The Melting Points of the Inert Gas Solids

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The melting points of the heavy inert gases and of some other simple molecules show an excellent linear correlation with the depths of their diatomic potential wells, and the slope of the correlation line is in accord with Lindemann's theory of melting

INTRODUCTION

Here is a simple question.[≠] Why do the melting points of the inert gases (Ne–Xe) increase as we ascend the periodic table? A common response is 'they get heavier'. This is not the correct answer. Isotopes and isotopomers interact through the same potentials, and at the classical level, the Gibbs free energy of solids and liquids have a very weak (logarithmic) dependence on mass through their translational motion, yet they have very similar melting points. Moreover, at the classical level p-V isotherms are mass independent. Notably, mass is not a parameter in the Monte Carlo computer simulation of solid-liquid melting.

Here are some examples of melting points (in brackets) taken from Ref. 1 and the NIST physical properties data base:[2] CH_4 (90.6 K), CD_4 (89.8 K), C_6H_6 (278.6 K), C_6D_6 (280 K), H_2O (273.15 K), H_2O^{18} (273.4 K), D_2O (277 K). Significant increases in mass lead to changes in the melting point that are usually only about one percent or less, sometimes up, sometimes down. Any differences are primarily due to vibrational zero point energies, which are a quantum effect. The largest mass difference in the above list is for H_2O/D_2O because hydrogen bonds have large zero point energies. Helium is also an exception because it is a quantum system.

An early, phenomenological theory of melting was given by Lindemann.[3] This was based on the idea that if the average displacement of the atoms from their lattice sites exceeded a certain fraction of the lattice spacing (later studies showed this to be about 1/10), then above the sublimation pressure the solid would melt. This idea has been supported by theoretical calculations, and by neutron diffraction experiments on supercooled liquids and frozen glasses.[4,5]

Lindemann used his idea to produce a mathematical expression for the melting point, which in the classical limit is indeed mass independent. Although very simple, Lindemann's assumption is still the basis of many melting models, as illustrated by a recent publication.[6] In this

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≠ This question was posed by John N. Murrell at the Brijuni Conference on Interdisciplinary Topics in Chemistry and Physics 2006.

paper we go further and show that his model gives a simple and surprisingly accurate explanation of the melting points of inert gas solids, and indeed of some other simple solids, a result that to our knowledge has not been published before.

Although this paper emphasises melting points a similar mass dependence applies to boiling points as illustrated by a few examples:[1,2,7] ^{20}Ne (27.084 K), ^{22}Ne (27.211 K), CH_4 (111.6 K), CD_4 (111.7 K), C_6H_6 (353 K), C_6D_6 (352 K).

A MODIFIED LINDEMANN MODEL

For small displacements from an equilibrium position we can restrict the potential to harmonic terms as

$$V(r) = -\varepsilon + (1/2)(r - r_e)^2 k \qquad (1)$$

where ε is the depth of the well, r_e the equilibrium distance and k the force constant. Now k will usually depend on the form of the potential (*e.g.*, the exponent in the Morse function), but for the well-established Lennard-Jones (m,n) family of potentials k depends only on ε and r_e. For example, for the (6,12) potential, which we can write in the form

$$V(r) = \varepsilon((r_e/r)^{12} - 2(r_e/r)^6) \qquad (2)$$

$$k = 72\varepsilon/r_e^2 \qquad (3)$$

The equipartition theorem shows that at equilibrium both the potential and kinetic energies are equal to $k_B T/2$, where k_B is Boltzmann's constant. The Lindemann hypothesis is that melting occurs when the root mean square displacement exceeds a fraction f of the equilibrium distance, hence we can make the equality

$$k_B \, T_m = k \, r_e^2 f^2 \qquad (4)$$

and for the (6,12) potential

$$T_m = 72\varepsilon \, f^2 \, / \, k_B \qquad (5)$$

We see again that the melting point T_m is independent of mass and for the (6,12) potential (or others of that family), is proportional to ε.

Figure 1 shows that this prediction holds very well for the inert gases, and from the slope of the line we deduce $f = 0.09$, which is very close to the generally accepted Lindemann value of 0.1. The well depths were taken from the compilation given in Ref. 9.

The figure also includes data for O_2, N_2, CH_4, and CF_4, and although the simple (6,12) law is not expected
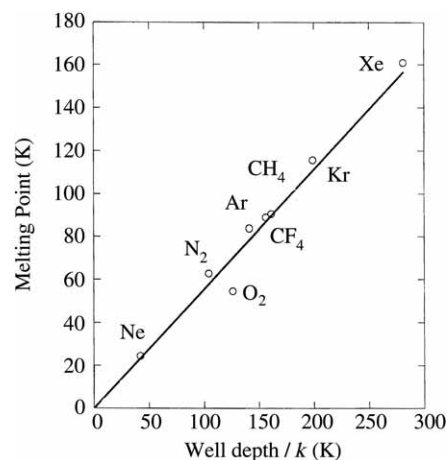

Figure 1.

to be as accurate for these systems, their melting points lie surprisingly close to the inert gas line.

A simple thermodynamic argument supports the idea that ε is the most important factor in determining melting points. At the melting point the Gibbs energy of solid and liquid are the same, hence we can write

$$T_m = \Delta H_m \, / \, \Delta S_m \qquad (6)$$

And as the volume change on melting is small, ΔH_m is approximately equal to ΔU_m, which, in the case of the inert gas solids, will be proportional to ε. Thus the linear relation between T_m and ε in our figure is to be expected. However, the fact that the slope of the line is in accord with Lindemann's model has implications for ΔS_m, and suggests a common factor for the entropy of melting, just as there is for the entropy of vaporisation, (Trouton's rule). For the inert gases the entropies of fusion per atom lie between 1.64 k_B (Ne) and 1.71 k_B (Xe).[7]

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SAŽETAK

Tališta krutina plemenitih plinova

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Tališta krutina teških plemenitih plinova i nekih jednostavnih molekula linearno se koreliraju s dubinom njihovih potencijalnih jama, a nagib korelacijskoga pravca slaže s Lindemannovom teorijom taljenja.