

Phase Change Materials : A Numerical Method for the Behaviour Predictions

Zohir Younsi ^a, Annabelle Joulin ^a, Laurent Zalewski ^a,
Stéphane Lassue ^{a,*}, and Daniel R. Rousse ^b

^a LAMTI, Faculté des Sciences Appliquées de l'Université d'Artois, Technoparc FUTURA 62400 Béthune Cedex, France

^b Université du Québec à Chicoutimi, Chicoutimi, G7H 2B1, Canada

Abstract

The storage of thermal energy as latent heat of fusion has attractive features over sensible heat due to its high storage density and isothermal nature of the storage process at melting temperature. Latent heat thermal energy storage systems find application in space craft, refrigerated cargo transport, solar energy system, greenhouses, heating and cooling of buildings, etc.

The use of phase change material (PCM) for thermal storage in buildings was one of the first applications considered for such materials along with typical sensible heat storage reservoirs and enclosures. Hence, the LAMTI is studying the thermal behaviour of phase change materials so as to incorporate bricks of such materials into passive solar components. However, optimized performances calls for parametric studies of relevant properties and dimensions and therefore require an appropriate design tool.

This paper presents the first research effort of our group to formulate, implement, and validate a numerical method in order to optimize the design of solar passive walls involving phase change materials (PCM). The fusion of the commercially available PCM27 (hydrated salt), engineered by Cristopia, was studied. The proposed enthalpy based method is found excellent to predict the fusion but still fails to adequately reproduce the exact solidification pattern measured for the PCM 27. Further work is then undergoing to improve the model.

Keywords: Numerical predictions, enthalpy based method, melting and solidification, phase change material.

1. Introduction

The thermal latent energy storage provides more attractive features than its sensible counterpart. This is mainly due to its high energy storage density and to the isothermal nature of the storage process at the melting temperature of the material. Latent heat thermal energy storage systems find application in space craft, refrigerated cargo transport, solar energy system, greenhouses, and, with respect to this paper, also in heating and cooling of buildings.

The use of phase change material (PCM) for thermal storage in buildings was one of the first applications considered for such materials along with typical sensible heat storage reservoirs and enclosures. Today, PCM are the subject matter of several review papers: encapsulated materials used in plasterboard or packed beds are reviewed in a paper by Regin, Solanki, and Saini [1]; PCM in buildings applications are the subject of the syntheses by Tyagi and Buddhi [2] and Zhang *et al.* [3] while general storage applications are reviewed in that of Sharma *et al.* [4] and Farid *et al.* [5]. Cassedy's work [6] provides an overview of the applications.

In this context, the overall objective is here to insert PCM in a passive solar component such as the « composite Trombe wall » investigated by Zalewski *et al.* [7, 8]. However, optimized performances require parametric studies of relevant properties and dimensions, and therefore an appropriate design tool. Although heat transfer in a building wall is mostly one-dimensional, in vertical enclosures filled with liquid that undergoes a temperature difference between the vertical surfaces, natural convection occurs and two-dimensional effects have to be accounted for. This paper here presents the first steps of an effort aimed at formulating, implementing, and validating a numerical method to be used as such.

The objective of the present study is to propose a suitable two dimensional numerical method for the investigation of the fusion process of a specific PCM brick.

The next section discusses briefly the phenomenon to be simulated while the third section presents the mathematical description and the numerical procedure. The fusion of the specific PCM to be used in our application is then investigated. The numerical code is first validated by comparing the obtained results with 1D

*Corresponding author. Tel.: +0 33 (0)320640271 Fax: 0 33 (0)3211780; E-mail: stephane.lassue@univ-artois.fr

analytical, 2D numerical and experimental melting result available in the literature or obtained experimentally. Concluding remarks close the paper.

2. Physical phenomenon

This section is only an overview of the basic difficulties encountered when a prediction method based on the solution of a mathematical model is required. The topic is discussed in an excellent textbook on the subject by Bejan [9] and Burmeister [10]. A specific recent review of mathematical modeling of latent heat thermal energy storage using PCM is provided by Verna and Singhal [11]. During the early stages of the melting process, conduction is the dominant mode of heat transfer even within the liquid phase. This is followed by a short transition phase for which both conduction and natural convection occur. Then, as the melt volume increases, natural convection becomes dominant [12].

