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LETTER TO THE EDITOR

Quantum nucleation in the physical kinetics of phase transitions

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Abstract. Theories of the physical kinetics of first-order phase transitions are usually based on the notion that a stable phase droplet within a metastable phase environment is formed by thermal activation over a free energy barrier. Some features of quantum tunnelling through the barrier are explored here.

The central problem in the theory of the physical kinetics of first-order phase transitions is the computation of the probability of forming a domain of stable phase within an environmental metastable phase. For the case of a stable fluid droplet, formed within a metastable fluid, the classical thermal activation view has been very well studied (Lifshitz and Pitaevskii 1981).

Briefly, the physical considerations of the classical nucleation problem are as follows: (i) The surface tension σ (of the stable droplet phase of radius R) determines a free energy barrier yielding the metastability of the environmental phase. (ii) The critical radius of the droplet R_c is the point at which the droplet free energy barrier reaches a maximum, and this parameter can be computed from laboratory data by comparing the 'bulk' and 'surface' free energy contributions to the barrier free energy (Landau and Lifshitz 1980).

$$V(R) = 4\pi\sigma R^2 - \frac{2}{3}(4\pi\sigma/R_c)R^3. \quad (1)$$

(iii) To leading exponential order, the thermal activation probability of the droplet is determined by the maximum in the free energy barrier height

$$V^* = \max_R V(R) = (4\pi/3)\sigma R_c^2, \quad (2)$$

i.e. the probability is given by

$$P^* = \exp(-4\pi\sigma R_c^2/3k_B T). \quad (3)$$

The purpose of this letter is to explore the notion that quantum tunnelling through the barrier can appreciably contribute to the physical kinetics of phase transitions. This notion can be probed by using well developed methods of treating collective coordinates via quantum mechanics (Gervais 1979). In particular, a variational theorem (Widom and Clark 1983) allows one to find sufficient, but not necessary, conditions for the quantum nucleation of stable phase droplets within a metastable phase. These conditions will now be derived.

In the collective coordinate method, the leading exponential behaviour is determined by the WKBJ quantum nucleation tunnelling barrier factor

$$B = (2/\hbar) \int_0^{R_{\max}} [2M(R)V(R)]^{1/2} dR, \quad (4)$$

where

$$R_{\max} = \frac{3}{2}R_c, \quad (5)$$

and $M(R)$ is the 'local mass' of the collective coordinate R . To compute this effective local mass, one may consider a stable droplet of mass density $\rho + \Delta\rho$ in a metastable fluid environment of mass density ρ . In order that the droplet may grow in size, a radially directed hydrodynamic velocity field need exist for resulting mass flow in the metastable phase,

$$v_r = -(\Delta\rho/\rho)(R/r)^2 \dot{R}, \quad r > R. \quad (6)$$

The resulting hydrodynamic kinetic energy is then given by

$$K = \frac{1}{2} \rho \int_R^\infty v_r^2 (4\pi r^2 dr), \quad (7)$$

and this determines the effective mass $M(R)$,

$$K = \frac{1}{2} M(R) \dot{R}^2, \quad (8)$$

via equations (6), (7) and (8); i.e.

$$M(R) = (4\pi/\rho)\Delta\rho^2 R^3. \quad (9)$$

From equations (1), (4), (5) and (7), one can deduce the barrier factor

$$\hbar B = K_1 |\Delta\rho| (\sigma/\rho)^{1/2} R_c^{7/2}, \quad (10)$$

where K_1 is a pure number of order unity. The nature of the variational theorem in the WKBJ scheme indicates that the actual quantum nucleation probability (to leading exponential order) obeys

$$P \geq \exp(-(K_1/\hbar) |\Delta\rho| (\sigma/\rho)^{1/2} R_c^{7/2}). \quad (11)$$

By comparing equations (3) and (11), one arrives at the central results of this work.

(i) The temperature scale which determines the quantum nucleation regime is given by

$$T^* = (4\pi/3K_1)(\hbar/k_B) |\Delta\rho|^{-1} (\sigma\rho/R_c^3)^{1/2}, \quad (12)$$

where all of the parameters on the right-hand side of equation (12) can be experimentally determined. (ii) A sufficient, but not required, condition for quantum nucleation to play the dominant role in the kinetics of the phase transition is that the temperature obey

$$T \leq T^*. \quad (13)$$

Finally, we note that the viscosity η plays an important part in the classical kinetics of the phase transition, i.e. if η is the viscosity of the metastable phase environment of the nucleated stable droplet, then the heating rate (Landau and Lifshitz 1959) of the hydrodynamic flow velocity in equation (6) is given by

$$\dot{Q} = 8\pi(\Delta\rho/\rho)^2 (\eta R) \dot{R}^2. \quad (14)$$

Via the dissipative function (Landau and Lifshitz 1976), equation (14) implies a 'frictional force',

$$f = -\gamma(R)\dot{R}, \quad (15)$$

for the collective coordinate R , in which the frictional coefficient is given by

$$\gamma(R) = 8\pi(\Delta\rho/\rho)^2(\eta R). \quad (16)$$

Such frictional effects do not invalidate the variational estimate given in equations (12) and (13).

It is hoped that the sufficient, but not necessary, conditions given in equations (12) and (13) will be of help to those physical chemists interested in regimes in which quantum nucleation should play an important role in the physical kinetics of phase transitions.

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