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DOI:

[10.1016/j.enconman.2017.12.040](https://doi.org/10.1016/j.enconman.2017.12.040)

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*Document Version*

Peer reviewed version

*Citation for published version (Harvard):*

Yu, Q, Romagnoli, A, Al-Duri, B, Xie, D, Ding, Y & Li, Y 2018, 'Heat storage performance analysis and parameter design for encapsulated phase change materials', *Energy Conversion and Management*, vol. 157, pp. 619-630. <https://doi.org/10.1016/j.enconman.2017.12.040>

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Checked for eligibility: 13/12/2017

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# Heat storage performance analysis and parameter design for encapsulated phase change materials

Qinghua Yu <sup>a,b</sup>, Alessandro Romagnoli <sup>c</sup>, Bushra Al-Duri <sup>a</sup>, Danmei Xie <sup>b</sup>, Yulong Ding <sup>a</sup>,  
Yongliang Li <sup>a,\*</sup>

<sup>a</sup> Birmingham Centre for Energy Storage, School of Chemical Engineering, University of  
Birmingham, Birmingham B15 2TT, United Kingdom

<sup>b</sup> School of Power and Mechanical Engineering, Wuhan University, Wuhan 430072, PR  
China

<sup>c</sup> School of Mechanical and Aerospace Engineering, Nanyang Technological University,  
Singapore 639798, Singapore

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\*Corresponding author. Tel.: +44 (0) 121 414 5135, Email: [y.li.1@bham.ac.uk](mailto:y.li.1@bham.ac.uk) (Y. Li)

20 **Abstract**

21 This paper establishes a thermo-mechanical model considering the liquid density  
22 variation to explore the comprehensive energy storage performance of two types of small-  
23 sized encapsulated phase change materials (PCMs) as well as effects of shell thickness. The  
24 study shows that the varying ranges of internal pressure, melting temperature and latent heat  
25 are markedly diminished during melting of PCMs after taking into account the liquid density  
26 variation. The decrease of shell thickness leads to a decrease of maximum internal pressure  
27 and a larger decrease of critical cracking pressure, which will increase the risk of shell  
28 cracking. The decrease in shell thickness slows down the increase in melting temperature and  
29 the decrease in latent heat during the melting process, which consequently reduces the  
30 melting time and increases the stored latent energy. These results indicate that reducing shell  
31 thickness of encapsulated PCMs is favourable for elevating energy charging rate and energy  
32 storage capacity while it is harmful to mechanical stability. The Cu/Ni capsule has smaller  
33 critical core/shell size ratio to avoid cracking than the salts/SiC capsule, while the former  
34 offers a shorter melting period. This implies that physical properties of materials of PCM  
35 capsules should be carefully considered for improving mechanical stability and melting  
36 dynamics. This study is helpful for selection of appropriate shell thickness and materials to  
37 achieve excellent comprehensive energy storage performance of encapsulated PCMs.

38

39 *Keywords:* Phase change materials; Encapsulation; Melting; Thermal energy storage.

## Nomenclature

### Roman letters

$a$	shell thickness (m)
$c_p$	specific heat ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )
$E$	Young's modulus (Pa)
$ES$	stored energy (J)
$f$	fraction
$g$	Gibbs free energy ( $\text{kJ}\cdot\text{kg}^{-1}$ )
$h$	enthalpy ( $\text{kJ}\cdot\text{kg}^{-1}$ )
$L$	latent heat ( $\text{kJ}\cdot\text{kg}^{-1}$ )
$P$	pressure (Pa)
$r$	radius (m)
$s$	entropy ( $\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$ )
$t$	time (s)
$T$	temperature (K)
$u$	displacement (m)
$V$	volume ( $\text{m}^3$ )

### Greek letters

$\alpha$	thermal expansion coefficient ( $\text{K}^{-1}$ )
$\beta$	isothermal compressibility ( $\text{Pa}^{-1}$ )
$\gamma$	heating rate ( $^{\circ}\text{C}\cdot\text{min}^{-1}$ )

$\delta, \mu$	Lamé's constant
$\lambda$	thermal conductivity ( $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ )
$\nu$	Poisson's ratio
$\rho$	density ( $\text{kg}\cdot\text{m}^{-3}$ )
$\sigma$	stress (Pa)
$\varphi$	relaxation factor

### Subscripts

0	reference or initial
$c$	shell
$e$	external surface of shell
$eq$	equivalent
$i$	shell/PCM interface or PCM
$l$	liquid
$m$	melting or melting front
$r, \theta, \varphi$	spherical coordinates system
$s$	solid
$t$	tensile strength

### Superscripts

*	holistic
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## 40 **1. Introduction**

41 High-temperature thermal energy storage (HTTES) provides an effective solution to  
42 overcome the mismatch between energy supply and demand associated with concentrated  
43 solar power generation [1, 2] and industrial waste heat recovery [3]. HTTES is also crucial to  
44 the round-trip efficiency enhancement of recently developed compressed air energy storage  
45 [4-6] and liquid air energy storage systems [7, 8]. Latent heat storage-based solid-liquid  
46 transition of phase change materials (PCMs) has attracted increasing attention because of  
47 high energy storage densities with small temperature variations [9]. However, the applicable  
48 PCMs for HTTES, such as molten salts and metals, exhibit high chemical corrosion in the  
49 liquid phase. Therefore it is essential to encapsulate PCMs in suitable shell materials to  
50 prevent leakage of liquid PCMs. The encapsulation of PCMs can also significantly increase  
51 heat transfer surface area and establish barriers for PCMs against harmful reactions with the  
52 environment [10]. The formed spherical PCM capsules offer stable geometric and chemical  
53 structures like solid balls or particles, which are easy to handle.

54 The spherical PCM capsules can be used for thermal energy storage in the form of  
55 packed beds [11, 12] or fluidized beds [13, 14]. The diameters of the PCM capsules used in  
56 packed beds generally measure tens of millimetres [15]. This kind of large-sized capsule is  
57 fabricated by filling in a precast container (i.e. shell) with PCM [16]. There will be some void  
58 or porosity inside this kind of capsule [17]. In contrast, the diameters of the capsules used in  
59 fluidized beds generally measure a few millimetres or hundreds of micrometres [18, 19]. This  
60 kind of small-sized capsule is manufactured by coating or plating PCM pellets with shell  
61 materials, which does not introduce voids inside the capsule [20, 21]. In comparison with  
62 packed beds, fluidized beds offer more advantages including temperature uniformity along  
63 the bed and excellent heat transfer between the carrier fluid and the PCM. However, since  
64 small-sized capsules have no voids inside, shell cracking may occur due to volume expansion

65 during phase transition of PCM from solid to liquid and this has to be considered in the  
66 design of PCM capsules [22]. Mathur et al. [23] developed PCM capsules tolerating PCM  
67 volume expansion by incorporating sacrificial polymer as the first shell layer which  
68 decomposes below the melting point of PCM to gas leaving a void in the capsule. Obviously,  
69 the resulting void layer reduces the heat storage density and charging/discharging rate.  
70 Zhang et al. [24] examined encapsulation of copper (Cu) as PCM with a thick chromium-  
71 nickel (Cr-Ni) bilayer. The results showed that there was no leakage or crack from the outside  
72 view of the capsule after charge-discharge thermal cycles. However, the integrity of the  
73 capsule is attributed to a sufficiently thick shell, which leads to a reduction of heat storage  
74 density by 70% with respect to the pure copper. Further, the shell thickness has considerable  
75 impact on the melting dynamics of PCM, which is closely related to the energy charging rate.  
76 Therefore, it is crucial to precisely tailor the shell thickness of PCM capsules to obtain  
77 excellent comprehensive heat storage performance, including good mechanical stability (i.e.  
78 no cracking), high heat storage density and fast charging/discharging processes.

79         Since it is difficult to directly measure the thermal and mechanical parameters within  
80 encapsulated PCMs, especially at high temperature, numerical simulation or analysis has  
81 become a very powerful tool. Several researchers have explored the heat storage performance  
82 of encapsulated PCMs for HTTES by numerical method. Zhao et al. [25] compared the  
83 charging/discharging time for encapsulated PCMs between different heat transfer fluids using  
84 numerical simulations of heat transfer regardless of volume variation. Lopez et al. [26]  
85 established a model for a solid sphere of PCM salts encapsulated in an elastic graphite shell  
86 with a mobile internal wall and a fixed external wall to explain the behaviour of graphite/salt  
87 composites during melting. The pressure inside the shell increases linearly as melting  
88 continues, leading to a continuous increase in the melting point and continuous decrease in  
89 latent heat. Pitié et al. [27] incorporated Lamé equations into the model to describe the

90 thermo-mechanical behaviour of a spherical PCM coated by silicon carbide (SiC) shell with a  
91 free, mobile, external wall by specifying volume friction of melted salts. The analysis  
92 indicates that the coated PCM with a low volumetric expansion resulting in a small pressure  
93 change is vital to avoid cracking. Parrado et al. [28] analysed the temperature and pressure  
94 evolutions during the melting and solidification processes of Cu-encapsulated nitrates using a  
95 decoupled model between heat transfer and mechanical deformation. However, this work did  
96 not consider the variation in density of the liquid PCM which cannot be ignored at high  
97 pressures [27]. Although the shell thickness of PCM capsules need be adjusted to make a  
98 compromise between mechanical stability and heat storage density, little work has been  
99 conducted on its effects on the comprehensive heat storage performance.

