On the Application of Laplace Pressure in the Science of Sintering

A. F. Lisovsky
Institute for Superhard Materials, National Academy of Sciences of Ukraine, Avtozavodska 2, Kiev, 04074 Ukraine

Abstract:
An equation of the Laplace pressure derived using the Gibbs thermodynamic method have been discussed and the correct applications of the equation have been substantiated. It has been shown that the expression is applicable only to macrovolumes for the description of surfaces with a constant curvature, but not to the description of nanodispersed systems and surfaces with variable curvature. The expression of the Laplace pressure applicable to a crystal and the cavity limited by a surface of any geometrical shape have been derived.

Keywords: Sintering, Laplace pressure

1. Introduction

The Laplace pressure value is defined as the product of the surface tension by interfacial area curvature. In spite of the very simple expression, its interpretation and application in the literature is ambiguous. In this expression in parallel with the surface tension the free surface energy is used [1, 2]. It is applied to nano- and macrodispersed systems to describe the moving forces of the particle consolidation [2 – 4]. In this case the notion of the “effective Laplace pressure” is introduced, which requires a clear physical interpretation. Because of this the necessity has arisen to describe the derivation of the equation of the Laplace pressure based on the philosophy of thermodynamics and taking into account the results obtained to substantiate the area of its correct application.

2. Thermodynamic study

To solve this problem, have been used a method of virtual changes of the system parameters when the system is in equilibrium state. Let us consider a system consisting of phases 1 and 2 and phase 2 is inside phase 1 and is restricted by arbitrary closed surface $S_{12}$. Phases 1 and 2 may be solid, liquid, or gaseous and set up various combinations on the condition that there is interfacial surface $S_{12}$. The following limitations are imposed on the system:

$$T_1 = T_2 = T_{12} = T = \text{const}$$

$$\vartheta_1 + \vartheta_2 + \vartheta_{12} = \vartheta = \text{const}$$

$$V_1 + V_2 = V = \text{const}$$

$$m_1 + m_2 + m_{12} = m = \text{const}$$

Corresponding author: lisovsky@ism.kiev.ua
where $T$ is the temperature, $\vartheta$ is the entropy, $V$ is the volume, $m$ is the amount of the component, indices 1, 2, and 12 indicate that the values they define refer to the corresponding phase or interface.

To simplify the description it is assumed that the system is one-component. Limitation (1) indicates that there are no temperature gradients in the system. Limitations (2) and (3) are responsible for the conditions of the system interaction with the environment. The constancy of the entropy points to the thermal insulation of the system, while the constancy of the volume points to the mechanical insulation. Limitation (4) indicates that the system does not exchange mass with the environment. Under these conditions the thermodynamic potential of the system is internal energy $U$. For the system under consideration we have

$$U = U_v + U_s$$

where $P$ is the pressure, $\mu$ is the chemical potential, $\gamma$ is the surface tension, $S$ is the interfacial area; indices $v$ and $s$ show that the values they indicate belong to the volumetric and surface phases, respectively.

In the state of equilibrium the system internal energy is the lowest and under any virtual variations in the region near the equilibrium is zero, i.e.

$$\delta U = T_1 \delta \vartheta_1 + T_2 \delta \vartheta_2 + T_{12} \delta \vartheta_{12} - P_1 \delta V_1 - P_2 \delta V_2 - V_1 \delta P_1 - V_2 \delta P_2 - \gamma_{12} \delta S_{12}$$

$$+ m_1 \delta m_1 + m_2 \delta m_2 + m_{12} \delta m_{12} + \mu_1 \delta m_1 + \mu_2 \delta m_2 + \mu_{12} \delta m_{12} = 0$$

For the system considered it is assumed that in the equilibrium state the chemical potentials of phases and interfacial area $S_{12}$ are the same, i.e.

$$\mu_1 = \mu_2 = \mu_{12} = \mu = \text{const.}$$

It follows from Eq. (9) with allowance made for limitation (1) that for macrophasess under virtual changes of interfacial area $\delta S_{12}$ pressures $P_1 = \text{const}$, $P_2 = \text{const}$, and $\gamma_{12}$ is also const. Only under these conditions and limitation (1) equality (9) is true.

