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# Volumes of critical bubbles from the nucleation theorem

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A corollary of the nucleation theorem due to Kashchiev [*Nucleation: Basic Theory with Applications* (Butterworth-Heinemann, Oxford, 2000)] allows the volume $V^*$ of a critical bubble to be determined from nucleation rate measurements. The original derivation was limited to one-component, ideal gas bubbles with a vapor density much smaller than that of the ambient liquid. Here, an exact result is found for multicomponent, nonideal gas bubbles. Provided a weak density inequality holds, this result reduces to Kashchiev's simple form which thus has a much broader range of applicability than originally expected. Limited applications to droplets are also mentioned, and the utility of the $p_{T,x}$ form of the nucleation theorem as a sum rule is noted. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2354493]

## I. INTRODUCTION

Bubble nucleation occurs in processes involving boiling or cavitation.[1] In many cases, e.g., polymeric foam processing,[2] vulcanism,[3] and cosmological phase transitions in the early universe,[4] the size of the critical bubbles produced by nucleation is an important boundary condition influencing the subsequent evolution of the process. While it is generally a routine matter to determine the critical bubble size from theory,[1–15] experimental values are difficult to obtain because of the scarcity of measured bubble nucleation rates.[8,16]

Using a version of the nucleation theorem[5,17–29] (NT) to analyze measured nucleation rates, experimental values for the molecular content of critical droplets have been obtained for many years.[19,20] For multicomponent systems, this exact version of the NT (Refs. 19–21 and 27) provides the excess number of molecules $\Delta n_i$ of species $i$ for the critical cluster as a derivative of the reversible work of critical nucleus formation $W$,

$$\Delta n_i = -\left(\frac{\partial W}{\partial \mu_{\alpha,i}}\right)_{T,\mu_j}. \tag{1}$$

Here, $\mu_{\alpha,i}$ is the chemical potential of component $i$ in the bulk, metastable mother ($\alpha$) phase, and the chemical potentials of the other components, $j \neq i$, are also held fixed (subscript $\mu_j$) in taking this partial derivative. For droplet nucleation this result correlates nicely with intuitive notions of cluster size since the number of dilute vapor phase molecules displaced by the droplet is very small, and we have as an excellent approximation $\Delta n_i = n_i^*$, where $n_i^*$ is simply the number of molecules of type $i$ in the critical cluster. For pure bubble nuclei, this simple interpretation fails because the value of $\Delta n_i$ is dominated by the number of dense liquid phase molecules displaced by the bubble phase and will be a negative number;[21] for a mixture, $\Delta n_i$ will be negative for at least one species. This difficulty of interpretation was overcome by Kashchiev,[5] who found a corollary to the NT that allows one to determine critical bubble volumes, as in Ref. 16, from measured nucleation rates.

This corollary, Eq. (14.13) of Ref. 5, was derived for low density, ideal gas bubbles in a pure metastable liquid. It reads

$$V^* = \left(\frac{\partial W}{\partial P_\alpha}\right)_T = -kT\left(\frac{\partial \ln J}{\partial P_\alpha}\right)_T, \tag{2}$$

where $V^*$ is the volume of the critical bubble nucleus with respect to the equimolecular dividing surface (EDS), $P_\alpha$ is the pressure of the metastable liquid phase, and $J$ is the nucleation rate, given as usual by

$$J = A\exp(-W/kT), \tag{3}$$

with the good assumption that $A$ is independent of $P_\alpha$.

Here, I generalize this result for multicomponent nonideal systems and show that Kashchiev's result is an excellent approximation under much less restrictive conditions than he assumed. Applications to critical droplet properties are also noted. Lastly, another recent result of Kashchiev,[29] termed the $p_{T,x}$ form of the NT and used here in generalizing Eq. (2), is shown to serve as a sum rule constraining results found independently by applying the NT to experimental data using different sets of independent variables.

## II. THERMODYNAMIC DERIVATION

The thermodynamic formalism used is similar to that of Oxtoby and Kashchiev.[21] The total system is at constant temperature $T$ and its volume is split into two parts,

$$V = V_\alpha + V_\beta, \tag{4}$$

where $\alpha$ and $\beta$ denote the original phase and the new (nucleated) phase, respectively. Following Gibbs,[30] the interface volume equals zero, and the actual values of $V_\alpha$ and $V_\beta$ are determined by the location of a thermodynamic dividing surface. The same dividing surface also determines the number of molecules, $n_{\phi,i}$, of each species $i$ in each phase $\phi$ under the assumption that each phase is a uniform system with constant species densities $\rho_{\phi,i}$,

