

Physical model for the latent heat of fusion

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Abstract

The atomic movement induced on melting has to overcome a viscous drag resistance. It is suggested that the latent heat of fusion supplies the required energy for this physical process. The viscosity model introduced here allows computation of the latent heat from viscosity, molar volume, melting temperature, and atomic mass and diameter. The correlation between these parameters and the latent heat was calculated for monoatomic melts formed from body and face centered cubic structure. The correlation coefficients are 0.97 and 0.95 respectively.

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1. Introduction

Despite the enormous importance of the liquid–solid phase transformation there is still no satisfactory theory able to describe this process. One of the key missing elements is an understanding of the latent heat of fusion (L_f). The latent heat of fusion is the energy which has to be supplied to the system in order to complete the phase transformation. This energy is absorbed at constant temperature when the solid transforms to liquid. Since the temperature remains constant, the corresponding entropy change is the difference between the entropy (S) of the two phases

$$\Delta S = S_{\text{liquid}} - S_{\text{solid}} \quad (1)$$

then the latent heat of fusion is

$$L_f = T_m \Delta S, \quad (2)$$

where T_m is the melting temperature in degrees of Kelvin. The melting or solidification of a crystalline solid is always a first order transition and heat is absorbed

or released at the melting temperature (Fig. 1a). There is only one exception to this general rule [1,2] the transition of solid helium to liquid helium II (Fig. 1b). Not every solid–liquid phase transformation requires latent heat for its transition [3,4]. Non-crystalline solids or glasses do not have a well defined melting temperature and latent heat is not required for the completion of their phase transformation (Fig. 1c). This Letter explores the physical process behind the latent heat and presents a new model to explain different transformations of crystalline, non-crystalline solids, and helium.

2. Proposed model

Investigating the fundamental characteristics of the solid and liquid phases, one of the most striking differences between them is the atomic position stability. In solids the atomic positions are well defined while in liquids the position stability is lost. The induced atomic movement at melting most likely will generate viscous resistance. It is suggested that the energy of the latent heat of fusion is utilized to overcome this viscous resistance. This physical explanation of the latent heat is con-

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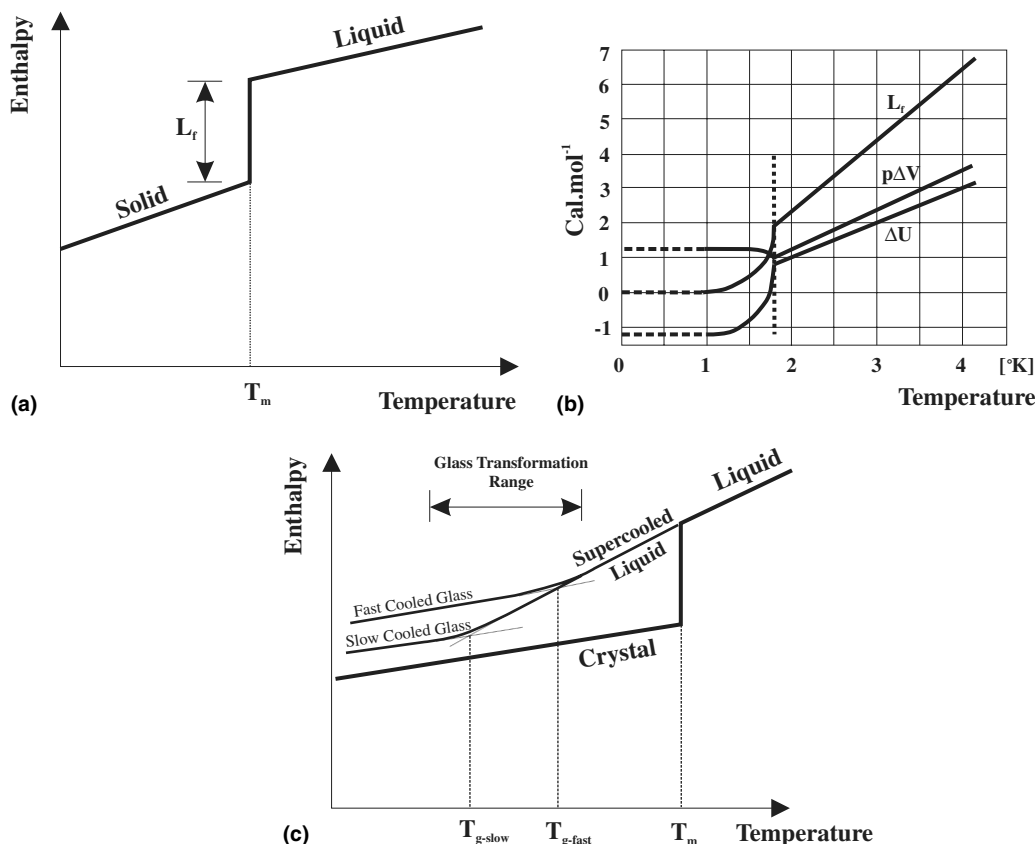


Fig. 1. Melting and solidification. (a) Crystalline solids. (b) Solid helium–liquid helium II. (The molar latent heat of fusion L_f , $p\Delta V$, and the change in internal energy, $\Delta U = L_f - p\Delta V$, for helium from [2].) (c) Glasses.

sistent with the zero viscosity of helium II and with the glass transformation. If the latent heat supplies the energy for the viscous drag, then liquid with zero viscosity should not require latent heat for its phase transformation. The transition between solid and liquid helium II requires no energy (Fig. 1b).

