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# Containerless nucleation behavior and supercooling degree of acoustically levitated graphene oxide nanofluid PCM

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ABSTRACT

Acoustic levitation constitutes an alternative experiment technology for avoiding contamination from container walls or other external objects. Graphene oxide nanofluid drop was acoustically levitated and solidified, and supercooling degree of nanofluid drop at different cooling temperatures was measured. The supercooling degree of nanofluid drop can be reduced by 59.79% in comparison to that of the deionized water, and the reduction of supercooling degree gradually weakens with the decrease of cooling temperature. Based on Wenzel's wetting model, the authors established a new physical model of nanosheet to analyze the effect of rough surface on the nucleation behavior and supercooling degree, revealing that only on the upper or lower surfaces of the nanosheets can crystal nucleus form and grow, and nucleation on the thickness surface is difficult. Furthermore, a model for predicting nucleation rate of nanofluid was proposed, suggesting that the nucleation rate increases significantly with the increasing of supercooling degree.



# Comportement de nucléation sans creuset et degré de surfusion d'un PCM nano fluide en oxyde de graphène lévité acoustiquement

*Mots clés :* Oxyde de graphène ; Nano fluide ; Lévitation acoustique ; Degré de surfusion ; Taux de nucléation

## 1. Introduction

Phase change materials (PCMs) are always the focus of attention due to their high energy storage density in ice storage applications. But most PCMs exist big supercooling degrees (Oró et al., 2012; Wang et al., 2014), which result in liquid PCMs not solidifying immediately at the freezing temperature, but starting crystallization only after a temperature well below the freezing temperature is reached. If nucleation does not happen

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**Nomenclature**

| | |
|---|---|
| $\gamma_W$ | the water surface free energy [J m$^{-2}$] |
| $\gamma_I$ | the ice surface free energy [J m$^{-2}$] |
| $\gamma_{IW}$ | the ice–water specific surface free energy [J m$^{-2}$] |
| $\gamma_I^d$ | the dispersion force of ice [J m$^{-2}$] |
| $\gamma_W^d$ | the dispersion force of water [J m$^{-2}$] |
| $\theta$ | the solid–ice contact angle |
| $\theta_{SW}$ | the solid–liquid contact angle |
| $r$ | the rough rate |
| $\Delta G$ | the Gibbs free energy change of system [J] |
| $V_n$ | the volume of crystal nucleus [m$^3$] |
| $\Delta G_m$ | the difference value of volume Gibbs free energy [J] |
| r | the radius of crystal nucleus [m] |
| R | the radius of spherical surface [m] |
| H | the enthalpy [J] |
| S | the entropy [J] |
| T | the thermodynamic temperature [K] |
| $L_V$ | the latent heat per unit volume [kJ kg$^{-1}$] |
| $T_m$ | the thermodynamic temperature of ice melting point [K] |
| $\Delta T$ | the subcooling degree [K] |
| $r^*$ | the critical nucleation radius [m] |
| $r_{max}$ | the maximum ice nucleus radius [m] |
| $K^-$ | the detachment frequencies |
| $D_c$ | the diffusion coefficient |
| $N_S$ | the number of molecule on clusters surface |
| $P_{eq}$ | the balance of probability distribution |
| $R_c$ | the cluster radius [m] |
| k | Boltzmann constant [J °C$^{-1}$] |
| $E_w$ | the diffusion activation energy of water [J mol$^{-1}$] |
| $N_A$ | Avogadro constant |
| $H$ | the thickness of nanosheet [m] |
| $I_n^0$ | the nucleation rate [1 cm$^{-3}$·s$^{-1}$] |
| $\rho$ | the graphene oxide density [g ml$^{-1}$] |
| n | the concentration of nanofluids [g ml$^{-1}$] |
| N | the total number of nanosheets |
| V | the volume of suspending droplet [ml] |
| $D_0$ | the average size of nanosheets [m] |
| $\Delta G_n^*$ | the heterogeneous nucleation energy [J] |

at all, the latent heat is not released and the PCMs only store sensible heat, which might be a serious problem in practical applications. Many scholars have developed a variety of methods to depress the supercooling degree of PCMs such as adding nucleation catalyst (Oda et al., 2004), and using ultrasonic technology (Liu et al., 2015). However, the effect of these methods is not ideal. The emergence of nanofluids provided an alternative way.

Nanofluid is engineered colloidal suspensions of nanoparticles in a base fluid (Choi, 1995). Many researches demonstrated nanofluid existing low supercooling degree (Chandrasekaran et al., 2014; Harikrishnan and Kalaiselvam, 2012; Liu et al., 2009; Wang et al., 2014). Some scientists believed that it was the contribution of nanoparticles suspended in nanofluid (Li and Zhu, 2009; Liu et al., 2015). They explained that nanoparticles can be served as nucleation agents in base fluid and the heterogeneous nucleation aroused by nanoparticles have a great positive effect on reducing the nucleation time and supercooling degree. But other scientists argued that the reduction of supercooling degree is not only the effect of nanoparticles, but also the contribution of rough container surface and the contaminant adhering on it (Hong et al., 2004; Matsumoto et al., 2006). Nucleation experiments were usually accomplished in containers such as test tubes, beakers and heat exchangers which exist rough wall surface and foreign substance. Obviously, two undesirable outcomes arise when we use these container experiment techniques. One is container wall or contaminant that will act as effective catalytic site that can lower the nucleation barrier, confusing the contribution of nanoparticles. The other is that once an ice crystal starts to grow from the container wall or the contaminant, nucleation stimulated by nanoparticles is no longer dominant and not considered to play a key role in altering the nucleation behavior. Therefore, containerless experiment technology should be the best choice.

Acoustic levitation is an important containerless experiment technology for avoiding the undesirable interference from container walls and has attracted much attention due to its wide applications in the fields of solidification kinetics (Diehl et al., 2009; Geng et al., 2012; Yan et al., 2014), fluid mechanics (Shitanishi et al., 2014), thermophysical property measurement (Mondragon et al., 2011) analytical chemistry (Chainani et al., 2013), etc. It utilizes acoustic radiation force generated from the nonlinear effect of intense sound field to balance gravity and levitates sample drops without contact. Furthermore, under acoustic levitation condition, the nucleation of nanofluid has some new characteristics. The shape deformation, bulk vibration, rotation of the levitated drop and ultrasonic cavitation effect can induce complicated internal flow and heat transfer. This will affect the nucleation process. Therefore, acoustic levitation provides an interesting condition for the study on nucleation behavior of nanofluid PCM.

In this article, we added graphene oxide into deionized water to prepare graphene oxide nanofluid and tested the supercooling degree of nanofluid drop levitated by ultrasonic wave. Basing on the Wenzel wetting model, we analyzed the mechanism of depressing supercooling degree by setting up new heterogeneous nucleation physics model from the perspective of the roughness which indirectly affects heterogeneous nucleation work and deduced the mathematical model of nucleation rate of graphene oxide nanofluid.

## 2. Experiment details

### 2.1. *Preparation of nanofluid and their stabilities*

The base fluid is deionized water and the suspension additive is graphene oxide. First, we add 10 mg, 20 mg, 30 mg, and 50 mg graphene oxide into 100 ml deionized water respectively, without adding any dispersant or stabilizer, and then disperse the mixture one by one with an ultrasonic oscillator (20 kHz) for 150 min, cooling them with ice water mixture at the same