magnitude of the rate calculated by Eq. (11) depends on the estimate of the underlying CNT, which often can be off by many orders of magnitude [17,18]. In our case however, we are only interested in the *deviations* arising from the pressure effect. By renormalizing Eq. (11) we get a reasonable and mostly model-independent estimate of this deviation [19]:

$$\frac{J_{\text{PE}}}{J_{\text{CNT}}} = \frac{b^2}{b^2 + q^2} \frac{J_{pV}}{J_{\text{CNT}}}. \tag{12}$$

Figure 1 shows the change of the rate as a function of the ratio of carrier gas to vapor molecules, N_c/N, which for perfect gases is the same as the ratio of carrier gas over vapor pressure, p_c/p. The calculation was performed for argon at 50 K and a supersaturation of $S = 869$ [20] and the latent heat h was calculated via the Clausius-Clapeyron relation. Figure 1 also shows the individual contributions coming from nonisothermal corrections, which always have a positive effect on the rate, and pV work, whose effect is always negative. The competition of both terms first leads to an increase in the rate with increasing carrier gas pressure due to better thermalization. Then, the penalty
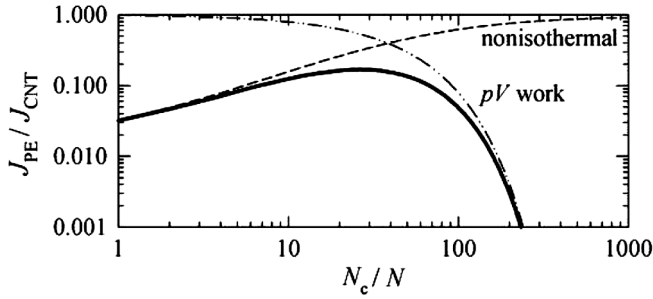
FIG. 1.   Deviation of the nucleation rate from CNT due to the full pressure effect, Eq. (12), as a function of the ratio of carrier gas over vapor molecules (solid line) arising from the two contributions of nonisothermal effects [dashed line, Eq. (10), and pV work (dash-dotted line, Eq. (7)] for argon at 50 K and $S = 869$.

of pV work takes over and leads to an overall decrease of the rate.

We have performed standard molecular dynamics simulations of Lennard-Jones argon nucleation at 50 K ($N_{Ar} = 343$, $S = 869$) and 80.7 K ($N_{Ar} = 512$, $S = 10.5$) with Lennard-Jones helium as carrier gas in order to verify the predictions of our model. Details of the simulation are similar to Ref. [16]. The rates were analyzed using a method based on mean first-passage times [21]. The studied N_c/N ratios range from 1 to 20. We have renormalized the simulation data to the first point of each series because we are only interested in the deviation arising from an increase of the amount of carrier gas. Figure 2 shows the simulation result together with the prediction of Eq. (12), which is also renormalized by the same fixed value. The agreement is quite remarkable. At 50 K, we only observed a slight increase in the rate with increasing amount of carrier gas. On the other hand, the rate already starts to
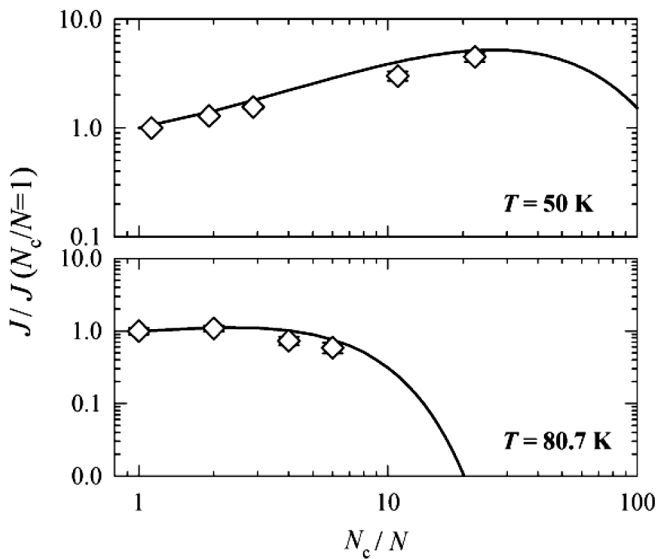

FIG. 2.   Comparison of MD results with theoretical prediction of the pressure effect, Eq. (12).

drop at a much smaller ratio of $N_c/N = 4$ at 80.7 K, again following the theoretical prediction remarkably close.

We now take a closer look at the influence of temperature on the pressure effect. Figure 3 again shows the pressure effect for argon, this time for three different nucleation temperatures. We took the supersaturations at each T to correspond to approximately the same rate from an earlier work [20]. The nonisothermal effects, Eq. (10), are only weakly depending on the supersaturation of the system. The pV-work term, however, gets more and more pronounced the higher the temperature. The reason for this is the huge change in the equilibrium vapor pressure by almost 3 orders of magnitude with increasing T. Hence, the same p_c/p ratio corresponds to a much higher total pressure in the system and the pV-work contribution is taking over earlier than at lower T. We have also framed a region of ratios that can be encountered experimentally [17]. In a typical experiment [4,5] to study the pressure effect, one would fix T and S and vary the total pressure by increasing the amount of carrier gas. We can do the same in Fig. 3, going from 3:1 to 20:1. At 50 K we observe a mild increase of the rate of about a factor of 2. There is practically no change in the rate at 65 K, at least none that would be detectable by available experimental techniques. Finally, at 80.7 K, we only observe a strong decrease of the rate of up to 2 orders of magnitude. Thus, we understand clearly how it is possible to observe only a positive, a negative, or no effect at all for the same substance. Both the sign at any given p_c/p ratio and the magnitude of the effect will strongly depend on the equilibrium vapor pressure (thus on the substance and temperature) and the experimental window of accessible p_c/p ratios.

