

Fundamentals of the Diffuse Interface Theory of Nucleation

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The basic assumptions of the diffuse interface theory of nucleation (bulk physical properties at the center of nuclei and size-independent interface thickness) are discussed in the light of field-theoretical calculations and light/X-ray reflectivity measurements. It is concluded that, contrary to recent suggestions, the basic assumptions of the diffuse interface theory are reasonable.

Introduction

Despite efforts and recent promising developments, a well proven theoretical description of vapor condensation is yet missing.¹ Nucleation rates predicted by the classical theory (CNT) deviate from experiments by several orders of magnitude.² The origin of this failure is the “capillary” approximation that assigns bulk liquid properties to the whole volume of the nucleus. This assumption is questionable for typical nuclei which contain 20 to a few hundred molecules. Experiments³ and computer simulations⁴ show that the interface is about two molecular layers thick; i.e., the nuclei should be nearly “all interface”. It is known for some time that this problem can be rectified by introducing a size-dependent surface tension.⁵ However, the correction cannot easily be determined, and (more or less justified) assumptions are made when performing the calculations. Phenomenological models based on different assumptions achieved quite a success in describing the condensation experiments.¹ It is, however, important to see whether the assumptions made are realistic or not. Computer simulations or first principles calculations with realistic molecular interactions offer a possibility to perform the test.

In this paper attention is focused on a recent phenomenological approach, the diffuse interface theory (DIT),⁶ which gave a substantially improved description of condensation of nonpolar,⁶ weakly polar^{6d} and metallic substances^{6c,d} without using adjustable parameters. This model can easily be generalized to other nucleation processes.^{6b,7} It is consistent with data on crystal nucleation in undercooled liquids (hydrocarbons,^{6b} metals,^{6b,7b} water^{7c}), oxide and metallic glasses.^{6b,7a,b,d,e} In the DIT the work of formation of droplets is expressed as

$$W = \int_V \{ \Delta h(\mathbf{r}) - T \Delta s(\mathbf{r}) \} d\mathbf{r} = \kappa \{ R_H^3 \Delta h_0 - R_S^3 T \Delta s_0 \} \quad (1)$$

where $\Delta h(\mathbf{r}) = \rho(\mathbf{r})[u(\mathbf{r}) - u_v] + p_v[1 - \rho(\mathbf{r})/\rho_v]$ and $\Delta s(\mathbf{r}) = \rho(\mathbf{r})[s(\mathbf{r}) - s_v]$ are the local volumetric enthalpy and entropy relative to the vapor (v); u , s , and ρ are the specific internal energy, entropy, and the number density of molecules; R_H and R_S are the positions of the enthalpy and entropy surfaces defined by $\kappa R_H^3 \Delta h_0 = \int_V \Delta h(\mathbf{r}) d\mathbf{r}$ and $\kappa R_S^3 \Delta s_0 = \int_V \Delta s(\mathbf{r}) d\mathbf{r}$; $\Delta h_0 = \Delta h(0)$ and $\Delta s_0 = \Delta s(0)$ are evaluated at the center of the droplet; $\kappa = 4\pi/3$ is the volume of the unit sphere, while the integrals are to be performed for the volume V of the inhomogeneous system (droplet + supersaturated vapor). It is assumed that (i) bulk properties exist at least at the centers of nuclei and (ii) that the characteristic thickness of the interface $R_S - R_H = \delta = \gamma/\Delta h_b$ independently of size, where γ and Δh_b are the interface tension and the volumetric heat of evaporation, respectively.

In this work a simple density functional theory (by van der Waals^{8a} and Cahn and Hilliard;^{8b–d} vdW/CH) is used for testing assumptions (i) and (ii). The results imply that under typical experimental conditions the assumptions of the DIT are reasonable. This contradicts the suggestions of a recent analysis.⁹ The origin of the disagreement is discussed.

Semiempirical Density Functional Theory

In the van der Waals/Cahn–Hilliard theory⁸ the work of formation of droplets is given as

$$W = \int_V \{ \rho(\mathbf{r})[f_h(\mathbf{r}) - f_{h,v}] + c[\nabla \rho(\mathbf{r})]^2 + p_v[1 - \rho(\mathbf{r})/\rho_v] \} d\mathbf{r} \quad (2)$$

where $f_h(\mathbf{r})$ and $f_{h,v}$ are the Helmholtz free energy per molecule of homogeneous fluids of density $\rho(\mathbf{r})$ and ρ_v , respectively, and c is a constant. The second term on the RHS of eq 2 is a simple nonlocal contribution which is responsible for the interface diffuseness. This formulation of the nonlocal term is only valid for smooth cross-interfacial variation of the density. The nucleus corresponds to an extremum of the functional W . The respective (spherically symmetrical) density distribution can be found by solving the Euler equation