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$$n_{\phi,i} = \rho_{\phi,i} V_\phi . \tag{5}$$

These densities are evaluated in the interior of each phase far from the interfacial zone. To conserve the total numbers of molecules of each species it is customary to introduce the so-called surface excess numbers of molecules $n_{s,i}$ that account for the deviations in the interfacial region of the actual density profiles from the idealized uniform densities of the two phases. The total number of molecules of species $i$ can then be written as

$$n_i = n_{\alpha,i} + n_{\beta,i} + n_{s,i} . \tag{6}$$

The specific values of the $n_{s,i}$ also depend on the choice of the dividing surface. Finally, the volume of each phase is defined as

$$V_\phi = \sum_i n_{\phi,i} v_{\phi,i} , \tag{7}$$

where $v_{\phi,i}$ is the partial molecular volume of phase $\phi$ far from the interface. Note that, in general, the $v_{\phi,i}$ are functions of composition that depend on the density, pressure, and temperature of the phase in question.

To derive an exact version of Eq. (2), start with an explicit definition for $\Delta n_i$,[21]

$$\Delta n_i = n_{s,i} + n_{\beta,i} - V_\beta n_{\alpha,i} / V_\alpha , \tag{8}$$

multiply both sides by $v_{\phi,i}$, sum over $i$, and solve for $V_\beta$ to find

$$V_\beta = \sum_i v_{\phi i}(\Delta n_i - n_{s,i}) \bigg/ \left( \sum_j v_{\phi j}(\rho_{\beta j} - \rho_{\alpha j}) \right), \tag{9}$$

for the critical volume of the freshly nucleated phase. This formal result involves the quantities $\rho_{\beta i}$ (and $v_{\beta i}$ when $\phi = \beta$) that cannot, at present, be determined experimentally. With known values of $\rho_{\beta i}$ and $v_{\beta i}$, the $n_{s,i}$ can be determined for a specific Gibbs dividing surface,[31] but this is feasible only for theoretical models of critical nuclei, including the virtual nucleus based on Gibbs idea of a reference phase.[30] Nevertheless, the sum involving the $n_{s,i}$ can be eliminated by making an appropriate choice for a Gibbs dividing surface. An obvious choice is to locate the dividing surface where

$$\sum_i n_{s,i} v_{\phi,i} = 0 . \tag{10}$$

With $\phi = \beta$, this corresponds to the Koenig[31] and Buff[32] dividing surface (KBDS) used in several recent papers[33–35] for droplets. As noted by Buff,[32] the KBDS is conjugate to the Gibbs surface of tension since the distance between these two dividing surfaces, known now as the Tolman length,[36] affects the curvature dependence of the surface tension.[31] The KBDS is, thus, the multicomponent analog of the EDS in one-component systems. With Eq. (10) and the identity $\Sigma_i \rho_{\phi,i} v_{\phi,i} = 1$, Eq. (9) simplifies to

$$V'_\beta = \sum_i v_{\beta i} \Delta n_i \bigg/ \left( 1 - \sum_j v_{\beta j} \rho_{\alpha j} \right), \tag{11}$$

where the prime designates the use of the KBDS. While simpler, Eq. (11) still contains the experimental unknowns $v_{\beta i}$. A second dividing surface, here termed the complementary KBDS (CKBDS), comes from putting $\phi = \alpha$ in Eq. (10). In this case Eq. (9) reduces to

$$V''_\beta = \sum_i v_{\alpha i} \Delta n_i \bigg/ \left( \sum_j v_{\alpha j} \rho_{\beta j} - 1 \right), \tag{12}$$

where the double prime indicates the use of the CKBDS. This simpler form still contains the experimental unknowns $\rho_{\beta j}$. The CKBDS seems not to have been used previously, but it is essential to this paper's main result.

## III. ONE-COMPONENT LIMIT

When the system contains only one component $(i=1)$, $v_\phi = 1/\rho_\phi$, the two dividing surfaces are degenerate and equal to the EDS for which $n_s = 0$, and Eqs. (11) and (12) reduce to

$$V_\beta = -\Delta n / (\rho_\alpha - \rho_\beta) . \tag{13}$$

Using the Gibbs-Duhem equation for the bulk mother phase at constant $T$, $V_\alpha dP_\alpha = n_\alpha d\mu_\alpha$, Eq. (1) can be recast as $\Delta n = -\rho_\alpha (\partial W / \partial P_\alpha)_T$, as shown before[22,26] in other ways. With this result, Eq. (13) then becomes

$$V_\beta = \frac{\rho_\alpha}{\rho_\alpha - \rho_\beta} \left( \frac{\partial W}{\partial P_\alpha} \right)_T , \tag{14}$$