Finally, we discuss some of the generic conclusions that can be drawn from our model with respect to different experimental situations. Since experiments greatly vary in the preparation, parameters, rate window, evaluation method, etc., a careful evaluation requires a comprehensive analysis that we leave for a future work. In general, we can distinguish between two different limiting behaviors of the
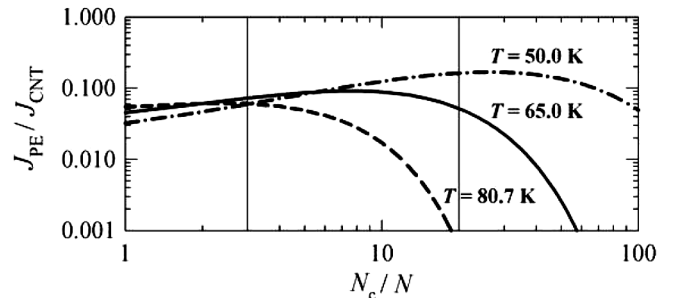

FIG. 3.   Pressure effect for argon at three different temperatures, 50 K (dash-dotted line), 65 K (solid line), and 80.724 K (dashed line) as a function of the ratio of carrier gas to vapor. The supersaturations at each temperature correspond to a base rate of about 10^{25} cm^{-3} s^{-1} [20]. The vertical lines frame a region of N_c/N ratios typically encountered in experiments.

pressure effect, depending on the relative influence of the pV-work term and, therefore, the total pressure $p_{tot} = p + p_c$. If $\frac{p_{tot}v_l}{k_BT} \ll \ln S$, the contribution of pV work can be neglected and the only noticeable contribution comes from nonisothermal effects. In that case, the possible influence of the pressure effect follows the dashed line in Fig. 1, and the only effect we could observe in an experiment would be a slight increase in the rate with increasing amount of carrier gas. Note also that we would not observe any pressure effect at all if we already started from high molar fractions of carrier gas. Interestingly, these are the conditions that we typically find in nucleation pulse chambers [22], where the total pressure varies only very little around 1 bar and where carrier gas fractions are high. Our analysis thus justifies why no effect is found in these experiments. In the opposite limit, when p_c/p is large and $\frac{p_{tot}v_l}{k_BT} \sim \ln S$, the system is perfectly thermalized but the dominating pV work leads to a significant overall decrease of the rate. Moreover, we can make an estimate of the changes in the critical size in terms of the CNT estimate [11],

$$n^* = \frac{32\pi}{3} \frac{v_l^2 \gamma^3}{\Delta \mu_{eff}^3}, \tag{13}$$

again replacing the chemical potential by the effective one, Eq. (6). Equation (13) shows that a further increase of the carrier gas pressure (or similarly p_{tot}) would also lead to an increase in n^*. In an experiment, this might be noticeable by an increase in the slope of a nucleation rate isotherm, which is connected to the critical size via the nucleation theorem [13]. However, care must be taken in that kind of analysis because the nucleation theorem in principle requires that the carrier gas pressure p_c is also fixed.

In summary, we have presented a simple model that is able to shed light on one of the biggest puzzles in current research of vapor-liquid nucleation: the "pressure effect." The investigation of this effect is often entangled between experimental uncertainties, wildly different experimental conditions and procedures, and theoretical interventions on different stages of the modeling of nucleation and growth. We have presented a physically very appealing way to disentangle most of these ambiguities by properly incorporating the presence of a carrier gas into CNT. Simulation results corroborate the validity of the model quite impressively. Still, we cannot discard the influence of other factors on the observed pressure effect. Nevertheless, these factors, if applicable, can be added easily to our model as secondary contributions to the more fundamental and inevitable physical roles that the presence of an ambient carrier gas plays in nucleation and which are accounted for in our model. For example, it is straightforward to include nonidealities of the vapor and carrier gas as well as the compressibility of the liquid, which surely will play a more prominent role the higher the pressure. Another

possible influence we have neglected here is a change in the kinetic prefactor. Finally, we deliberately separated the influence of a truly inert carrier gas pressure from other effects such as binary nucleation or surface adsorption. It is somehow misleading to include these under the same pressure effect tag because even though the strength of them may depend on pressure, their *origin* certainly is not the pressure of the carrier gas. In any case, the insights provided by the model presented in this Letter will undoubtedly be very helpful to quantify and remove the influence of the carrier gas on experiments. This opens the door to a more accurate evaluation of nucleation rates, which has important implications on many atmospheric and technological processes.

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