100 Therefore, this paper develops a new thermo-mechanical model to evaluate  
101 comprehensive heat storage performance of different types of spherical PCM capsules. This  
102 model takes into account density variations of the liquid phase PCM and pressure-dependent  
103 solid-liquid equilibria together with energy conservation and shell stress during the PCM  
104 melting process. On the basis of the model, the melting characteristics of PCM within a  
105 capsule are examined, including the evolutions of internal pressure, melting point, latent heat  
106 and stored energy as well as melting time frame. Special attention is paid to the effects of  
107 shell thickness on the melting characteristics, mechanical stability and energy storage  
108 capacity. The model is also applied to predict the minimum shell thickness to avoid cracking  
109 at specified PCM bead size and shell materials. This study provides a fundamental  
110 understanding of comprehensive energy storage performance of encapsulated PCM and  
111 significant references for tailoring shell thickness of encapsulated PCM to achieve optimum,  
112 comprehensive energy storage performance.

113

## 114 **2. Mathematical Models**

## 115 2.1. Geometry and main hypotheses

116 The geometry of a spherical capsule under melting of PCM is shown in Fig. 1,  
117 including a shell and liquid/solid PCM. The internal and external radii of the shell are  
118 referred to as  $r_i$  and  $r_e$ , respectively. The position of the melting front is labelled  $r_m$ . The radii  
119 or position of the melting front, vary during melting of the PCM.

120 The main hypotheses adopted to simplify the model are as follows [26, 27]: (a) specific  
121 heat  $c_{ps}$  and thermal conductivity  $\lambda_s$  are constant for the solid phase of PCM with non-  
122 deformability; (b) specific heat  $c_{pl}$  and thermal conductivity  $\lambda_l$  are constant for the liquid  
123 phase of PCM; (c) convection heat transfer inside the small-sized capsule is negligible; (d)  
124 viscous energy dissipation of the liquid is also negligible; (e) the liquid within the shell has  
125 uniform pressure; (f) the shell is considered to be homogeneous, isotropic and exhibiting  
126 linear elastic behaviour indicated by Young's modulus, with constant values of density  $\rho_c$ ,  
127 specific heat  $c_{pc}$  and thermal conductivity  $\lambda_c$ ; (g) the pressure and temperature are known  
128 and uniform at the external wall of the shell; (h) there are equalities of pressure and  
129 temperature at the PCM/shell interface. The spherical symmetry from the above hypotheses  
130 allows reduction of the original three-dimensional problem into a one-dimensional one under  
131 a spherical coordinates system  $(r, \theta, \varphi)$  for the melting process before shell cracking.

## 132 2.2. Heat transfer modelling for spherical capsule

133 The melting process of PCM is modelled using the enthalpy method based on a fixed  
134 grid [29] with directly solving the temperature field. According to the aforementioned main  
135 hypotheses (a-e), the energy conservation equation for the capsule can be written as

$$\left\{ \begin{array}{l} \frac{\partial [(\rho c_p)_{eq} T_i]}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \lambda_{eq} r^2 \frac{\partial T_i}{\partial r} \right) - \frac{\partial (\rho_{eq} \Delta h_m)}{\partial t} \quad \text{for } 0 \leq r \leq r_i, \\ \frac{\partial (\rho_c c_{pc} T_c)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( \lambda_c r^2 \frac{\partial T_c}{\partial r} \right) \quad \text{for } r_i < r \leq r_e, \end{array} \right. \quad (1)$$



136 where  $T_i$  and  $T_c$  represent the temperature distributions in the PCM and shell layers,  
 137 respectively;  $\Delta h_m$  denotes the melting enthalpy which can be defined as a product of latent  
 138 heat  $L_m$  and local liquid fraction  $f_l$ , i.e.  $\Delta h_m = f_l L_m = (1 - f_s) L_m$ ;  $f_s$  is local solid fraction;  
 139  $(\rho c_p)_{eq}$ ,  $\rho_{eq}$  and  $\lambda_{eq}$  denote the equivalent heat capacity, density and thermal conductivity,  
 140 respectively. They are given by

$$\begin{cases} (\rho c_p)_{eq} = \rho_s c_{ps} f_s + \rho_l c_{pl} (1 - f_s), \\ \rho_{eq} = \rho_s f_s + \rho_l (1 - f_s), \\ \lambda_{eq} = \lambda_s f_s + \lambda_l (1 - f_s). \end{cases} \quad (2)$$

141 where  $\rho_s$  and  $\rho_l$  denote the densities of solid and liquid phases of PCM, respectively. The  
 142 detailed derivation of Eqn. (1) for the PCM region is presented in Appendix A.

143 For the pure PCM with a fixed melting temperature  $T_m$  at a specified pressure, the local  
 144 solid fraction can be defined as

$$f_s(r, t) = \begin{cases} 0, & T_i \geq T_m \\ 1, & T_i < T_m \end{cases}. \quad (3)$$

145 Based on the hypotheses (g) and (h), boundary conditions of heat transfer can be  
 146 expressed as

$$\begin{cases} -\lambda_{eq} \frac{\partial T_i}{\partial r} = 0 \text{ at } r = 0, \\ \lambda_{eq} \frac{\partial T_i}{\partial r} = \lambda_c \frac{\partial T_c}{\partial r}, \text{ and } T_i = T_c \text{ at } r = r_i, \\ T_c = T_e(t) \text{ at } r = r_e, \end{cases} \quad (4)$$

147 where  $T_e(t)$  denotes the temperature at the external surface of shell. Initially,  $T_i(r, 0) =$   
 148  $T_c(r, 0) = T_0$ , which is a specified initial temperature in the simulations. Therefore,  $T_e(t) =$   
 149  $T_0 + \gamma t$ , where  $\gamma$  is the heating rate at the external surface of the shell.

150 The ratio of melted volume at a time  $t$  to the initial volume  $V_{s0}$  of solid PCM is denoted  
 151 by  $f^*(t)$ , which is referred to as liquid fraction in the following. The liquid fraction can be  
 152 calculated by

$$f^*(t) = 1 - \frac{3}{r_{i0}^3} \int_0^{r_i} r^2 f_s(r, t) dr. \quad (5)$$

153 where  $r_{i0}$  are the initial values of  $r_i$ .

154 The total energy stored within the PCM bead during melting mainly consists of latent  
155 energy and sensible energy, which can be written as

$$ES(f^*) = \int_0^{f^*} \rho_s V_{s0} L_m d\vartheta + \int_0^{V_{s0}} \int_{T(f^*=0)}^{T(f^*)} (\rho c_p)_{eq} d\vartheta dV. \quad (6)$$

### 156 2.3. Thermodynamic equilibrium dependent on pressure

157 It should be noted that liquid-solid phase equilibrium exists at the melting front, with an  
158 equality of Gibbs free energy between liquid and solid phases. The Gibbs free energy can be  
159 estimated by a second order Taylor expansion based on fundamental thermodynamic  
160 relations, which is expressed as [26]

$$g_j(T_m, P) = g_{j0} - s_{j0}(T_m - T_{m0}) + \frac{1}{\rho_{j0}}(P - P_0) - \frac{1}{2} \frac{c_{pj0}}{T_{m0}}(T_m - T_{m0})^2 \\ - \frac{1}{2} \frac{\beta_{j0}}{\rho_{j0}}(P - P_0)^2 + \frac{\alpha_{j0}}{\rho_{j0}}(T_m - T_{m0})(P - P_0), \quad (7)$$

161 where the index  $j = l$  or  $s$  represents liquid or solid phase;  $T_m$  is the melting temperature at  
162 the pressure  $P$ ;  $g_{j0} = g_j(T_{m0}, P_0)$  denotes the Gibbs free energy at  $T_{m0}$  and  $P_0$ ;  $T_{m0}$  is the  
163 melting temperature at  $P_0$  denoting reference pressure;  $s_j$  represents the specific entropy;  $\alpha_j$   
164 denotes the thermal expansion coefficient;  $\beta_j$  denotes the isothermal compressibility; and the  
165 subscript 0 refers to  $(T_{m0}, P_0)$  conditions. The detailed derivation of Eqn. (7) is presented in  
166 Appendix B.