With allowance made for the above Eq. (8) becomes

$$\delta U = T_1 \delta \vartheta_1 + T_2 \delta \vartheta_2 + T_{12} \delta \vartheta_{12} - P_1 \delta V_1 - P_2 \delta V_2 - \gamma_{12} \delta S_{12} + m_1 \delta m_1 + m_2 \delta m_2 + m_{12} \delta m_{12} = 0$$

The first three terms of Eq. (10) define the condition of the system thermal equilibrium, the next three define the condition of the mechanical equilibrium, and the last term define the condition of the system chemical equilibrium. These conditions are independent and can be written as follows:

$$T_1 \delta \vartheta_1 + T_2 \delta \vartheta_2 + T_{12} \delta \vartheta_{12} = 0$$

$$- P_1 \delta V_1 - P_2 \delta V_2 - \gamma_{12} \delta S_{12} = 0$$

$$\mu_1 \delta m_1 + \mu_2 \delta m_2 + \mu_{12} \delta m_{12} = 0.$$

Limitation (2) and the constant temperatures in the bulk of the system guarantee the implementation of condition (11a), limitations (4) and (9) ensure the implementation of condition (11c). Let us transform condition (11b) in the following way. According to limitation (3), $\delta V_1 = -\delta V_2$, therefore, from (11b) we found

$$P_2 - P_1 = \gamma_{12} \frac{\delta S_{12}}{\delta V_2}.$$

It is known from differential geometry that $\frac{\delta S}{\delta V} = K = R_1^{-1} + R_2^{-1}$, where $K$ is the surface curvature, $R_1$ and $R_2$ are the main radii of the curvature at the given point. Taking into account this dependence we have
\[ \Delta P_L = \gamma_{12} \left( \frac{1}{R_1} + \frac{1}{R_2} \right). \] (12)

Eq. (12) is a known dependence of the Laplace pressure on the surface tension and interfacial surface curvature. It may be derived for a multicomponent system as well. In this case an additional limitation should be imposed, namely, the system should consist of independent components. The Eq. (12) is true only if the limitations and assumption used in its derivation are allowed for.

3. Results and discussion

According to our thermodynamic study, the surface tension is used in Eq. (12) and not the free surface energy. In deriving Eq. (12) the Gibbs thermodynamic method was used, which was developed for macroobjects, therefore, the expression Eq. (12) is inapplicable to the nanosized objects. In the thermodynamics of nanosystems a new independent parameter appears, namely, nanoparticle size \( r \) [5], on which the chemical potential, surface tension, and thermodynamic functions depend. Because of this limitation (9) cannot be extended to nanodispersed systems, it is true for macroobjects only, hence, the applications of Eq. (12) is restricted to macrosystems only.

There is a contradiction in the expression of the Laplace pressure. Eq. (12) describes the pressure at a point of a curved surface, which contradicts the physical essence of the mere notion of the pressure, which is an integral characteristic and has the meaning only as applied to a certain surface area or to the bulk of the body. Because of this Eq. (12) may correctly be used only to describe a surface with constant curvature \( K \), i.e. spherical, cylindrical, or plane. To apply expression (12) correctly, it is necessary for presenting as follows

\[ \Delta P_L = \gamma_{12} K, \]

where \( K = (0, 1, 2) \).

For a plane surface the Laplace pressure equals zero, that’s why sometimes it is interpreted as an excessive pressure that is generated by a curved surface. Based on the above, the use of Eq. (12) for arbitrary curved surface \( (K \neq \text{const}) \) is incorrect. Laplace pressure is the excessive pressure of the phase created by the closed surface, and for its writing it is necessary to use a symbol \( \Delta P_L \).

Let's define the Laplace pressure in bodies of various geometrical shapes (fig. 1).

Fig. 1. Cavities formed by particles in a composite body (a, b,) and crystal (c).
The cavities are filled by vapor. A cavity (fig. 1a) is limited by a spherical surface. The spherical surface has a constant curvature, therefore, the pressure created by this surface can be defined by Eq. (12). According to Eq. (12), the Laplace pressure in the A area is $\Delta P_A = 0$, and in the B area is $\Delta P_B > 0$, thus $\Delta P_B >> \Delta P_A$ (fig.1b). Such a situation is impossible in a cavity filled by vapor. It is obvious that Eq.(12) is unsuitable for determination of the Laplace pressure in a cavity (fig.1b) and in a crystal (fig.1c). To solve this problem, we use the results reported in [6]. The author [6] has proved that pressure of crystal $P_r$ is described by the following expression

$$P_r = P_m + 2 \frac{\gamma}{l_i},$$

where $P_m$ is the medium pressure, $\gamma_{li}$ is the surface tension of face $s_i$ of a crystal, $l_i$ is the height of a pyramid constructed using face $s_i$ as the basis.

Expression $2 \frac{\gamma}{l_i}$ is called the Wulf constant, $W$, thus, $W = 2 \frac{\gamma}{l_i} = 2 \frac{A_i}{3} v$, where $v$ is the crystal volume, $A_i$ is the mechanical work of the formation of a whole crystal surface, $A_x = \Sigma s_i \gamma_{li}$. For a practical use it is necessary to find the average value of a surface tension $\gamma = \frac{\Sigma s_i \gamma_{li}}{s}$, where $s$ is the surface of a crystal. Taking into account these expressions, we have

$$\Delta P_L = P_r - P_m = \frac{2 \gamma s}{3 v} \tag{13}.$$ 

Eq. (13) can be applicable for closed cavities of any geometrical shape and for crystals. For the description of an equilibrium state of dispersed systems it is necessary to use Eq. (13), which is devoid of the contradictions inherent in the Eq. (12).