When non-crystalline solids solidify, the atomic movements are not restricted to crystal lattice sites as they are in crystalline solids. Instead, there is a continuous reduction mobility and the energy (latent heat) is released through the whole temperature range of the phase transformation. The lack of definite melting point and latent heat for non-crystalline solids (Fig. 1c) is consistent with the proposed physical explanation.

3. Calculations

The thermal velocity of the atoms in liquid is

$$v_{\text{therm}} = \sqrt{\frac{kT_m}{m}}, \quad (3)$$

where k is the Boltzmann constant, and m is the atomic mass. The maximum velocity difference between two atoms is $2v_{\text{therm}}$, while the minimum is zero. It will be as-

sumed that the average velocity difference between the atoms is v_{therm} . For Newtonian liquids the viscosity (η) is defined as

$$\eta = \frac{\tau}{\dot{\epsilon}}, \quad (4)$$

where τ is the shear stress, and $\dot{\epsilon}$ is the strain rate. The strain rate for atoms moving with the velocity difference of v_{therm} can be written as

$$\dot{\epsilon} = \frac{v_{\text{therm}}}{(n+1)d}, \quad (5)$$

where $(n+1)d$ is the distance between the center of the atoms. It was assumed that the atoms are displaced from each other by their atomic diameter (d) and n is the number of the coupled atoms between the two atoms moving with the velocity of v_{therm} .

The shear stress is the ratio of the viscous drag force (F_{vd}) and the surface of the sheared area (A)

$$\tau = \frac{F_{\text{vd}}}{A}. \quad (6)$$

The total sheared area or surface (A_{mol}) in one molar volume (V_{mol}) is estimated as

$$A_{\text{mol}} = \frac{V_{\text{mol}}}{(n+1)d}. \quad (7)$$

Table 1
Physical parameters of the liquids used for this investigation

Element	Crystal structure	Atomic diameter (10^{-10} m)	Liquid mol. vol. (10^{-6} m ³)	Viscosity (10^{-4} Pas)	Latent heat of fusion (kJ/mol)	Melting temp. (K)	Atomic-weight (amu)
Li	bcc	3.04	13.47	5.66	2.33	453.69	6.941
Na	bcc	3.72	24.77	6.87	2.60	370.96	22.990
K	bcc	4.72	47.22	4.41	2.40	336.80	39.098
Fe	bcc	2.52	7.938	58.0	13.81	1808.00	55.845
Rb	bcc	4.95	57.95	5.42	2.19	312.20	85.468
Cs	bcc	5.31	72.11	5.98	2.09	301.55	132.905
Ca	bcc	3.94	29.36	11.1	8.54	1112.00	40.078
Ar	fcc	3.84	28.17	2.80	1.21	83.78	39.948
Al	fcc	2.86	11.29	12.9	10.71	933.52	26.982
Ni	fcc	2.50	7.546	43.5	17.48	1726.00	58.693
Cu	fcc	2.56	8.003	43.2	13.26	1356.60	63.546
Ag	fcc	2.88	11.54	38.0	11.30	1235.08	107.868
Au	fcc	2.88	11.40	51.3	12.55	1337.58	196.967
Pb	fcc	3.50	19.40	26.0	4.77	600.65	207.200
Mg	hcp	3.20	15.34	11.0	9.04	922.00	24.305
Co	hcp	2.50	7.684	41.5	16.2	1768.00	58.933
Zn	hcp	2.66	8.627	33.0	7.32	692.73	65.390

The viscosity of Cu, Ni and Fe is from [5].

The viscosity of the rest of the metals is from [6].

The rest of the data are from [7].