167 Applying the liquid-solid equilibrium condition ( $g_l = g_s$ ), the melting temperature as a  
168 function of pressure is obtained:

$$T_m(P) = T_{m0} + \frac{-j + \sqrt{j^2 - 4ik}}{2i}, \quad (8)$$

169 with

$$\left\{ \begin{array}{l} i = \frac{c_{pl0} - c_{ps0}}{2T_{m0}}, \\ j = (s_{l0} - s_{s0}) - \left( \frac{\alpha_{l0}}{\rho_{l0}} - \frac{\alpha_{s0}}{\rho_{s0}} \right) (P - P_0), \\ k = - \left( \frac{1}{\rho_{l0}} - \frac{1}{\rho_{s0}} \right) (P - P_0) + \frac{1}{2} \left( \frac{\beta_{l0}}{\rho_{l0}} - \frac{\beta_{s0}}{\rho_{s0}} \right) (P - P_0)^2. \end{array} \right. \quad (9)$$

170 The enthalpy difference between the liquid and solid phases (i.e. latent heat  $L_m$ ) at  
171 thermodynamic equilibrium ( $g_l = g_s$ ) can be expressed as [26]

$$L_m(T_m, P) = \Delta s_m(T_m, P) T_m. \quad (10)$$

172 where  $\Delta s_m(T_m, P)$  denotes entropy difference between the liquid and solid phases. According  
173 to the Gibbs relation based on Gibbs free energy [30], Eqn. (7) allows writing

$$s_j \equiv - \left. \frac{\partial g_j}{\partial T} \right|_P = s_{j0} + \frac{c_{pj0}}{T_0} (T_m - T_{m0}) - \frac{\alpha_{j0}}{\rho_{i0}} (P - P_0), \quad (11)$$

174 and therefore

$$\Delta s_m = (s_{l0} - s_{s0}) + \left( \frac{c_{pl0} - c_{ps0}}{T_{m0}} \right) (T_m - T_{m0}) - \left( \frac{\alpha_{l0}}{\rho_{l0}} - \frac{\alpha_{s0}}{\rho_{s0}} \right) (P - P_0). \quad (12)$$

175 Similarly according to the Gibbs relation based on Gibbs free energy [30], the  
176 expression of PCM density can be derived from Eqns. (7) as

$$\frac{1}{\rho_j} \equiv \left. \frac{\partial g_j}{\partial P} \right|_T = \frac{1}{\rho_{j0}} [1 + \alpha_{j0} (T_m - T_{m0}) - \beta_{j0} (P - P_0)], \quad (13)$$

177 Some thermodynamic databases usually provide values of these parameters  
178  $s_{j0}, \rho_{j0}, c_{pj0}, \alpha_{j0}$  and  $\beta_{j0}$ . The variations of melting temperature, latent heat and density of  
179 PCM with pressure are involved in Eqns. (8-10) and (12-13).

#### 180 2.4. Pressure variation caused by phase change

181 Considering the spherical symmetry of the studied capsule shell before cracking in a  
182 spherical coordinates system  $(r, \theta, \varphi)$  and based on the hypothesis (f), the equilibrium  
183 equation of elastic mechanics can be simplified as [31]

$$\frac{d\sigma_{rr}}{dr} + \frac{2(\sigma_{rr} - \sigma_{\theta\theta})}{r} = 0, \quad (14)$$

184 where  $\sigma_{rr}$  and  $\sigma_{\theta\theta}$  denote normal stress components of the shell.

185 From the hypothesis (e), the liquid pressure inside the shell can be represented by  $P$ .

186 Based on hypotheses (g) and (h), the boundary conditions for the elastic deformation of the  
187 shell are

$$\sigma_{rr}(r = r_{i0}) = -P, \quad \sigma_{rr}(r = r_{e0}) = 0, \quad (15)$$

188 where  $r_{e0}$  are the initial values of  $r_e$ .

189 The temperature change  $\Delta T$  that the shell undergoes leads to thermal stress in the shell,  
190 which is proportional to the thermal expansion coefficient of the shell material  $\alpha_c$ . By  
191 combining strain-displacement and stress-strain relations with thermal stress [27], the stress-  
192 displacement relations are obtained as

$$\sigma_{rr} = \delta \left( \frac{du}{dr} + \frac{2u}{r} \right) + 2\mu \frac{du}{dr} - \alpha_c \Delta T (3\delta + 2\mu), \quad (16)$$

$$\sigma_{\theta\theta} = \delta \left( \frac{du}{dr} + \frac{2u}{r} \right) + \frac{2\mu u}{r} - \alpha_c \Delta T (3\delta + 2\mu), \quad (17)$$

193 where  $u$  denotes the shell displacement which only has radial component  $u_r$  (i.e.  $u = u_r$ );  $\delta$   
194 and  $\mu$  are Lamé's constants calculated with the Young's modulus  $E_c$  and Poisson's ratio  $\nu_c$  as

$$\delta = \frac{E_c \nu_c}{(1 + \nu_c)(1 - 2\nu_c)}, \quad \mu = \frac{E_c}{2(1 + \nu_c)}. \quad (18)$$

195 By merging Eqns. (16) and (17) into Eqn. (14), the simplified Lamé's equation is  
196 derived as

$$\frac{d^2u}{dr^2} + \frac{2}{r} \frac{du}{dr} - \frac{2u}{r^2} = 0. \quad (19)$$

197 Solving Eqn. (19) with the boundary conditions in Eqn. (15), yields the elastic  
198 description of the shell as

$$u(r) = \frac{r_{i0}^3}{r_{e0}^3 - r_{i0}^3} \left( \frac{r_{e0}^3}{4r^2\mu} + \frac{r}{3\delta + 2\mu} \right) P + r\alpha_c\Delta T, \quad (20)$$

$$\sigma_{rr}(r) = \frac{r_{i0}^3}{r_{e0}^3 - r_{i0}^3} \left( -\frac{r_{e0}^3}{r^3} + 1 \right) P, \quad (21)$$

$$\sigma_{\theta\theta}(r) = \frac{r_{i0}^3}{r_{e0}^3 - r_{i0}^3} \left( \frac{r_{e0}^3}{2r^3} + 1 \right) P. \quad (22)$$

199 The volume displacement for  $r = r_{i0}$  is written as

$$\Delta V = \frac{4}{3}\pi \left[ (r_{i0} + u(r_{i0}))^3 - r_{i0}^3 \right]. \quad (23)$$

200 During the melting process, the volume expansion of the PCM caused by the density  
201 difference between liquid and solid phases at a time  $t$  is

$$\Delta V = V_{s0} \left( \frac{\rho_s - \rho_l}{\rho_l} \right) f^*(t). \quad (24)$$

202 From Eqns. (23) and (24), it can be derived that

$$u(r_{i0}) = r_{i0} \left( \sqrt[3]{\frac{\rho_s - \rho_l}{\rho_l} f^*(t) + 1} - 1 \right), \quad (25)$$

203 which, combined with Eqn. (20), gives

$$P(t) = \frac{2(r_{e0}^3 - r_{i0}^3)E_c \left( \sqrt[3]{(\rho_s - \rho_l)f^*/\rho_l + 1} - (1 + \alpha_c\Delta T) \right)}{r_{i0}^3(2 - 4\nu_c) + r_{e0}^3(1 + \nu_c)}. \quad (26)$$

## 204 2.5. Equivalent critical pressure of cracking

205 The equivalent critical internal pressure as the shell cracking limit is calculated with the  
206 von Mises criterion. By virtue of the spherical symmetry, the von Mises stress in the shell  
207 reduces to [31]

$$\sigma_v = \sigma_{\theta\theta} - \sigma_{rr}, \quad (27)$$

208 which has the maximum value at  $r = r_{i0}$ . When the maximum von Mises stress reaches the  
209 tensile strength of the shell material  $\sigma_t$ , the shell will crack and loose the encapsulated PCM

210 [20, 22]. According to this situation, the equivalent critical pressure of cracking can be  
211 derived as

$$P_{eq} = \frac{2}{3} \left( 1 - \frac{r_{i0}^3}{r_{e0}^3} \right) \sigma_t \quad (28)$$

## 212 2.6. Solving procedure

213 In the proposed model, the melting process of PCMs is coupled with the internal  
214 pressure change via variation of the volume inside the shell, melting point, latent heat and  
215 liquid density. The above equations thus need iterations to obtain the melting dynamic  
216 characteristics, mechanical behaviour and heat storage performance. The flowchart of the  
217 solving procedure for the proposed model is illustrated in Fig. 2. The flowchart also includes  
218 the input and output parameters. In each time step,  $\Delta t$ , the solving procedure needs to  
219 repeatedly undergo internal iterations until satisfying convergence criteria, and then the  
220 calculated instantaneous results are output for analysis. The relaxation factor,  $\varphi$ , is used to  
221 speed up the convergence. If the melting process is not completed (i.e.  $f^*(t) < 1$ ), the  
222 solving procedure turns into the next time step. When  $f^*(t) = 1$ , the solving procedure is  
223 over and the resulting internal pressure is used to examine the mechanical behaviour of the  
224 shell combined with the equivalent critical pressure of cracking calculated by Eqn. (28).

225

## 226 3. Validation of the model

227 In order to validate the proposed model, the results calculated based on the model  
228 established in this paper were compared with those in literature for the melting process of salt  
229 particles coated in a graphite matrix [26] and a SiC shell [27] with the same properties and  
230 hypotheses. The heat conduction in the matrix or shell is not included for the two types of salt  
231 capsules. The properties of salts and SiC used in the model validation are listed in Table 1  
232 and Table 2, respectively. The graphite matrix was modelled as a thick shell with a non-

233 moving external wall [26]. The property of the graphite matrix required in the model  
234 validation is the rigidity modulus, which is 8 GPa. The input parameters are the same for the  
235 simulations of the melting process of the two types of salt capsules, which are listed in Table  
236 3. The radius of salt beads and the thickness of the graphite or SiC shell are set to 1 mm and  
237 200  $\mu\text{m}$ , respectively. The Fig. 3(a) shows the comparison between the current study and the  
238 literature [26] in the variations of solid fraction and internal pressure during melting of a  
239 single salt bead. The relative errors in the solid fraction and internal pressure are shown in  
240 Fig. 3(b). It can be found that the maximum relative errors are both less than 8%. Fig. 3(c)  
241 displays the comparison between the current study and the literature [27] in the variations of  
242 melting temperature and latent heat during melting of a single salt bead. The relative errors in  
243 the melting temperature and latent heat are depicted in Fig. 3(d). We can see that the  
244 maximum relative errors are both less than 6%. Except for tiny discrepancies in values, the  
245 results in all aspects obtained in this study agree satisfactorily with the literature [26, 27],  
246 indicating that the heat transfer model in Section 2.2 and the pressure-dependent  
247 thermodynamic equilibrium model in Section 2.3 together with the pressure variation model  
248 in Section 2.4 are sufficiently accurate. The established model can therefore be used to  
249 analyse the thermo-mechanical behaviour and evaluate heat energy storage performance of  
250 PCM capsules.