The first difficulty an analyst has to deal with, is the high nonlinearity of the governing equations which precludes the general use of analytical solutions. Other difficulties pertain to the time-dependence of location, shape, and orientation of the solid-liquid interface as well as that of the presence of a time-dependent « mushy » zone that may involve solid particles surrounded by the liquid phase next to the interface. Moreover, in the case of solidification, problems are even more complex: superfusion phenomena occur [13]. In the experimental counterpart of the numerical analysis proposed here, the solidification process analysis was found to be impossible to carry out because of the importance of superfusion within the PCM [14].

3. Proposed model

In the work presented here, the investigated material (hydrated salts) has a melting point (announced by the manufacturer) equal to 27°C [15]. The phase change material samples are 210x140x25 mm³ parallelipedic elements. As the bricks of PCM – called PCM27 – used have to be installed vertically in a wall, a two-dimensional behavior is assumed. Several approximate analytical solutions have been worked out for problems involving a pure substance [16] or even two substances [17,18]. But as soon as the geometry or the material are complex, they are no longer amenable to provide solutions.

Hence, numerical solutions of the governing equations are generally proposed. Some of these formulations are temperature-based methods while others base their mathematical model upon enthalpy. The first ones rely on the prediction of the front of fusion/solidification while the other, much easier to implement, does not.

In the mathematical model involved herein, the enthalpy formulation is used, because the following advantages take place: (1) the governing equations are similar to the single phase equations, (2) there is no explicit condition to be satisfied at the solid-liquid interface; (3) the enthalpy formulation involves the solution within a mushy zone, involving both solid and liquid material, between the two standard phases; and (4) the phase change problem becomes much easier to solve.

Independently of the formulation retained, several numerical methods have been used to implement PCM. Here, a finite volume method (FVM) formulated for the

solution on Cartesian grids was retained [19]. As both the weak formulation of the melting problem and the finite volume methods have been the subject of several publications, they will not be repeated here to avoid making this paper overly lengthy. The interested reader should consult the paper by Voller [20] or the text book by Patankar [19] for details.

3.1. Geometry and general boundary conditions

A validation procedure has been carried out to later simulate the melting of PCM 27 bricks.

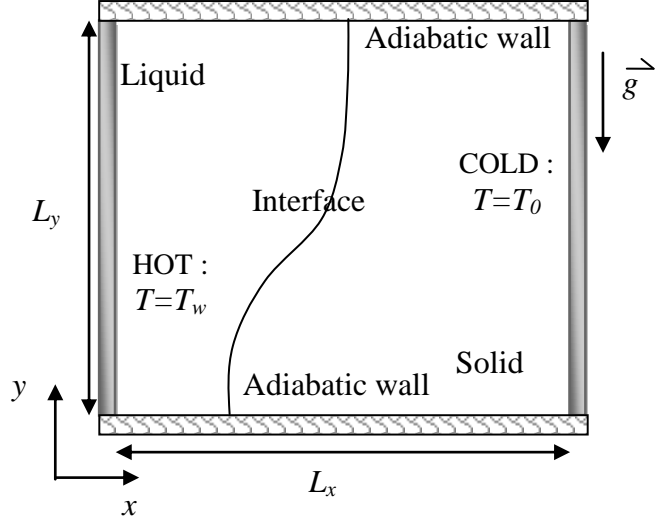


Fig. 1 : Schematic of the problem

Fig. 1 shows a rectangular two-dimensional cavity (brick) of length L_x and height L_y subject to the following boundary conditions:

- Heated surface (left surface, $x=0, y, t$)

$$u = v = 0 \quad T = T_w \quad (1)$$

- Solid / liquid interface ($x = x_c, y = y_c, t$)

$$u = v = 0 \quad T = T_F \quad (2)$$

- Cooling surface (right surface, $x = L_x, y, t$)

$$u = v = 0 \quad T = T_0 \quad (3)$$

- Top ($x, y = 0, t$) and bottom ($x, y = L_y, t$) surfaces

$$u = v = 0 \quad \frac{\partial T}{\partial y} = 0 \quad (4)$$

where $T_w > T_F > T_0$

3.2. Relevant assumptions

To obtain a solution of the governing equations [19,20], several assumptions are essential to understand the limits of the validity of the selected method:

1. The problem is two-dimensional.

Strictly speaking, edge effects should be taken into account for a single brick of material. But,

these bricks will be inserted into a wall into which the heat transfer is nearly one-dimensional. Hence, the two-dimensional behavior is retained to account for natural convection within the bricks.