$$2c[\rho'' + (2/r)\rho'] = \mu_h(\rho) - \mu_h(\rho_v) \quad (3)$$

under boundary conditions (a) $\rho(r) \rightarrow \rho_v$ for $r \rightarrow \infty$; and (b) $\rho'(r) \rightarrow 0$ for $r \rightarrow 0$, where r is the distance from the center of the nucleus, ' stands for differentiation with respect to r , and $\mu_h(\rho)$ is the chemical potential of the homogeneous fluid of density ρ . In this work a semiempirical version of the vdW/CH theory was developed. The thermodynamic properties of homogeneous fluid were obtained by integrating the van der Waals equation of state. Since fixed van der Waals parameters a and b give a reasonable representation of real fluids in only the vicinity of the critical point (far from the experimental regions), they were treated as temperature dependent parameters. At a fixed temperature a and b were chosen so as to reproduce the experimental equilibrium pressure (p_{eq}) and liquid density (ρ_l), while c was evaluated from the measured surface tension of the planar interface. Equation 3 was solved for $\rho(r)$ numerically by using a fourth order Runge-Kutta method.¹⁰

Results and Discussion

The most reliable data for homogeneous vapor condensation are available on nonane. Therefore, calculations were performed with the properties of this liquid at $T = 270.1$ K, with supersaturations $S_p = p/p_{eq}$ varied between 3 and 300. (The temperature falls into the experimental range, while the S_p range covers the experiments.^{2a,b}) Within the vdW/CH theory the

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enthalpy and entropy distributions are identified as $\Delta h(r) = \rho(r)[u_h(r) - u_{h,v}] + c[\rho'(r)]^2 + p_v[1 - \rho(r)/\rho_v]$ and $\Delta s(r) = \rho(r)[s_h(r) - s_{h,v}]$. The interfacial profiles calculated for various supersaturations are shown in Figure 1a. The radii of nuclei (position of the entropy surface) and the 10–90 % thickness (d_{10-90}) of the interface are depicted as a function of the excess number of molecules (i^*) in Figure 1b. The thermodynamic data at the center of nuclei are presented in Figure 1c. Note, that bulk properties are preserved in the center until d_{10-90} becomes comparable with the radius of the nucleus. This originates from the facts that the interface thickness d_{10-90} is roughly the half of the total thickness of the interface and that R_S^* lies approximately at the midpoint of the interface region; i.e., the interface reaches the center when $R_S^* \approx d_{10-90}$. This happens for very small droplets: $i^* \approx 9$. The characteristic thickness δ is shown as a function of size in Figure 1d. It is remarkable that δ has a maximum at very small sizes and decreases to the value for planar interface. Under typical experimental conditions (near the vertical line) the size-dependence is weak ($\delta \approx \text{constant}$).

Note, however, that the vdW/CH theory is based on a few approximations that may restrict its applicability. For example, the square-gradient approximation is known to give a poor description of the interface far from the critical point.¹¹ Furthermore, being a mean field calculation, the vdW/CH theory does not account for the capillary waves, which play an important role in determining the interface diffuseness.^{12,13} Therefore, it is essential to test the predicted interface structure. Relevant interfacial information may be obtained from light or X-ray reflectivity measurements. The predicted interface thickness is compared to the experimental data in Table 1. Despite the deficiencies of the model, the results are quite reasonable for nonpolar and metallic substances (about 25% lower than the experimental data). (A more significant underestimation (by 39–56%) was found for polar substances.¹⁴) Evidently, the agreement occurs by cancellation of errors of the applied approximations. Nevertheless, what counts from the viewpoint of testing the DIT is that an accurate surface tension and a reasonable interface thickness are ensured by the semiempirical vdW/CH approach.

Now we return to the validity of the DIT assumptions. To the author's knowledge no experimental data are available for d_{10-90} of nonane. Utilizing, however, that for nonpolar and metallic substances the vdW/CH theory underestimates d_{10-90} by typically 25%, we can estimate the respective value as $d'_{10-90} = 1.33 \times d_{10-90}$ (see dashed line in Figure 1b). It was found that the R_S^* vs i^* curves from the vdW/CH and the DIT are very close (to a good approximation the entropy surface coincides with the equimolar surface⁹) and that the critical nuclei predicted by the DIT for the experimental supersaturation ($S_p = 14.6$) contain $i^* = 39.4$ molecules. Then, $d'_{10-90} = 8.4$ Å which is smaller than $R_S^* = 13.4$ Å. Thus, *bulk properties are expected to prevail in a central region of ~ 10 Å diameter*. Comparable results were obtained under other experimental conditions.

