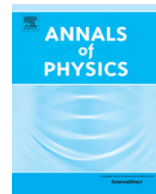




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# The role of the “Casimir force analogue” at the microscopic processes of crystallization and melting

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## ABSTRACT

Melting (crystallization), a phase transition from a crystalline solid to a liquid state, is a common phenomenon in nature. We suggest a new factor, “the Casimir force analogue”, to describe mechanisms of melting and crystallization. The Casimir force analogue is a force occurring between the surfaces of solid and liquid phases of metals caused by different energy density of phonons of these phases. It explains abrupt changes in geometry and thermodynamic parameters at a melting point. “The Casimir force analogue” helps to estimate latent melting heat and to gain an insight into a solid–liquid transition problem.

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## 1. Introduction

Melting (crystallization) is a phase transition from a crystalline solid (topologically distinguished by a long-range order in the arrangement of atoms) to a liquid state (characterized by absence of a long-range order), which is a very common phenomenon in nature. Studies on atomic mechanisms of melting and crystallization started well before the beginning of the XX century and are still going on due to great scientific and practical relevance of this phenomenon [1–6].

In classical thermodynamics, melting (crystallization) is described as a first-order phase transition that occurs when a certain critical temperature of melting  $T_m$  is reached. The process of melting (crystallization) is accompanied by a dramatic change in volume and absorption (release) of latent

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heat of fusion. There are several known models of melting (crystallization) [7–12]. Despite the fact that many aspects of these phenomena are now thoroughly studied, the physical mechanism of melting (crystallization) is still rather debatable [2–6]. The challenge is that the theory of first-order phase transitions and the Lee–Yang theory [13], in particular, contains no references to specific criteria which could help to determine system parameters under which phase transition occurs [2,3,14].

We reckon that some difficulties arising during the analysis of this sophisticated problem can be eliminated by taking into consideration a new factor that used to be neglected. In this work it is referred to as the “Casimir force analogue”.

## 2. Model description

To simplify further discussions, let us consider a simple model system of two half-spaces at a small distance  $x$  from each other, one of which is a solid S-phase at temperature  $T_m - \Delta T$  where  $\Delta T$  is an infinitesimal deviation from melting (crystallization) temperature  $T_m$ , and the other is a liquid L-phase (melt) at temperature  $T_m + \Delta T$ . Both are placed in a thermostat at an average temperature of  $T_m$ .

To describe melt-liquid behavior, we shall use a free-volume model [15–19]. Based on this model, the liquid equation at temperature  $T$  looks as follows [16,17]:

$$p + p_i^l = \delta' \frac{kT}{V}, \quad (1)$$

where  $p$  and  $p_i^l$  represent external and internal “thermal” pressure respectively,  $k$  is the Boltzmann constant,  $V$  stands for volume per atom. For simple liquids,  $\delta'(T)$  parameter may be approximately calculated using the following formula:

$$\delta' \approx \left( \frac{\partial \ln V_f}{\partial \ln V} \right)_T, \quad (2)$$

where  $V_f$  stands for fluctuation free volume of liquid associated with displaced center of gravity of particles from their equilibrium position in the center of a cell due to some thermal motion. In accordance with [18],  $V_f$  shall be calculated based on the following equation:

$$V_f = \int_V \exp(-E(\vec{r})/kT) d\vec{r}, \quad (3)$$

where  $E(\vec{r})$  denotes potential energy of a particle in a cell that depends on the radius vector of its deviation from the cell center  $\vec{r}$ . Assuming that liquid atoms are hard spheres of  $V_0$  volume, we can show that [19]:

$$V_f = (V - V_0)^3 / V_0^2. \quad (4)$$

Eqs. (2) and (4) bring us to an obvious conclusion:  $\delta' = 3V / (V - V_0)$  and by inserting  $\delta'(T)$  in Eq. (1), we can write a liquid equation in the following form:

$$(p + p_i^l)(V - V_0) = 3kT. \quad (5)$$

This equation is similar to that of the Van der Waals. The same result was obtained by Henry Eyring [19] based on somewhat different approximations. A more rigorous calculation is given in [18].

By inserting (4) into (2), we shall rewrite (1) so that it explicitly includes fluctuation free volume  $V_f$ :

$$p + p_i^l = \delta(T) \frac{3kT}{V_0} \quad (6)$$

where  $\delta(T)$  shall be calculated using the following formula:

$$\delta(T) = (V_f / V_0)^{-1/3}. \quad (7)$$

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