2. The horizontal walls are adiabatic.

This allows for a one-dimensional comparison with standard solutions for the Neumann problem, and the vertical heat fluxes (y-direction) will indeed be quite negligible compared to those in the horizontal direction (x-direction).

3. Conduction occurs in both phases.

This is strictly true with thermophysical properties that may differ.

4. Natural convection occurs in the liquid phase.

The Neumann one-dimensional solution is only for conduction but the two-dimensional solutions proposed here will account for natural convection within the liquid phase.

5. Radiative heat transfer is neglected.

The temperature gradients are small and the overall temperatures are low. Consequently, it is assumed that any radiation heat transfer is accounted for in the effective thermal conductivity.

6. The flow in the liquid phase is Newtonian, laminar, incompressible, and the Boussinesq approximation holds.

7. Viscous dissipation is neglected.

The liquid phases of either ice or gallium as well as that of PCM 27 have low viscosities and this assumption holds.

8. Thermophysical properties are constant.

Solid region:

$$\frac{\partial T}{\partial t} = \alpha_s \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right] \quad (5)$$

Liquid region:

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad (6)$$

$$\rho_l \left(\frac{\partial u}{\partial t} + u \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} \right) = -\frac{\partial p}{\partial x} + \mu \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) + Bu \quad (7)$$

$$\rho_l \left(\frac{\partial v}{\partial t} + u \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} \right) = -\frac{\partial p}{\partial y} + \mu \left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) + \rho g \beta (T - T_{ref}) + Bv \quad (8)$$

$$\left(\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} \right) = \alpha_l \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) - \frac{L}{c_l} \frac{\partial f}{\partial t} \quad (9)$$

Although different in the liquid and the solid phases, densities, heat capacities and thermal conductivities are assumed to remain constant with time and independent of temperature. Properties for PCM 27 are determined experimentally while standard properties are taken from the literature for water and gallium. In the liquid phase, an effective thermal conductivity is obtained and this eases the comparison with the standard one-dimensional Neumann solutions.

9. The PCM material is pure, homogeneous and isotropic.

This is certainly not the case for a hydrated salt for the crystallization of PCM27, but once again the main idea is to propose a design tool and the assumption is not too bad as the fusion process displays much less discontinuities than its solidification counterpart.

10. The effect of thermal expansion is neglected.

Indeed, the brick involves an air space within its polyolefin envelope that will act as a buffer to take the solidification related expansion. Accounting for expansion does not modify the overall thermophysical properties observed here.

During the fusion process, three different states coexist, the fully liquid state, the solid state and the "mushy" region, involving a mixture of solid particles surrounded by liquid. In the modeling, source terms are added in the momentum equations to account for this mushy region.

3.3. Mathematical model

Based on the aforementioned assumptions, the governing equations for the heat transfer melting process are as follows:

In the enthalpy-porosity approach, the condition that sets the velocities in the solid regions is provided by appropriately defining a parameter B in the momentum equations [21]. The basic principle is to reduce gradually the velocities from a finite value in the liquid to zero in the solid, over the computational cell that undergoes phase change. This can be achieved by assuming that such cells behave like a porous media with a porosity equal to the liquid fraction. In order to achieve this behavior, an appropriate definition of B is:

$$B = -\frac{C(1-f)^2}{(f^3+b)} \quad (10)$$

which is the Carman-Kozeny relation. In this model, $f = 1$ in the liquid region while $f = 0$ in the solid region while it takes a value between 0 and 1 in the mushy zone. The constant C has a large value to suppress the velocity as the cell becomes solid and b is a small constant used to avoid a division by zero when a cell is fully located in the solid region, that is when $f = 0$. The choice of the constants is arbitrary. However, the constants should ensure sufficient suppression of the velocity in the solid region and should not influence the numerical results significantly. In this work, $C = 1 \times 10^9$ $\text{kg} / \text{m}^3 \text{ s}$ and $b = 0.0003$ are used [22].