Finally, the nucleation rate was calculated for the vdW/CH theory as $J = J_0 \exp(-W^*/kT)$, where the classical prefactor $J_0 = \rho_v^2 \rho_l^{-1} [2\gamma/(\pi m)]^{1/2}$ was used (m is the molecular mass). Under experimental conditions $T = 270.1$ K and $S_p = 14.6$ the vdW/CH prediction ($J_{\text{vdW/CH}} = 1.15 \text{ cm}^{-3} \text{ s}^{-1}$) falls between the experimental value ($J_{\text{exp}} = 1.78 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$) and that from the CNT ($J_{\text{CNT}} = 0.51 \text{ cm}^{-3} \text{ s}^{-1}$), however, much closer to the latter. This shows that the size-dependent correction to the surface tension in the vdW/CH theory is rather small. Comparable results were obtained for other experimental conditions. It is worth noting, that the DIT predictions are in a much better

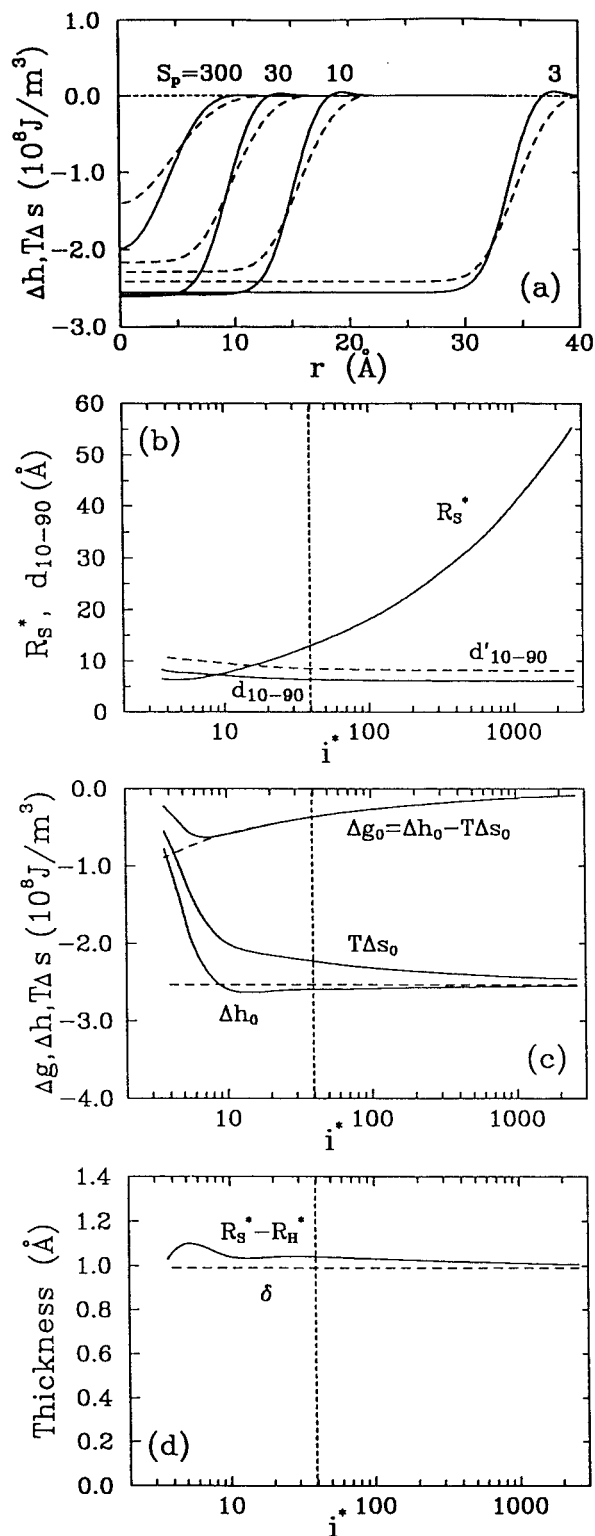


Figure 1. Characteristics of nuclei vs. size, as predicted by the semiempirical van der Waals/Cahn–Hilliard theory for nonane at 270.1 K: (a) Interfacial enthalpy (solid line) and entropy density (dashed line) profiles at supersaturations $S_p = 3, 10, 30$, and 300. (b) The radius of droplets, R_S^* and the 10–90% thickness of the interface, d_{10-90} (solid lines) vs the excess number of molecules, i^* . The enhanced thickness $d'_{10-90} = 1.33 \times d_{10-90}$ (dashed line) is also shown. The vertical dashed line stands for the experimental point $T = 270.1$ K and $S_p = 14.6$, for which $i^* = 39.4$. (c) Thermodynamic properties at the center of nuclei (solid lines) vs i^* . For the sake of comparison, the bulk volumetric enthalpy and Gibbs free energy differences (dashed lines) are also indicated. (d) Distance of the enthalpy and entropy surfaces (solid line) and its value for the planar limit (dashed line) as a function of i^* .