251

#### 252 **4. Results and discussions**

253  $\text{NaNO}_3\text{-KNO}_3$  eutectic salts [26, 27] and Cu [21, 24], as typical high temperature PCMs  
254 applicable to different temperature regions, have attracted much attention. Based on the  
255 melting point, corrosion inhibition, mechanical strength and thermal conductivity, SiC and Ni  
256 are potential encapsulating materials for salts and Cu, respectively. In this study the SiC-  
257 encapsulated salt and Ni-encapsulated Cu are selected as an illustration to demonstrate heat

258 transfer and mechanical behaviour of encapsulated PCMs during melting using the validated  
259 models. The adopted approach and resulting characteristics could be extended to other types  
260 of encapsulated PCMs. The thermodynamic properties of salts and Cu as PCMs at  
261 atmospheric pressure  $P_0$  are listed in Table 1. The properties of SiC and Ni as shell materials  
262 are listed in Table 2. It should be noted that the actual properties of the shell depend on actual  
263 fabricated effect. The radius of the solid PCM bead is prescribed as 1 mm. The temperature at  
264 the external surface of the shell is specified as increasing from 220°C for the salt capsule and  
265 1080°C for the Cu capsule at a heating rate of 5°C/min until the PCMs are totally melted in  
266 the simulations. The time step is set to 0.1 s. These input parameters are summarized in Table  
267 3.

#### 268 *4.1 Effects of shell thicknesses on thermo-mechanical behaviour of salt capsules*

269 Fig. 4(a) illustrates the evolution of internal pressure under different shell thicknesses  
270 during the melting process of salts ( $f^*$ : 0  $\rightarrow$  1). The main finding is that the increasing rate of  
271 internal pressure decreases with the decrease in shell thickness. As a consequence of PCM  
272 volume expansion during the melting process, the internal pressure will progressively  
273 increase and the shell will strain due to the increasing pressure. The pressure is no longer  
274 subject to linear with respect to the liquid fraction and the calculated maximum internal  
275 pressure will not reach an incredible value of over 3000 MPa, which is different from cases  
276 investigated without considering density change dependent on pressure in the work of Pitié *et*  
277 *al.* [27]. Fig. 4(b) compares the equivalent critical pressure as the cracking limit of SiC to the  
278 calculated maximum internal pressure in the SiC shell for different shell thicknesses. The  
279 maximum internal pressure and equivalent pressure both decrease with the decrease in shell  
280 thickness, while the latter has a larger decreasing rate. An intersection point between the  
281 maximum internal pressure and equivalent pressure appears at shell thickness  $a = 67 \mu\text{m}$ . It  
282 indicates that the shell can avoid cracking during the melting process of salts for  $a \geq 67 \mu\text{m}$ ,



283 whereas the shell will crack at some melting stage for  $a < 67 \mu\text{m}$ . The cracking point is  
284 marked according to the equivalent pressure of cracking limit represented by the horizontal  
285 line for  $a = 50 \mu\text{m}$  as shown in Fig. 4(a). The corresponding liquid fraction at the cracking  
286 point is 0.53. Through calculation according to Eqn. (28) and the calculated maximum  
287 internal pressure for  $a = 50 \mu\text{m}$ , we can infer that if the tensile strength of SiC could be  
288 augmented over 2.26 GPa the shell with  $a = 50 \mu\text{m}$  can also avoid cracking. According to  
289 Eqns. (26) and (28), the maximum internal pressure and equivalent critical pressure both  
290 depend on the ratio of core radius to shell thickness  $r_{i0}/a$ . Therefore, the condition of  
291 avoiding cracking for different size SiC-shell/salts-core capsules can be deduced by the  
292 critical shell thickness of  $67 \mu\text{m}$  for the salt bead of a 1 mm radius, which is  $r_{i0}/a \leq 14.9$ .

293         According to Eqn. (13), the density of the liquid PCM is dependent on the pressure.  
294 Although the isothermal compressibility of the liquid PCM is very small, the density  
295 variation cannot be ignored at high pressures. Fig. 5(a) elucidates the evolution of the density  
296 of liquid salts as a function of liquid fraction. Under the action of increasing internal  
297 pressures as shown in Fig. 4(a), the density of liquid salts gradually increases with the liquid  
298 fraction and its difference with that of solid salts gradually diminishes. Therefore, the volume  
299 expansion rate caused by phase change will be decreased, which slows down the pressure  
300 change at high pressures as shown in Fig. 4(a). The melting temperatures of coated salts at  
301 different melting stages under different shell thicknesses are shown in Fig. 5(b). It can be  
302 found that the melting temperature visibly increases as the melting process carries on. The  
303 coated salts must be heated up to at least 510.9 K, which is 14.8 K higher than the melting  
304 temperature at atmospheric pressure, to achieve complete melting for  $a = 200 \mu\text{m}$ . According  
305 to Eqns. (8) and (9), it is evident that the melting temperature mainly depends on the internal  
306 pressure. Thus variations of the melting temperature with the liquid fraction and shell  
307 thickness show the trends similar to the internal pressure. Fig. 5(c) shows the variation of

308 latent heat of salts during the melting process under different shell thicknesses. As both the  
309 internal pressure and melting point rise, the latent heat remarkably decreases. For  $a = 200$   
310  $\mu\text{m}$ , the latent heat reduces from 105 kJ/kg to 87.2 kJ/kg. This results in the effect of a loss in  
311 stored heat energy by absorption of latent heat. The decrease of shell thickness minimises the  
312 decrease of latent heat during the melting process and thus can increase the storage capability.

313 Due to the progressive increase of melting temperature, the wall temperature of the  
314 capsule should be increased continuously to trigger ongoing melting. Fig. 6(a) depicts the  
315 required wall temperature corresponding to different melting stages under different shell  
316 thicknesses of salt capsules at a heating rate of  $5^\circ\text{C}/\text{min}$ . The required maximum wall  
317 temperature for completely melting is 513.3 K at  $a = 200 \mu\text{m}$ . The required maximum wall  
318 temperature is reduced with the decrease in shell thickness. Fig. 6(b) displays the heat  
319 transfer rate at the salt capsule wall during the melting process under different shell  
320 thicknesses. The heat transfer rate has little change with the decrease in shell thickness for  
321 liquid fraction  $f^* \leq 0.1$ , while it increases with the decrease in shell thickness for  $f^* > 0.1$ .  
322 This is attributed to the smaller decrease of latent heat for a thinner shell as shown in Fig.  
323 5(c).

#### 324 *4.2 Effect of shell thickness on heat storage performance of salt capsules*

325 Fig. 7(a) demonstrates the melting time of coated salts under different shell thicknesses.  
326 The melting rate in the early stage of the melting process is less than that in the late stage for  
327 various shell thicknesses. This is due to the slow change of melting temperature in the early  
328 stage and its abrupt increase in the late stage. The shell thickness has no effect on the start  
329 time of the melting process, while the decrease in shell thickness speeds up the melting  
330 process and thus brings forward the end time of melting. This is consistent with the lower  
331 melting temperature for thinner shell thickness. The shortened melting period will be a  
332 benefit to the charging efficiency of heat energy.

333 The energy stored in the salt beads during the melting process is also examined for  
334 capsules with different shell thickness as shown in Fig. 7(b). The stored latent energy  
335 increases linearly with the liquid fraction, while the stored sensible energy sharply increases  
336 in the early stage of the melting process and slightly increases in the late stage. The change  
337 trends of the stored sensible energy are determined by the changes in melting temperature and  
338 wall temperature. In the early stage of the melting process, the stored sensible energy and  
339 latent energy represent a similar share of the total energy. In the late stage of melting, the  
340 stored latent energy is larger than the stored sensible energy. From this figure, we can also  
341 find that the capsule with a thicker shell stores larger sensible energy, while the capsule with  
342 a thinner shell stores larger latent heat during the melting process. The difference in the  
343 stored sensible energy for different shell thicknesses progressively decreases during the  
344 melting process, whilst the reverse is observed for the stored latent energy. The curves of  
345 stored total energy as shown in Fig. 7(b) show that the salt bead coated by a thinner shell  
346 offers better energy storage capacity.