The relevant dimensionless parameters are then :

$$Ra = \frac{\rho^2 c_l g \beta L_y^3 (T_w - T_F)}{\mu k_l} \quad (11)$$

$$Ste = \frac{c_l (T_w - T_F)}{L} \quad (12)$$

$$Pr = \frac{c_l \mu}{k_l} \quad (13)$$

which are respectively, the Rayleigh, Stefan, and Prandtl numbers. The overall formulation is nondimensionalized to enable comparisons with several test cases found in the literature. This dimensionless model is provided elsewhere [23].

3.4. Numerical procedure

As recommended by Patankar [19], a single algorithm can be used where all the governing equations for the heat transfer melting process can be casted into a general form:

$$\frac{\partial(\rho\phi)}{\partial t} + \nabla \cdot (\rho V\phi) = \nabla \cdot (I\nabla\phi) + S \quad (14)$$

where S is a source term.

In this method, the absorption of latent heat during melting is included as a source term S_h in the energy equation. Latent heat content of each control volume in the PCM is evaluated after each energy equation iteration cycle. Based on the latent heat content, a liquid fraction for each control volume is determined. For control volumes containing a liquid phase of PCM, f is set to 1, and for control volumes containing solid phase, f is set to 0. The control volumes with values of f between 0

and 1 are treated as mushy. Even though the phase change is assumed to be isothermal, the idea of mushy zone is introduced to gradually switch off the velocities from liquid to solid at the interface.

The conservation equations are discretized by a finite-volume method on a uniform Cartesian grid. The coupled energy-liquid fraction, resulting from the use of an enthalpy formulation, is handled by the procedure suggested by Brent and al. [21]. The SIMPLER algorithm is used to solve the coupled continuity and momentum equations. This code is fully implicit in time, for transient computations, and the convection-diffusion terms are treated by the hybrid scheme [19]. A line by line solver based on the TDMA (tri-diagonal matrix algorithm) is used to solve iteratively the algebraic discretized equations.

The general form of the discretized equation for any variable ϕ is given by

$$A_p \phi_p = \sum_i A_i \phi_i + S \quad (15)$$

For each iteration, the solid-liquid interface has to be determined. In this work, it is based on the value of the liquid fraction. The liquid fraction is updated using the equation:

$$f_p^{k+1} = f_p^k + \omega \frac{\Delta t A_p^k h_p^k}{\rho L \Delta V} \quad (16)$$

where ω is an appropriate under-relaxation factor.

To prevent the calculation of unrealistic values for f , variations of f_p from one iteration to the next are limited by use of

$$f_p^{k+1} = \begin{cases} 1 & \text{if } f_p^{k+1} > 1 \\ 0 & \text{if } f_p^{k+1} < 0 \end{cases} \quad (17)$$

Hence, despite the particular additions to the momentum and energy equations with respect to a standard mathematical description, the procedure proposed by Patankar [1980] can readily be used to obtain discretized algebraic equations, to incorporate boundary conditions, to solve, and to provide relevant dependent variables via an adequate post-processing.

Suffice it to say that for a given time step, when a converged solution is obtained for the discretized algebraic equations, the dimensionless liquid fraction is updated until no further change is detected in the solution for this particular time step. Then, the procedure proceeds with the next time step until t_{\max} is reached.

4. Melting of PCM 27

The first test problem used to assess the correct implementation and set-up of the numerical analysis tool is that of ice melting for which several numerical [24] and experimental [25] solutions can be found.

As a second benchmark problem, the melting of gallium was considered. Several solutions involving temperature and enthalpy based methods can be found in the literature [26-28].

Specific results for these two problems are not presented here to avoid making this paper overly lengthy. The interested reader should consult [23].

Then, following the assessments against results found for ice and gallium, PCM 27 was considered for simulation using the proposed FVM method. The thermophysical properties of relevant parameters used here were measured and reported in Table 1.

Table 1 : Data specifications for the melting PCM 27.