agreement with the measured nucleation rates.⁶ The difference between nucleation rates from the DIT and vdW/CH originates

TABLE 1: Comparison of the Experimental and Predicted 10–90% Interface Thickness

substance		d_{10-90} (Å)		$d_{vdW/CH}/d_{exp}$	T/T_c
		exp	vdW/CH		
Ar	np	7.9 ^a	6.0	0.76	0.60
CCl ₄	np	5.1–6.0 ^b	4.3	0.72–0.84	0.53
Cs	m	~3.3 ^c	2.4	0.73	0.14
Hg	m	6.2 ^d	4.6	0.74	0.17
H ₂ O	p	3.3 ^b	2.0	0.61	0.46
CH ₃ OH	p	4.8 ^b	2.1	0.44	0.58

^a Reference 3a. ^b Reference 3b. ^c Molecular dynamics result from ref 4c, that reproduces X-ray reflectivity of ref 3c. ^d Reference 3d. ^e The experimental data are from X-ray reflectivity measurements, with the exception of the datum for Ar, which originates from ellipsometry. (notations: vdW/CH, semiempirical van der Waals/Cahn–Hilliard theory; T_c , critical temperature; np, nonpolar; p, polar; m, metallic.

dominantly from the weak size-dependence of the characteristic thickness δ predicted by the latter. It appears that the size-independent δ is a better approximation of the real behavior than the size-independent c assumed in the vdW/CH model. In essence, the vdW/CH calculations imply that the basic assumptions of the DIT are reasonable, a conclusion further stressed by the finding that the DIT gives an improved description for a variety of nucleation processes.^{6,7}

These results contradict a recent analysis by Talanquer and Oxtoby⁹ who applied a simple perturbative density functional theory (PDFT) for a Lennard-Jones (LJ) fluid. While the nucleation rates predicted by the PDFT agree well with those from the DIT in a wide range of experimental conditions, the interface thickness and the physical properties at the center of nuclei are strongly size-dependent. It is suggested that the success of the DIT is at least partly fortuitous.

The origin of the disagreement on the validity of the DIT assumptions is that in the PDFT the interface is much broader (relative to the size of nuclei) than in the vdW/CH theory. (This prevents the appearance of bulk properties at the center of nuclei and influences the distance of the enthalpy and entropy surfaces.) As shown above, the interface thickness predicted by the semiempirical vdW/CH theory is reasonably close to the experimental data. In contrast, the PDFT cannot be directly compared to experiments, since the LJ potential is a rough approximation of the intermolecular forces acting in real substances.¹⁵ Strictly, the PDFT analysis (ref 9) is relevant to the LJ system. Its validity is further restricted by the applied approximations which are manifested in the absence of capillary waves and in surface tension and interface thickness figures¹⁶ that significantly exceed the respective data from computer simulations.^{4a,12} However, the PDFT is successful as an advanced semiempirical model. Choosing its free parameters so as to reproduce the equilibrium pressure, liquid density, and surface tension of nonane, it predicts nucleation rates remarkably improved over those of the classical theory (comparable with the results of the DIT).¹⁷ The respective interfaces are relatively narrow.¹⁸ This raises the possibility that the contradiction between ref 9 and the present work is apparent, and analyses of the DIT in terms of the *semiempirical* versions of the PDFT and vdW/CH lead to closer results than expected from calculations for the LJ fluid. Work is underway to clarify this issue.

Conclusion

The validity range of the diffuse interface theory of vapor condensation has been studied in the framework of the density functional approach. Contrary to a recent analysis, the present semiempirical van der Waals/Cahn–Hilliard model implies that the basic assumptions of the diffuse interface theory (bulk

thermal properties at the center of nuclei and size-independent interface thickness) are reasonable.

Note Added in Proof: A recent self-consistent-field lattice theory for chain molecules by Schlangen et al. (Schlangen, L. J. M.; Koopal, L. K.; Lyklema, J. *J. Phys. Chem.* **1996**, *100*, 3607) describes the surface tension of *n*-alkanes fairly well with model parameters fitted to the temperature dependence of the experimental vapor pressure. The full interface thickness for octane at 290 K is $d = 15$ Å. Similar results ($d_{10-90} = 7.2$ Å, and $d \approx 15$ Å) were reported (Harris, J. G. *J. Phys. Chem.* **1992**, *96*, 5077) for decane at 300 K on the basis of molecular dynamics simulations in which the methyl and methylene groups were treated as Lennard-Jones atoms with realistic bond lengths, bond angle potentials, and torsion potentials. These data indicate that the full thickness $d \approx 2d_{10-90} = 16.8$ Å obtained in this work for nonane at 270 K is quite reasonable.

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