347 The shell can also store some sensible heat during the salt melting process. As shown in  
348 Table 4, the thermal energy storage density, including the sensible heat stored in the shell, is  
349 compared for salt capsules with different shell thickness. Both the mass-based and volume-  
350 based energy storage densities notably increase with a decrease in the shell thickness. They  
351 increase by about 35.4 kJ/kg (55.1%) and 63.5 MJ/m<sup>3</sup> (37.6%), respectively, as the shell  
352 thickness reduces from 200 μm to 50 μm. The calculations indicate that the different sized  
353 capsules have the same energy storage density when they have the same  $r_{i0}/a$  value. The  
354 results imply that enhancing the tensile strength of shell materials to enable the thinner shell  
355 for encapsulated salts has great promise in further promotion of thermal energy storage  
356 density.

#### 357 *4.3 Comparative analysis between salt and Cu capsules*

358 Further simulations indicate that the effects of shell thickness of the Ni-shell/Cu-core  
359 capsule on the comprehensive energy storage performances are similar to those of the SiC-  
360 shell/salts-core capsule. However, due to the differences in the thermophysical and  
361 mechanical properties, the maximum internal pressure and equivalent critical pressure are  
362 notably different between the two types of capsules. Fig. 8(a) compares the equivalent critical  
363 pressure as the cracking limit of Ni to the calculated maximum internal pressure in the Ni  
364 shell for different shell thicknesses. This figure indicates that the Ni shell can accommodate  
365 the volume expansion of copper bead as the shell thickness is 400  $\mu\text{m}$ , which coincides with  
366 the experimental result of Zhang *et al.* [24]. From the intersection point between the  
367 maximum internal pressure and equivalent critical pressure, it can be inferred that the critical  
368 shell thickness for the Cu capsule is 248  $\mu\text{m}$  for the Cu bead of 1 mm in radius. Similarly, it  
369 can also be derived that the condition for avoiding cracking for different sized Ni-shell/Cu-  
370 core capsules is  $r_{i0}/a \leq 4.0$ . By comparing Fig. 8(a) with Fig. 4(b), it is found that the  
371 maximum internal pressure in the Cu capsule is much higher than that in the salt capsule at  
372 the same shell thickness. This can be easily explained, based on Eqn. (26), by the discrepancy  
373 between the two types of PCMs in the relative density difference  $(\rho_s - \rho_l)/\rho_l$ , as shown in  
374 Fig. 8(b). From this figure, it can be seen that the relative density difference of Cu is larger  
375 than that of salts at the same shell thickness of 200  $\mu\text{m}$  during the whole melting process. The  
376 larger relative density difference results in a higher internal pressure. Meanwhile, it can be  
377 found that the equivalent critical pressure of the Cu capsule is much less than that of the salt  
378 capsule by comparing Fig. 8(a) with Fig. 4(b). This is because the Ni as the shell of Cu  
379 capsule has smaller tensile strength than SiC as listed in Table 2. Therefore, a larger relative  
380 density difference and a smaller tensile strength lead to a smaller critical  $r_{i0}/a$  for avoiding  
381 cracking of the Cu capsule in comparison with the salt capsule.

382 The above results indicate that the capsules have optimum comprehensive energy  
383 storage performance when they possess the critical shell thickness. Fig. 9 displays the  
384 comparison between the salts and Cu capsules with the respective critical shell thickness in  
385 the melting point increment during the melting process and the melting time. As shown in Fig.  
386 9(a), the melting point increment of Cu is higher than that of salts in the early stage of  
387 melting, while the increment of Cu is lower in the late stage. This feature is determined by  
388 the thermodynamic properties and internal pressure according to the Eqns. (8) and (9).  
389 Although the maximum internal pressure in the Cu capsule is higher than that in the salt  
390 capsule, the eventual melting point increment of Cu is lower. This is different from the  
391 change tendency that the melting point increases with the internal pressure. The discrepancy  
392 indicates that the thermodynamic properties of PCMs play a critical role in the variation of  
393 melting point. Corresponding to the melting point increment, the Cu capsule exhibits slower  
394 melting rate in the early stage and faster melting rate at the late stage than the salt capsule for  
395 an equal sized PCM bead, as shown in Fig. 9(b). Further, it can be found in Fig. 9(b) that the  
396 melting period of a Cu bead is about 54 seconds lower than that of a salt bead at the same  
397 radius of 1 mm.

398

## 399 **5. Conclusions**

400 A thermo-mechanical model allowing for liquid PCM density variation at high  
401 pressures was set up to elaborate the behavior of a spherical capsule during melting of PCM  
402 for HTTES. The melting dynamic characteristics of PCM are notably different from those  
403 without considering the liquid density variation in the work of Pitié *et al.* [27]. The internal  
404 pressure is no longer increasing linearly with the increase of liquid fraction and the increasing  
405 rate gradually reduces. Hence the internal pressure does not increase to an incredibly high

406 value during the melting process. Accordingly, the changing rates of the melting point and  
407 latent heat of PCM during the melting process progressively decrease until nearly zero.

408 On the basis of the developed model, the effects of shell thickness on the  
409 comprehensive energy storage performances of a PCM capsule have been explored. When  
410 the size of PCM core is fixed, the decrease of shell thickness reduces the internal pressure  
411 increment, and thus diminishes the varying ranges of melting point and latent heat, which  
412 results in a diminution of melting period and an augmentation of stored latent energy in the  
413 capsule. Therefore increasing the ratio of core radius to shell thickness is beneficial for  
414 promoting the energy charging rate and energy storage capacity. However, there exists a  
415 maximum ratio of core radius to shell thickness to avoid shell cracking, which is 14.9 and 4.0  
416 for SiC-shell/salts-core and Ni-shell/Cu-core capsules, respectively. The maximum ratio of  
417 core radius to shell thickness can be elevated by enhancing the tensile strength of shell  
418 materials and/or selecting PCMs with small relative density difference between solid and  
419 liquid phases. In addition, the thermodynamic properties should be carefully considered in the  
420 selection of PCMs, which leads to different melting point increments and melting periods.  
421 This is confirmed by the fact that Cu capsules exhibit smaller melting point increment and  
422 shorter melting period than salt capsules for the same core radius with their respective critical  
423 shell thicknesses. Provided that the properties of PCMs and shell materials meet the main  
424 hypotheses described in Section 2.1, and that the PCMs have a fixed melting temperature at a  
425 specified pressure, the model can be applied to selection of materials and shell thickness to  
426 achieve excellent mechanical stability, fast energy charging rate and high energy storage  
427 capacity simultaneously for different types of encapsulated PCMs in HTTES applications.

428

429 **Acknowledgement**

430           The authors would like to acknowledge the financial support of the Engineering and  
431 Physical Sciences Research Council (EPSRC) of the United Kingdom (Grant Nos.  
432 EP/N000714/1 and EP/N021142/1), National Natural Science Foundation of China (Grant No.  
433 51606135) and Natural Science Foundation of Hubei Province (Grant No. 2016CFB156).

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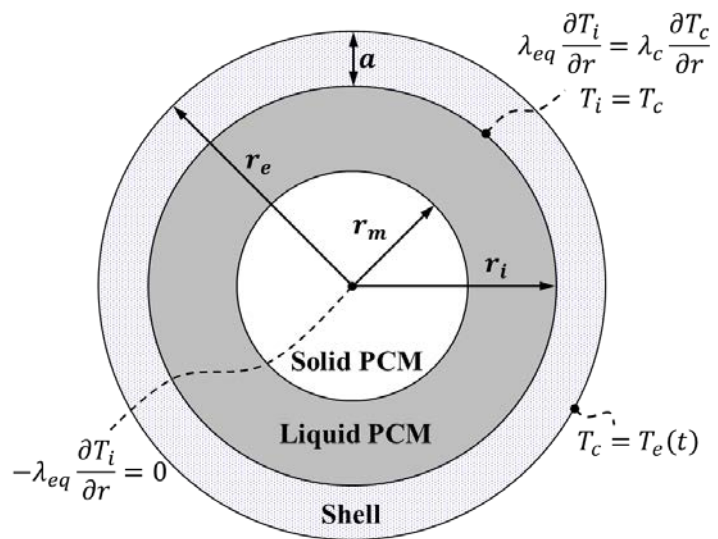


Fig. 1. Geometry of the spherical PCM capsule with boundary conditions.