Variable	Solid	Liquid
k (W/m.K)	0,577	0,813
c_p (J/kg.K)	1751,5	2225
α (m ² /s)	$1,93 \times 10^{-7}$	$2,39 \times 10^{-7}$
ρ (kg/m ³)	1710	1530
L (kJ/kg)	172,42	
T_F (K)	300,15	
T_0 (K)	288,15	
T_w (K)	323,15	

4.1. Numerical details and results

The first thing done was the implementation of the exact one-dimensional analytical solution for the melting of a homogeneous solid so as to compare it with a numerical implementation of a one-dimensional finite volume method. This 1D FVM was to be used as a comparison method for the 2D FVM proposed here [X].

Several domain discretizations were studied for the 2D simulations. Mesh redeployment has been used to refine the discretization along the active wall ($x=0$). A 80x40 grid was found to be satisfactory to obtain converged solutions, insensitive to further refinements.

The time step used was found to be problem dependent; different temperature scales (differences between the hot and the cold surfaces) were found to require different time steps. A time step of $t=1$ s was found to be appropriate for all cases. Calculations were carried out for conditions used in the experiments [8].

The relevant dimensionless parameters for the problem are: $R = 0,12$; $Ra = 1,34 \times 10^6$; $Pr = 273,85$; $Ste = 0,2968$; $c_s/c_l = 0,79$; and $k_s/k_l = 0,71$.

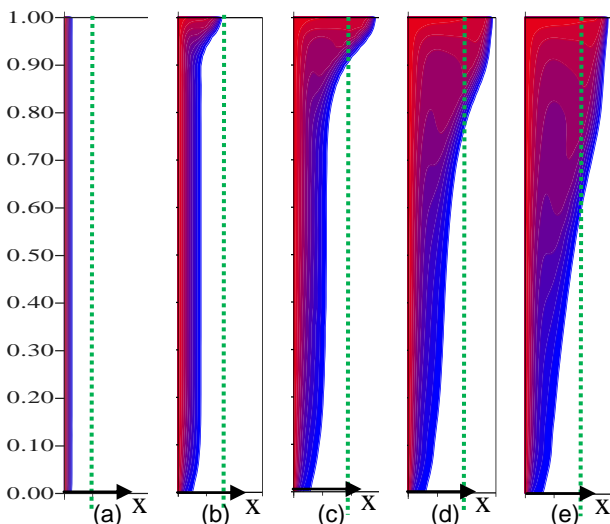


Figure 2: Location of the fusion front for several times: (a) 1 000s; (b) 10 000s; (c) 20 000s; (d) 30 000s; and (e) 40 000s. The dashed line is the corresponding 1D solution.

Figure 2 shows the calculated melting interface location for five different times ($t=1000s$, $t=10000s$, $t=20000s$, $t=30000s$, and $t=40000s$) after the onset of melting. At the time $t=1000s$, the melt interface is almost vertical, suggesting the dominance of the conduction mode of heat transfer. The dashed line, representing the one-dimensional semi-infinite solid solution, overestimates this location. As the melting process continues, the process of fusion is more and more dominated by the convection mode. As time increases, this buoyancy induces the motion of the fluid due to the temperature gradient, and then causes the melt volume at the top to move at a faster rate compared to the fluid at the bottom. This is obvious for the melt interfaces at times $t=10000-40000s$, which are curved due to the effect of the natural convection, thus augmenting the overall melting process. For $t=40000s$, Fig.2(e), the front is shown to be ahead of the 1D prediction in the top of the cavity while it is lagging behind at the bottom.

Here, one may think that the overall one-dimensional results (predictions or analytical solution) of the front location are not too wrong as the area behind the curve is quite corresponding to that behind the dashed line. However, this is misleading as the aspect ratio is $R=0,12$, that is the thickness of the brick is small (indeed it is 1 inch or $L_x=25$ mm) compared to its height. With higher aspect ratios, the discrepancies augment and the one-dimensional solutions fail to predict the phenomenon. One dimensional solutions should then be avoided.

As the overall objective is to propose a suitable tool for the design of passive walls involving such PCM bricks, the validity of the predictions have to be determined against suitable experimental data and preferably by another mean as well.