which differs from Kashchiev's approximate form by the ratio $\rho_\alpha / (\rho_\alpha - \rho_\beta)$. From this exact form, we see that Kashchiev's result for bubbles is accurate to 10% (which generally exceeds experimental accuracy) when $\rho_\beta \approx \rho_\alpha / 10$ and that it is not necessary to assume that the $\beta$ phase is an ideal gas. A vapor whose density was 10% of a liquid would typically be highly nonideal. Using density functional theory (DFT), Shen and Debenedetti[9] have found critical bubbles with a high density bubble phase. Even for a bubble phase density equal to one-half the liquid density, $\rho_\beta \approx \rho_\alpha / 2$, Kashchiev's approximate formula would only underestimate the critical bubble volume by a factor of 2, which corresponds to a modest 26% underestimate for the critical radius, assuming a spherical bubble. Thus, by comparison with the exact result [Eq. (14)], we conclude that Eq. (2) is capable of giving fairly accurate estimates for the EDS value of $V_\beta$ even under extreme conditions (high density and nonideal bubble phase) not considered in its original domain of applicability.

When the $\beta$ phase is a droplet in a low density vapor, $\rho_\alpha << \rho_\beta$, Eq. (13) yields the well-known result[19,21] that the molecular content of the nucleus, defined as $n_\beta$, is essentially equal to the excess number of molecules, $V_\beta \rho_\beta = n_\beta \approx \Delta n$. This result reaffirms the long-known importance of the EDS for one-component droplet nucleation.[32,37–39] Since $\rho_\beta$ is unknown, the value of $V_\beta$ cannot be determined.

## IV. MULTICOMPONENT FORM

### A. Generalized Kashchiev formula and sum rule

In an isothermal $N$ component system $W$ may be regarded either as a function of the $N$ chemical potentials $\mu_{\alpha,i}$ or as a function of $P_\alpha$ and $N-1$ appropriate composition variables, say, the mole fractions $x_i$ in the $\alpha$ phase. We then obtain directly from the chain rule,

$$\left(\frac{\partial W}{\partial P_\alpha}\right)_{T,x} = \sum_i \left(\frac{\partial W}{\partial \mu_{\alpha,i}}\right)_{T,\mu_j}\left(\frac{\partial \mu_{\alpha,i}}{\partial P_\alpha}\right)_{T,x}, \tag{15}$$

where the subscript $x$ indicates a partial derivative taken at fixed composition. This simplifies to

$$(\partial W/\partial P_\alpha)_{T,x} = -\sum_i v_{\alpha,i}\Delta n_i, \tag{16}$$

with the aid of Eq. (1) and the familiar thermodynamic relation, $(\partial \mu_{\alpha,i}/\partial P_\alpha)_{T,x} = v_{\alpha,i}$. Equation(16) was recently derived by Kashchiev,[29] who termed it the $p_{T,x}$ form of the NT. With this equality, Eq. (12) becomes the multicomponent analog of Eq. (14),

$$V''_\beta = \chi\left(\frac{\partial W}{\partial P_\alpha}\right)_{T,x} = -kT\chi\left(\frac{\partial \ln J}{\partial P_\alpha}\right)_{T,x}, \tag{17}$$

where

$$\chi^{-1} = 1 - \sum_i v_{\alpha,i}\rho_{\beta,i}. \tag{18}$$

This generalized Kashchiev formula differs essentially from Eq. (2) only by the multiplicative factor $\chi$, and it reduces to Eq. (14) in the one-component limit. Since the composition and pressure of the mother phase are usually well-controlled experimental parameters, the main formal obstacle to applying this corollary of the nucleation theorem to the analysis of data is the experimentally unknown value of $\chi$. While Eq. (16) is essential in deriving Eq. (17), it also has potential value as a sum rule if the two sides of Eq. (16) are evaluated independently. This can be done, in a sense, by finding the $\Delta n_i$, as usual, from a nucleation rate surface[20] that is a function of the $N$ independent $\mu_{\alpha,i}$ and by determining $(\partial W/\partial P_\alpha)_{T,x}$ using a nucleation rate surface that is a function of $P_\alpha$ and $N-1$ mole fractions. Of course, the two surfaces are not fully independent because they rely on the same rate data. Thus, Eq. (16) actually serves to check the internal consistency of the data and data conversion procedures employed in the mathematical construction of the surfaces, but this should still be worthwhile.