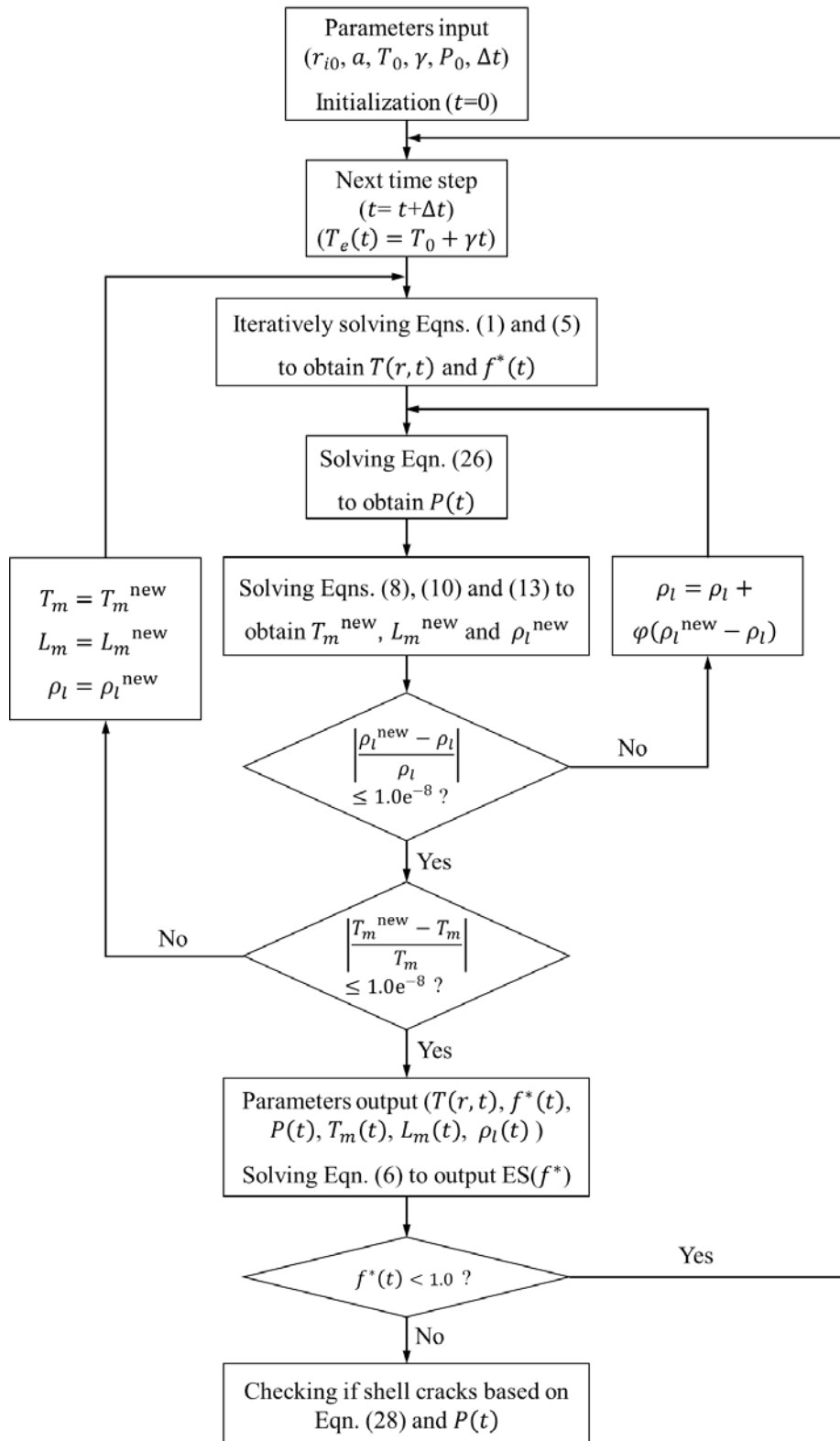
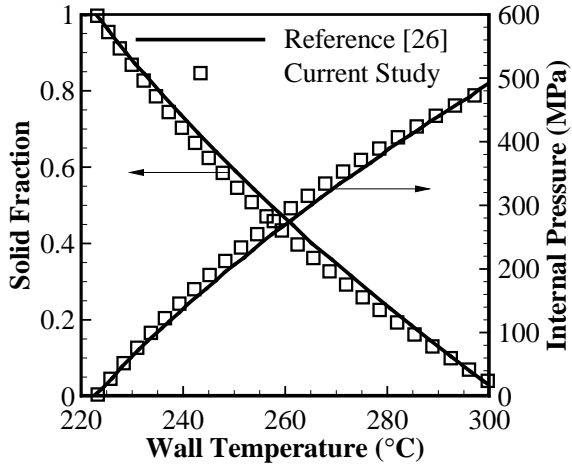
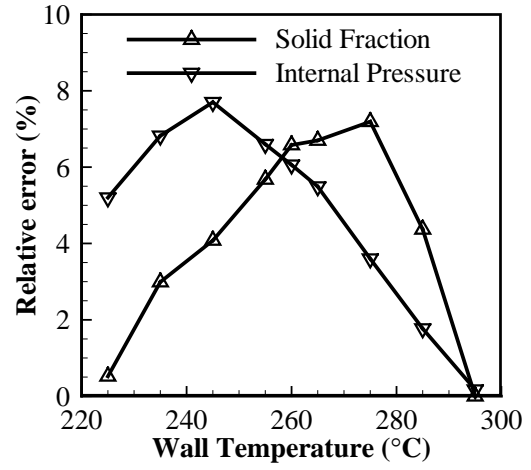


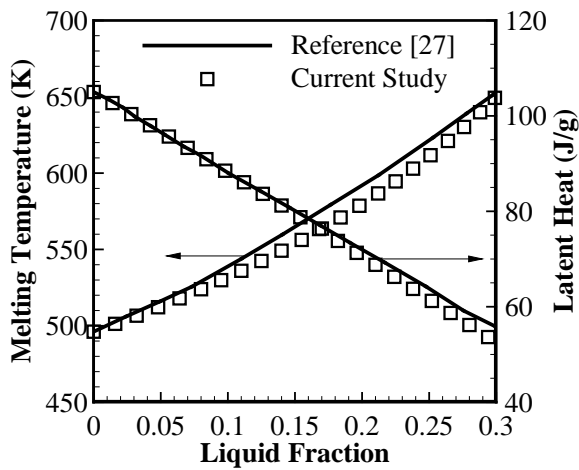
Fig. 2. Flowchart of solving procedure for the proposed model.



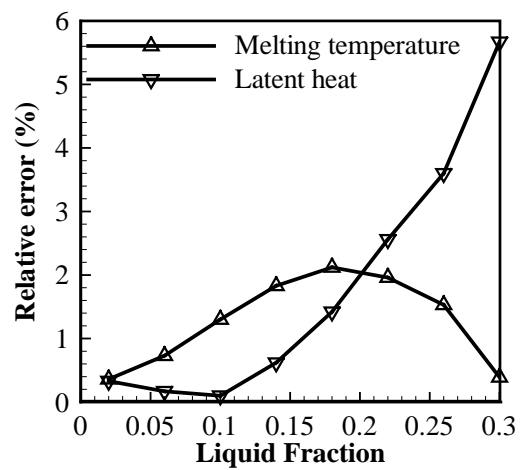
(a)



(b)

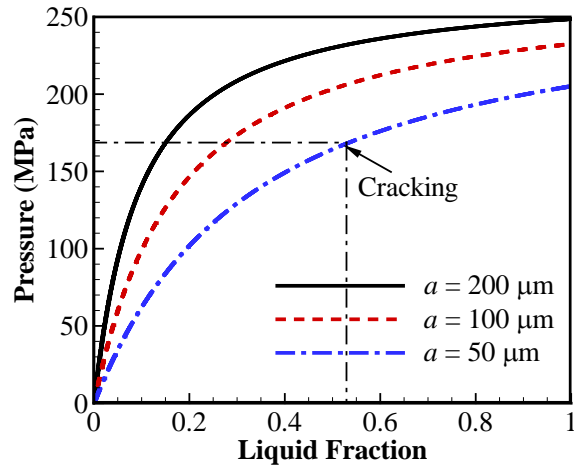


(c)

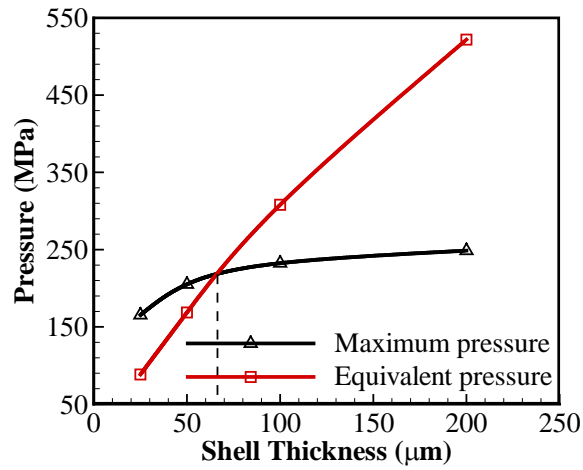


(d)

Fig. 3. Comparison with references: (a) Evolution of solid fraction and internal pressure with wall temperature; (b) Relative errors calculated from (a); (c) Evolution of melting temperature and latent heat with liquid fraction; (d) Relative errors calculated from (c).