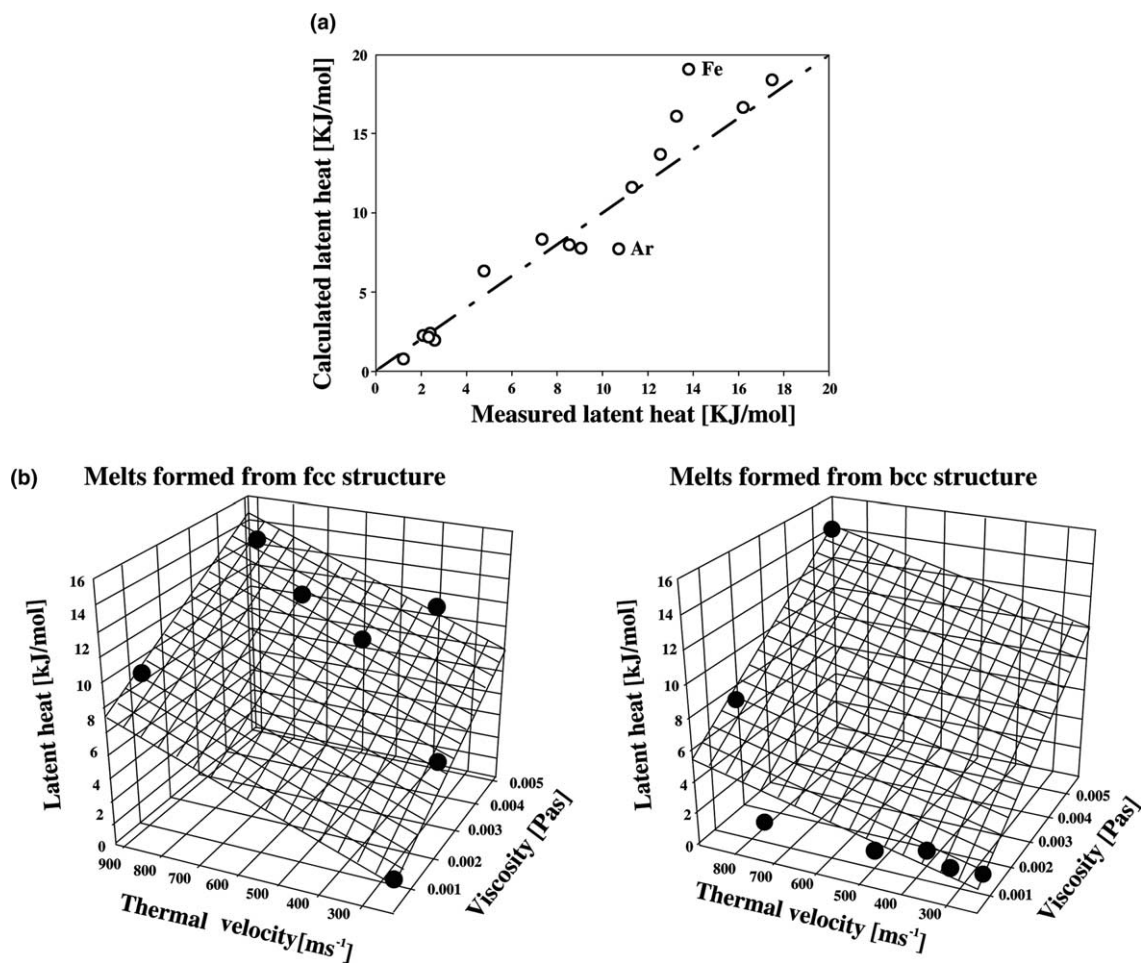


Fig. 2. Correlations (a) between the measured and calculated latent heat (The latent heat was calculated by using Eq. (10). The determined average of n was used for the appropriate crystal structure.) (b) between thermal velocity, viscosity, and latent heat.

The viscous drag force for one mol of liquid then is

$$F_{\text{vd-mol}} = \tau A_{\text{mol}} = \eta \dot{\epsilon} A_{\text{mol}} = \eta \frac{V_{\text{therm}}}{(n+1)d} \frac{V_{\text{mol}}}{(n+1)d}$$

$$= \frac{1}{(n+1)^2} \frac{\eta v_{\text{therm}} V_{\text{mol}}}{d^2}. \quad (8)$$

The estimated distance between the neighboring potential wells is equivalent to the atomic diameter. The energy (E_{mol}) needed to move all the atoms from one potential well to the next one is

$$E_{\text{mol}} = F_{\text{vd-mol}} d. \quad (9)$$

If this extra energy is supplied at the melting temperature then the displacement of the atoms becomes possible. The required latent heat for melting is therefore,

$$L_f = E_{\text{mol}} = \frac{1}{(n+1)^2} \frac{V_{\text{mol}}}{d} \eta v_{\text{therm}}. \quad (10)$$

Eq. (10) has been tested using experimental data of liquids formed from three different crystal structure. The physical properties of the 17 elements used for the investigation are listed in Table 1. The observed latent heat values correlates well with the predicted values of Eq. (10) and with the physical properties in Table 1 (Fig. 2). The calculated correlation coefficients between all the variables and the latent heat are 0.97 and 0.95 for liquids formed from body centered cubic (bcc) and from face-centered-cubic (fcc) structure, respectively.

The number of coupled atoms should be constant for melts formed from the same crystal structure. Using Eq. (10), the number of the coupled atoms was calculated

$$n = \sqrt{\frac{\eta v_{\text{therm}} V_{\text{mol}}}{d L_f}} - 1. \quad (11)$$

The average values and their standard deviations are 1.93 (± 0.28), 1.47 (± 0.31), and 1.57 (± 0.18) for liquids formed from bcc, fcc, and hexagonal close-packed structure, respectively. The calculated 1–2 coupled atoms for the different melts seem to be reasonable.

4. Conclusions

It is proposed that the energy of the latent heat of fusion is required to overcome viscous drag resistance introduced at melting. Assuming that the atoms are moving with their thermal velocity in the liquid, the viscous resistance working against this movement was calculated for melts formed from highly symmetrical packing arrangements. The calculated energies correlate well with the experimentally determined latent heat values.

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