Experimental results are presented in a companion paper to this one along with the details that pertain to the genuine experimental apparatus used for thermophysical property measurements and PCMs bricks behavior determination [8]. Moreover, Fluent 6 as used as a validation tool for the simulation of the proposed bricks.

In Figure 3, the heat flux (left axis) and the temperature (right axis) variations in the PCM are presented with respect to time as the materials undergoes heating from 15°C to 50°C (that is complete melting). The results are presented for the material adjacent to the inner surface of the brick's envelope, that is the material which is in the immediate vicinity of the heated surface.

The physical interpretation of the results is provided in the companion paper to this one and is not repeated here [8]. Nevertheless, Fig.3 shows that both numerical methods provided excellent correspondence with experimental results. The temperature profile clearly indicates the phase change that takes place while the material next to the wall is between 27°C (the melting point) and 32°C .

5. Conclusion

In this paper, a numerical work is conducted to study the thermal characteristics of the fusion process of a PCM heated on a vertical wall of a rectangular enclosure. This work has not been reported before.

An enthalpy-based mathematical model is proposed to analyze PCM for latent storage. Solution is obtained by using a control volume-based finite element method.

The convection-dominated melting in a rectangular cavity is also investigated numerically using the commercial code Fluent. The work first shows that one-dimensional

solutions should not be used although the aspect ratio is very low.

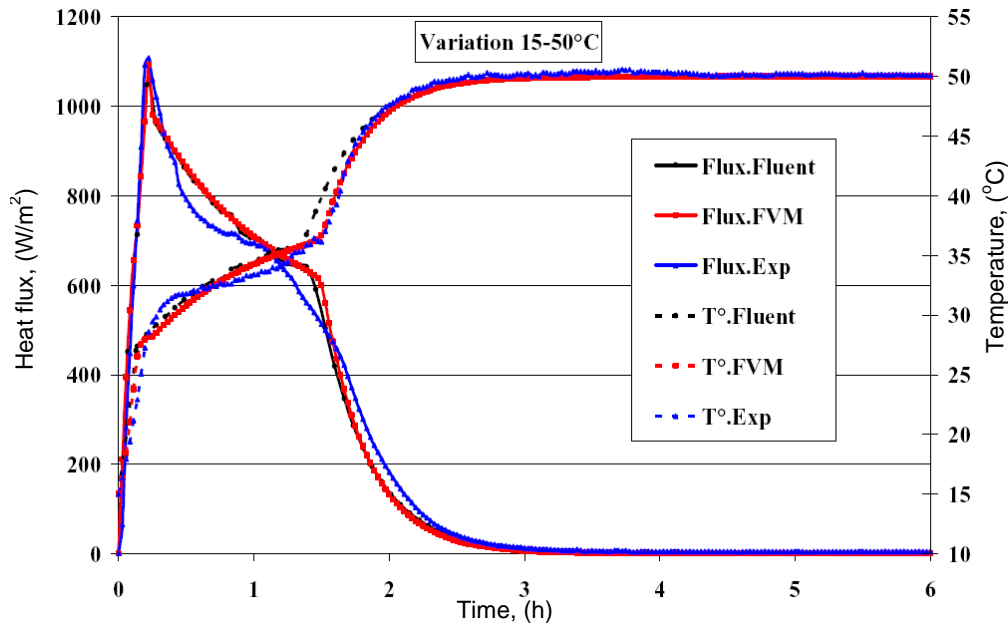


Fig.3: Variation of the heat flux (left) and temperature (right) of a brick of phase change material initially at 15°C when the temperature of the left wall ($x=0$) is suddenly raised to 50°C.

After several adjustments to obtain appropriate discretization, time step, and relaxation factor, the method has been used to reproduce experimental results obtained by other means for the material investigated here [15]. Numerical predictions provided confidence in the correct formulation and implementation of the proposed method. The method could now be used in a global design tool to investigate the idea of incorporating bricks of PCM 27 within passive solar walls.

Acknowledgments

The authors are very grateful to the program ANR-PREBAT which financed the work and to Artois Comm and the Nord Pas de Calais Region for financing the Phd thesis of Zohir Younsi.

The fifth author is grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Discovery grant.

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