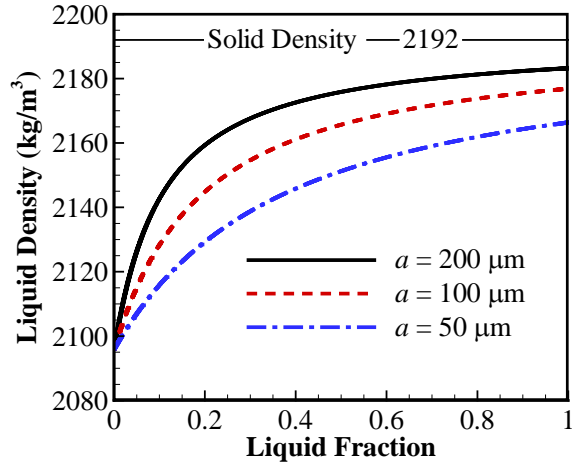


(a)

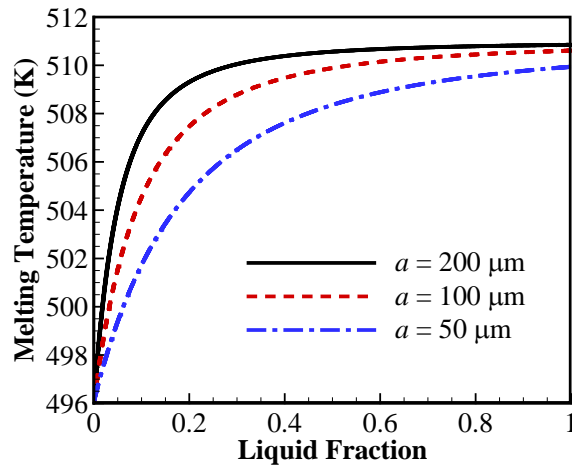


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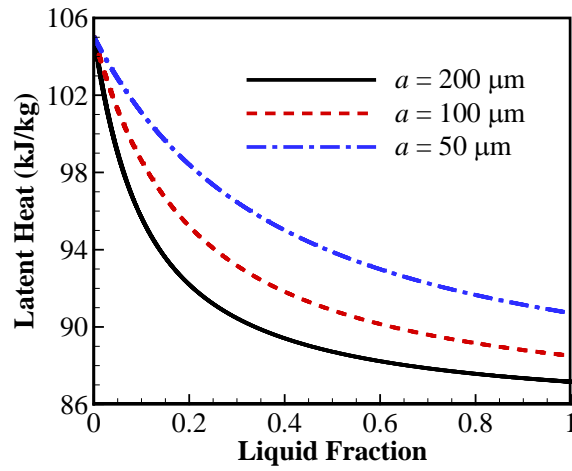
Fig. 4. Internal pressures under different shell thicknesses of salts capsule: (a) Evolution of pressures during melting; (b) Comparison between the calculated maximum internal pressures and pressures equivalent to the von Mises criterion strength of SiC as the cracking limit of materials. Critical position of cracking is labelled in (a).



(a)



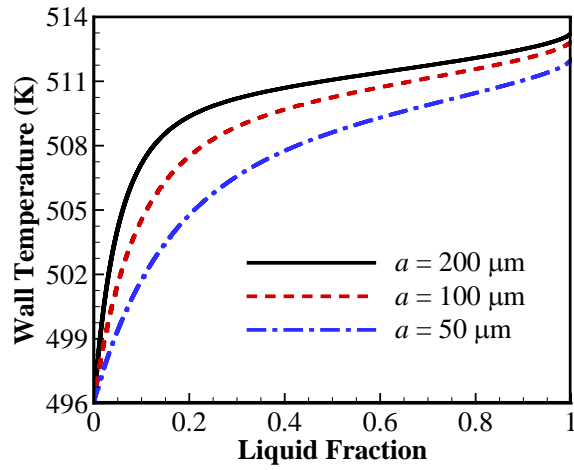
(b)



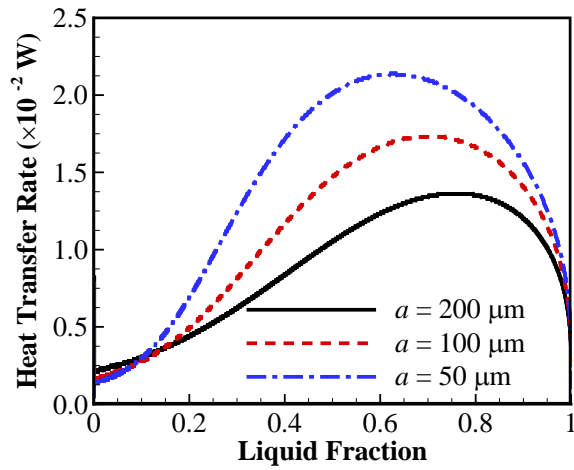
(c)

Fig. 5. Effects of shell thickness on the thermos-physical properties of salts during melting: (a) Evolution of liquid density; (b) Evolution of melting temperature; (c) Evolution of latent heat.



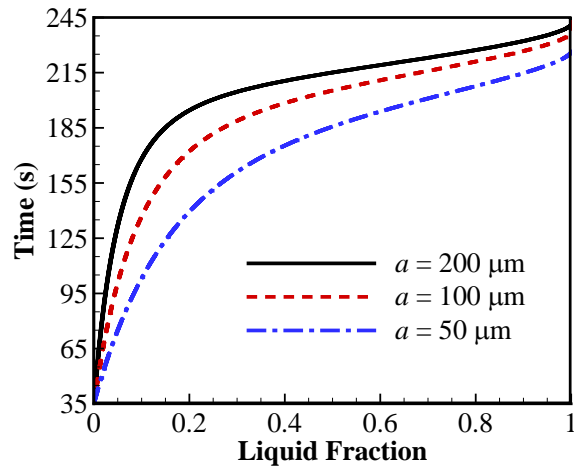


(a)

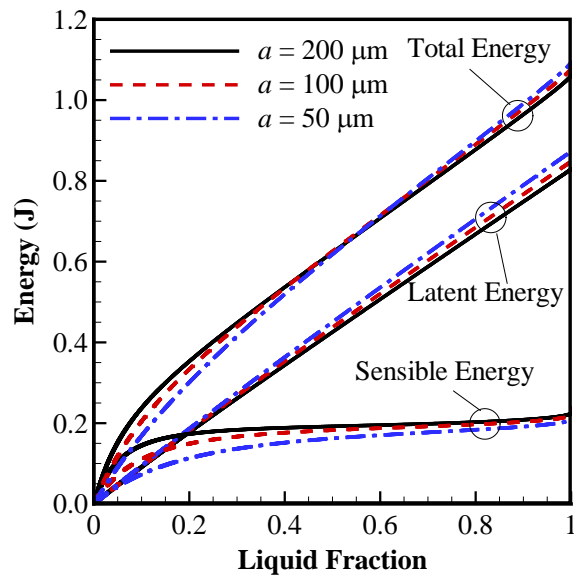


(b)

Fig. 6. Evolutions of wall temperature (a) and heat transfer rate (b) during melting under different shell thicknesses of salts capsule.

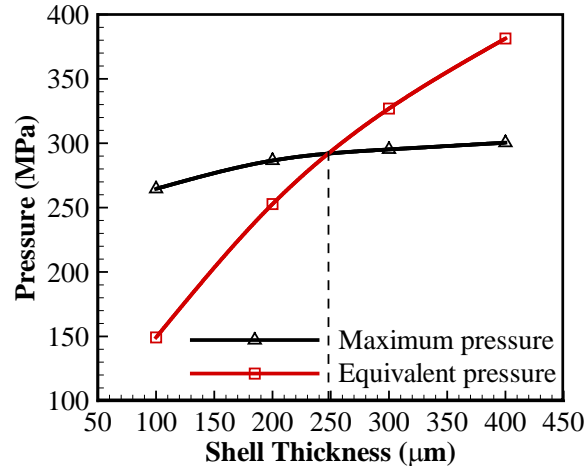


(a)

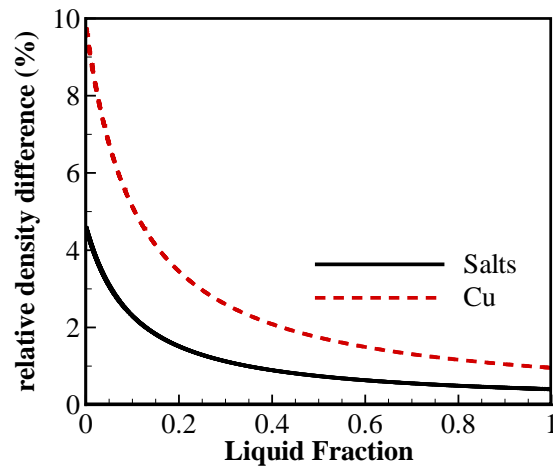


(b)

Fig. 7. Effects of shell thickness of salts capsule: (a) Melting time; (b) Evolution of stored energy.

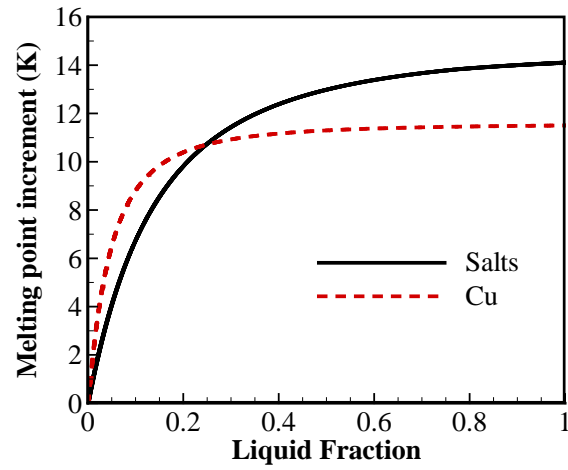


(a)

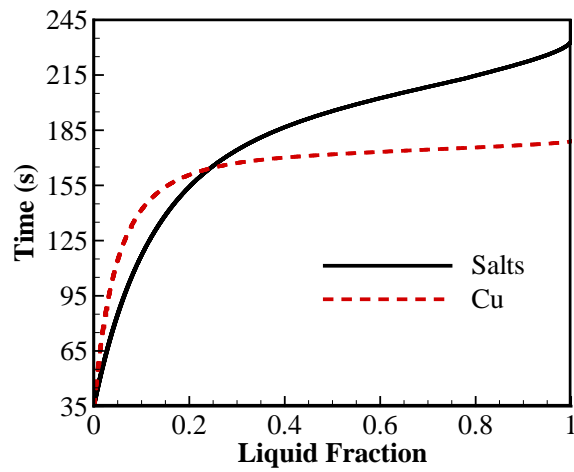


(b)

Fig. 8. (a) Comparison between the calculated maximum internal pressures and pressures equivalent to the von Mises criterion strength of Ni as the cracking limit of materials under different shell thicknesses of Cu capsule; (b) Comparison of relative density difference of solid and liquid phases between salts and Cu at a same shell thickness of 200  $\mu\text{m}$ .