### B. Bubble nuclei

The simple form of Eq. (2) is rigorously recovered only when $\chi \to 1$. For example, because of the identity, $\Sigma_i \rho_{\alpha,i} v_{\alpha,i} = 1$, and the strong inequality, $\rho_{\beta,i} << \rho_{\alpha,i}$, expected on physical grounds if the bubble phase were a highly dilute gas mixture, we then would have $\Sigma_i \rho_{\beta,i} v_{\alpha,i} << 1$. In this case, Eq. (17) simplifies to

$$V''_\beta = \left(\frac{\partial W}{\partial P_\alpha}\right)_{T,x} = -kT\left(\frac{\partial \ln J}{\partial P_\alpha}\right)_{T,x}, \tag{19}$$

which can be evaluated solely from experimental data. On the other hand, it is only necessary that the bubble phase densities satisfy the weaker inequality, $\Sigma_i \rho_{\beta,i} v_{\alpha,i} < 0.1$, for Eq. (19) to have an accuracy generally exceeding what is experimentally attainable. For some binary systems, DFT calculations by Talanquer and Oxtoby[7] and Talanquer *et al.*[10] have shown that the bubble phase density of the mother phase "solute" may be quite "liquid like," so that even this weaker inequality may not be obeyed. Then the factor $\chi$ in Eq. (17) exceeds unity by more than 10%, and the bubble volume estimated using Eq. (19) is only a lower bound to the correct result. Nevertheless, based on the order of magnitude arguments made for the one-component case, these lower bounds should be reasonably close to the correct values.

### C. Droplet nuclei

Droplet nucleation is most often studied in nearly ideal vapor mixtures for which the relations $v_{\alpha,i} = kT/P_\alpha = 1/\rho_\alpha$ are quite accurate ($\rho_\alpha$ is the total density of the $\alpha$ phase). Then Eq. (17) immediately simplifies to

$$V''_\beta = (\partial W/\partial P_\alpha)_{T,x}/(1-\rho_\beta/\rho_\alpha). \tag{20}$$

Although the total density of the new droplet phase $\rho_\beta$ is experimentally unknown, we expect, generally, $\rho_\beta/\rho_\alpha >> 1$. When this inequality holds, it yields an excellent approximation for the total molecular content $n''_\beta = V''_\beta \rho_\beta$, within the CKBDS,

$$n''_\beta \approx -\rho_\alpha(\partial W/\partial P_\alpha)_{T,x} \approx \sum_i \Delta n_i. \tag{21}$$

Note that the exact form of the right-hand equality, rearranged slightly, is given by Eq. (16). If we apply the dilute vapor approximation to Eq. (11), $\Sigma_j v_{\beta j}\rho_{\alpha j} << 1$, we obtain the result

$$V'_\beta \approx \sum_i v_{\beta i}\Delta n_i, \tag{22}$$

which is mainly of formal interest due to the presence of the experimentally unknown quantities $v_{\beta i}$. By comparison with Eq. (7) with $\phi = \beta$, it should be reasonable, although not rigorous, to make the identifications $n'_{\beta,i} \approx \Delta n_i$ for the molecular content of species $i$ in the droplet. As for unary droplets, the values of $V'_\beta$ and $V''_\beta$ cannot be determined.

## V. CONCLUSIONS

The main result of this paper [Eq. (17)] is an exact expression for $V''_\beta$, the volume of a critical nucleus as defined by the CKBDS. Unlike the original NT [Eq. (1)], which is invariant to the choice of dividing surface,[21] the critical volume depends in an essential way on such a choice. In accordance with the Gibbsian formulation of interfacial thermodynamics, the volume of the nucleus is determined by the location of the chosen dividing surface. The present choice, the CKBDS, is advantageous in that it leads to the simple pressure derivative term in Eq. (17), but it also produces the factor $\chi$ [Eq. (18)], whose experimental evaluation is not possible at present. Nevertheless, for bubble nucleation, arguments given above imply that in many circumstances $\chi \approx 1$, so that this corollary of the NT yields a well-defined value for $V''_\beta$ that can be found solely from experimental variables. In several instances it has been shown theoretically that the bubble phase is not dilute in all components.[7,9,10] In these cases, the approximation $\chi \approx 1$ will not be satisfied, and an accurate value for $V''_\beta$ requires a more precise estimate for $\chi$ from molecular theory. In any case, the corollary with $\chi = 1$ always results in a lower bound for $V''_\beta$. One could invoke

Gibbs' idea of a reference phase to determine the values of $\rho_{\beta i}$ and $v_{\beta i}$ needed to fully evaluate $V'_\beta$ and $V''_\beta$, but for bubbles this approach seems destined to yield low density phases and, thus, the value $\chi \approx 1$. A final point to note is that the corollary neither assumes nor yields information about the shape of the critical bubble; only its volume is determined.

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