In the literature [2, 3, 4, 7] the Laplace pressure is used to describe the motive force of the particle consolidation process. On the strength of the above contradiction in using Eq. (12) to describe the pressure in a cavity, formed by several particles, depending on a geometrical shape at different regions of the cavity various combinations of the Laplace pressure can be obtained. In order to apply the Laplace pressure for cavities of an arbitrary geometrical shape, the author [4, p. 39] introduce the so-called “effective Laplace pressure”, which is described by expression

$$P_L = -\frac{\partial F_s}{\partial V} = -\frac{3\sigma}{r_0} (1 - \Theta)^2, \tag{14}$$

where $F_s$ is the free surface energy, $V$ is the volume, $\sigma$ is the specific free surface energy, $r_0$ is the average radius of powder particles, $\Theta$ is the porosity.

During the particle consolidation the Helmholtz free energy decreases, therefore, $\frac{\partial F_s}{\partial V} < 0$, and expression $\frac{\partial F_s}{\partial V} > 0$. In Eq. (14) the right member $-\frac{3\sigma}{r_0} (1 - \Theta)^2$ is of a negative value, hence, $-\frac{\partial F_s}{\partial V} = -3\frac{\sigma}{r_0} (1 - \Theta)^2$. It seems likely that Eq. (14) should be presented as follows: $P_L = -\frac{\partial F_s}{\partial V} = -\frac{3\sigma}{r_0} (1 - \Theta)^2$. 
Authors of [3, 4, 7] think that at the consolidation of particles the Helmholtz free energy, $F$, changes only as a result of the reduction of the solid–gas interface. Thus, the changes of the Helmholtz free energy in volumetric phases and changes of the component chemical potentials are ignored. From Eq. (14) only negative values of the Laplace pressure can be obtained. It should be noted that according to Eq. (14), $P_L$ is not the Laplace pressure but an unknown parameter of the porous medium. In this connection it is desirable that the authors of [3, 4, 7] give a clear physical interpretation of the effective Laplace pressure and the negative Laplace pressure terms, which they used in [3, 4, 7].

The application of Eq. (12) gave erroneous results of research [2]. In this case the researcher used also the “negative pressure” term. The Laplace pressure can be of a positive value only. A negative pressure makes no physical sense.

In our opinion, in some phenomenological models for the description of the particle consolidation it is advisable to use the expression of shrinkage pressure $P_{sh}$ [8], which is an integral characteristic of the whole group of particles, and is devoid of contradictions inherent in the Eqs. (12) and (14),

$$P_{sh} = \frac{1}{3} (2g\gamma_{sv} - \gamma_{ss}) \frac{\partial S_{ss}}{\partial V},$$

where $g$ is the coefficient that allows for a change of the contact and interfacial areas of particles, $\gamma_{ss}$ and $\gamma_{sv}$ are the surface tensions respectively on the contact and interfacial areas of particles, $S_{ss}$ is the contact area.

This equation is easily transformed to the form [8]

$$P_{sh} = k(2g\gamma_{sv} - \gamma_{ss}) \frac{1}{r}\left(\frac{1-u}{u}\right)^{\frac{1}{3}} \hat{O}(u),$$

where $r$ is the particle size, $u$ is the gas phase content, expressed in terms of fractions, $k$ is the coefficient that allows for a change in geometric shapes of particles and cavities, formed by particles, $\hat{O}(u)$ is the nondimensional parameter which takes into account changes in the cavity geometry in the process of consolidation of particles.

The shrinkage pressure $P_{sh}$ is not the Laplace pressure. Pressure $P_{sh}$ is the parameter of a porous system.

4. Conclusions

The Laplace pressure is the excessive pressure of the phase created by the closed surface. Known equation of the Laplace pressure may correctly be used only as applied to macroobjects for the description of surfaces with constant curvature. The use of the derived expression for the description of nanodispersed systems and surfaces with variable curvature is incorrect. To define the Laplace pressure in the cavities limited by any curvilinear surface or in crystals it is necessary to use expression $\Delta P_L = \frac{2}{3} \frac{S}{V} \cdot \gamma$. 

References


Садржај: Разматрана је једначина за Лапласов притисак која је изведена коришћењем Гибсове термодинамичке методе и приказана је њена примена. Показано је да се израз може применити само на макрозапремине за опис површина са сталном кривином али не на опис нанодиспергованих система и површина са варирајућом кривином. Изведен је израз за Лапласов притисак који се може применити на кристал и удушње ограничено површином било каквог геометријског облика.

Кључне речи: Синтеровање, лапласов притисак.