# SCALING PROPERTIES OF THE CRITICAL NUCLEUS IN CLASSICAL AND DENSITY FUNCTIONAL NUCLEATION THEORIES

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**Abstract-** Scaling relations are developed for the number of molecules in the critical nucleus, $g^*$, and the nucleation barrier height, $W^*$. Density functional (DF) calculations for vapor-liquid nucleation confirm these relations and show systematic departure of the ratio $W^*/(g^*\Delta\mu)$ from its classical value, 1/2, with increasing difference in chemical potential between the supersaturated vapor and bulk condensed phase, $\Delta\mu$. Discrepancies between classical and DF nucleation theories and between the classical theory and experiment are interpreted using these results.

**Keywords-** Nucleation, Clusters, Phase transitions, Density-functional theory

## INTRODUCTION

It has been recognized in recent years that homogeneous vapor-liquid nucleation plays a central role in many atmospheric processes. Accordingly, considerable attention has been paid to formulation of phenomenological theories, which try to predict nucleation rates quantitatively starting from macroscopic, measurable properties of fluids (for a review, see [1]). However, at present it is not clear that any of these theories is overall more successful than the classical nucleation theory [2]. On the other hand, more fundamental theoretical approaches that aim to describe the properties of nucleating clusters on a molecular level have been developed [3,4] in parallel with more sophisticated experimental techniques [1]. In this paper, we derive scaling properties for the critical nucleus which are in harmony with novel findings from both experimental and theoretical studies, and which it is hoped will guide the phenomenological efforts in a more productive direction.



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## THEORY

Consider the nondimensional ratio $W^* / (g^* \Delta\mu)$ where $W^*$ is the nucleation barrier height, $g^*$ is the number of molecules in the critical nucleus, and $\Delta\mu$ is the free energy difference between the vapor, at a given saturation ratio $S$, and the bulk condensed phase driving the phase change. This ratio can be written in the following general form:

$$\frac{W^*}{g^* \Delta\mu} = \frac{1}{2} - f(g^*, \Delta\mu) \tag{1}$$

where $f$ gives the departure from classical nucleation theory. In Refs. 4 and 5 it is shown that the derivative of $W^*$ with respect to $\Delta\mu$ equals $-g^*$. Differentiation of Eq. 1 using this result gives:

$$\Delta\mu \frac{d}{d\Delta\mu} g^* + 3g^* = 2 \frac{d}{d\Delta\mu} (f g^* \Delta\mu). \tag{2}$$

In the classical theory, $f = 0$, and the solution of Eq. 3 for $g^*$ is a homogeneous function of the form

$$g^* = C(T)(\Delta\mu)^{-3} \tag{4}$$

in agreement with the Kelvin relation.

An interesting result of the DF calculations is that Eq. 4 seems to have a validity beyond the capillarity drop approximation of CNT. This is shown in Fig. 1. To the extent that Eq. 4 is valid, the right hand side of Eq. 2 must also equal zero. For this homogeneity class of systems we have shown that the barrier height differs from the result of classical nucleation theory (CNT) by a constant value at fixed temperature [6]:

$$W^*_{CNT} - W^* = D(T) \equiv n^*_s \Delta\mu / 2 \tag{5}$$

where $n^*_s$ is the area of the surface of tension times the superficial density. A second consequence of homogeneity (Eq. 4) is the following:

$$\frac{W^*}{g^* \Delta\mu} = \frac{1}{2} - \frac{D(T)}{C(T)}(\Delta\mu)^2 \tag{6}$$

showing recovery of CNT along the coexistence curve, $\Delta\mu = 0$, and quadratic dependence in the departure from CNT with increasing $\Delta\mu$. This behavior is seen in the results of the DF calculations shown in Fig. 2.

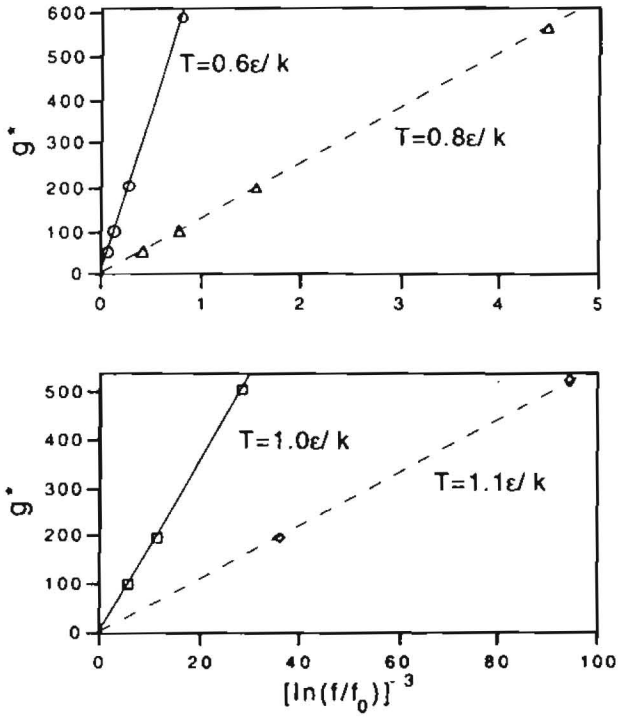


*Fig. 1 Density functional results for $g^*$ (markers) and comparison with scaling (lines) from Eq. 4. Temperatures are given in reduced units $kT/\varepsilon$ where $\varepsilon$ is the characteristic energy for the Lennard-Jones system of Ref. 3. Note for the abcissa that the fugacity ratio is* $\ln(f/f_0) = \Delta\mu / kT$.

## SUMMARY

Measurements of nucleation rate provide a direct probe of $W^*$, $g^*$, and, for multicomponent systems, nucleus composition [4,5]. In addition to providing an excellent description of the DF results, the scaling theorems (Eqs. 4-6) are shown to be supported by such measurements [6]. Finally, the scaling theorems constrain the departure from CNT and therefore can guide the construction of phenomenological nucleation theories.

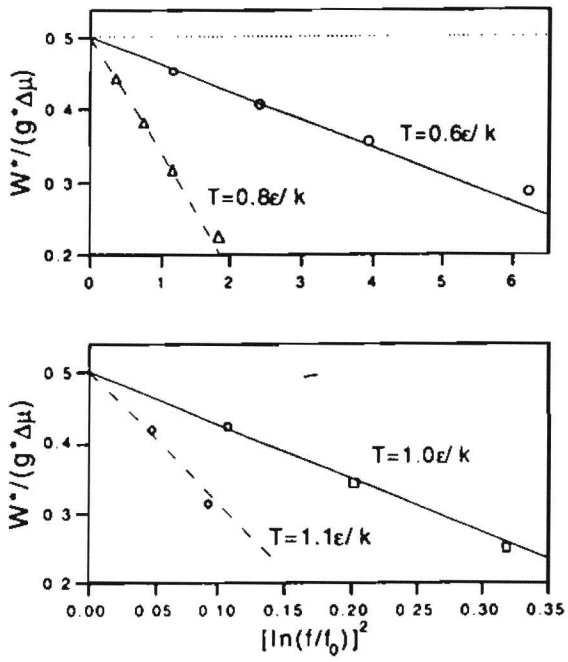


*Fig. 2. Density functional results for $W^*/(g^*\Delta\mu)$ (markers) and comparison with scaling (lines) from Eq. 6. Temperatures are as reported in Fig. 1. DF results at each temperature are for the same conditions as in Fig. 1. Horizontal lines are the prediction of classical nucleation theory.*

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