(a)



(b)

Fig. 9. Comparison of melting dynamics between salts and Cu capsules with the respective critical shell thickness: (a) Melting point increment; (b) Melting time.

Table 1 Properties of salts [26, 32] and Cu [33-35] used in simulations.

	Properties	Symbol	Salts	Cu	Unit
Liquid state	Density	$\rho_{l0}$	2096	8020	$\text{kg}\cdot\text{m}^{-3}$
	Specific heat	$c_{pl}$	1500	643	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
	Compressibility	$\beta_l$	$1.86\times 10^{-10}$	$3.00\times 10^{-10}$	$\text{Pa}^{-1}$
	Thermal expansion	$\alpha_l$	$3.7\times 10^{-4}$	$1.05\times 10^{-4}$	$\text{K}^{-1}$
	Thermal conductivity	$\lambda_l$	0.8	166	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Solid state	Density	$\rho_{s0}$	2192	8800	$\text{kg}\cdot\text{m}^{-3}$
	Specific heat	$c_{ps}$	1430	477	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
	Compressibility	$\beta_s$	0	0	$\text{Pa}^{-1}$
	Thermal expansion	$\alpha_s$	0	0	$\text{K}^{-1}$
	Thermal conductivity	$\lambda_s$	1	394	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
L $\leftrightarrow$ S	Melting temperature at $P_0$	$T_{f0}$	223	1083	$^{\circ}\text{C}$
	Latent heat at $(T_{f0}, P_0)$	$L_{f0}$	105	207	$\text{kJ}\cdot\text{kg}^{-1}$

Table 2 Properties of SiC [36] and Ni [37] in simulations.

Properties	Symbol	SiC	Ni	Unit
Density	$\rho_c$	3227	8890	$\text{kg}\cdot\text{m}^{-3}$
Specific heat	$c_{pc}$	950	456	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$
Thermal expansion	$\alpha_c$	$4\times 10^{-6}$	$1.34\times 10^{-5}$	$\text{K}^{-1}$
Thermal conductivity	$\lambda_c$	120	80	$\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$
Young's modulus	$E_c$	454	200	GPa
Poisson's ratio	$\nu_c$	0.164	0.31	--
Tensile strength	$\sigma_t$	1858	900	MPa

Table 3 Input parameters used in simulations.

Parameters	Symbol	Salts capsule	Cu capsule	Unit
Radius of solid PCM bead	$r_{i0}$	1	1	mm
Shell thickness	$a$	25~200	100~400	$\mu\text{m}$
Initial temperature	$T_0$	220	1080	$^{\circ}\text{C}$
Heating rate of external surface	$\gamma$	5	5	$^{\circ}\text{C}\cdot\text{min}^{-1}$
Initial pressure	$P_0$	$1.01\times 10^5$	$1.01\times 10^5$	Pa
Time step	$\Delta t$	0.1	0.1	s

Table 4 Thermal energy storage density of a single capsule containing a salts bead with a radius of 1 mm.

Shell thickness ( $\mu\text{m}$ )	Mass-based energy storage density (kJ/kg)	Volume-based energy storage density (MJ/m <sup>3</sup> )
200	64.2	168.8
100	84.2	206.3
50	99.6	232.3



## Appendix

### A. Derivation of Eqn. (1)

Fig. A-1 presents an arbitrary control volume  $V$  undergoing a phase change. In the volume  $V$  the total enthalpy  $H$  can be written as the sum of sensible enthalpy  $h$  and latent heat  $\Delta h_m$ , i.e.

$$H = h + \Delta h_m = c_p T + \Delta h_m. \quad (\text{A-1})$$

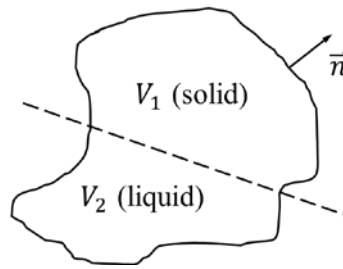


Fig. A-1 An arbitrary control volume.

Based on the volume  $V$  an energy balance will give

$$\frac{d}{dt} \int_V \rho H dV = \int_S -\rho H \vec{u} \cdot \vec{n} dS + \int_S \lambda \nabla T \cdot \vec{n} dS, \quad (\text{A-2})$$

where  $V = V_1 + V_2$ ;  $S$  is the surface area;  $\vec{u}$  is the velocity; and  $\vec{n}$  is the normal vector of external surface. Applying a divergence theorem, Eqn. (A-2) becomes

$$\int_V \left[ \frac{\partial(\rho H)}{\partial t} + \nabla \cdot (\rho H \vec{u}) - \nabla \cdot (\lambda \nabla T) \right] dV = 0. \quad (\text{A-3})$$

Since  $V$  is arbitrary and if the flow is negligible, Eqn. (A-3) can be expressed as

$$\frac{\partial(\rho H)}{\partial t} - \nabla \cdot (\lambda \nabla T) = 0. \quad (\text{A-4})$$

Combining Eqns. (A-1) and (A-4) yields

$$\frac{\partial(\rho c_p T)}{\partial t} = \nabla \cdot (\lambda \nabla T) - \frac{\partial(\rho \Delta h_m)}{\partial t}. \quad (\text{A-5})$$

which can be easily transformed into Eqn. (1) for the PCMs region under a spherical coordinates system with spherical symmetry.

### B. Derivation of Eqn. (7)

The Gibbs free energy  $g_j(T_m, P)$  can be estimated by a second order Taylor expansion around  $g_{j0}(T_{m0}, P_0)$ :

$$\begin{aligned}
g_j(T_m, P) = & g_{j0} + \left. \frac{\partial g_j}{\partial T_m} \right|_{P_0} (T_m - T_{m0}) + \left. \frac{\partial g_j}{\partial P} \right|_{T_{m0}} (P - P_0) \\
& + \frac{1}{2} \left. \frac{\partial^2 g_j}{\partial T_m^2} \right|_{P_0} (T_m - T_{m0})^2 + \left. \frac{\partial^2 g_j}{\partial P^2} \right|_{T_{m0}} (P - P_0)^2 \\
& + \left. \frac{\partial^2 g_j}{\partial T_m \partial P} \right|_{P_0, T_{m0}} (T_m - T_{m0})(P - P_0),
\end{aligned} \tag{B-1}$$

The Gibbs relation based on Gibbs free energy is defined as [30]

$$dg_j = -s_j dT_m + \frac{1}{\rho_j} dP \tag{B-2}$$

which combined with the fundamental relation for the total differential yields

$$\left. \frac{\partial g_j}{\partial T_m} \right|_P = -s_j, \quad \left. \frac{\partial g_j}{\partial P} \right|_{T_m} = \frac{1}{\rho_j} \tag{B-3}$$

The differential relationship of the entropy can be written as [30]

$$ds_j = \frac{c_{pj}}{T_m} dT_m - \left. \frac{\partial(1/\rho_j)}{\partial T_m} \right|_P dP, \tag{B-4}$$

which similarly yields

$$\left. \frac{\partial s_j}{\partial T_m} \right|_P = \frac{c_{pj}}{T_m} \tag{B-5}$$

The thermal expansion coefficient and isothermal compressibility are defined as [30]

$$\alpha_j = \rho_j \left. \frac{\partial(1/\rho_j)}{\partial T_m} \right|_P, \quad \beta_j = -\rho_j \left. \frac{\partial(1/\rho_j)}{\partial P} \right|_{T_m}. \quad (\text{B-6})$$

Based on Eqns. (B-3), (B-5) and (B-6), we get

$$\begin{cases} \left. \frac{\partial^2 g_j}{\partial T_m^2} \right|_P = - \left. \frac{\partial s_j}{\partial T_m} \right|_P = - \frac{c_{pj}}{T_m}, \\ \left. \frac{\partial^2 g_j}{\partial P^2} \right|_{T_m} = \left. \frac{\partial(1/\rho_j)}{\partial P} \right|_{T_m} = - \frac{\beta_j}{\rho_j}, \\ \left. \frac{\partial^2 g_j}{\partial T_m \partial P} \right|_{P, T_m} = \left. \frac{\partial(1/\rho_j)}{\partial T_m} \right|_P = \frac{\alpha_j}{\rho_j}. \end{cases} \quad (\text{B-7})$$

By reporting Eqns. (B-3) and (B-7) in Eqn. (B-1), Eqn. (7) is derived.