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Title
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Permalink

Journal

ISSN

Authors
Lilley, D
Jain, A
Prasher, R

Publication Date

DOI

Peer reviewed

A Simple Model for the Entropy of Melting of Monatomic Liquids

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We present an analytical model for calculating the entropy at melt of monatomic liquids. The model is motivated by the concept of a rough potential energy surface (PES). It offers a simple, physical explanation for Richard's Melting rule, and provides a material-dependent correction to Trouton's Vaporization rule. Without employing any adjustable parameters, the model agrees closely with experimental entropy of melting values for monatomic liquids. When combined with the phonon theory of liquids, it allows for estimation of entropy over the entire liquid range.

Due to the difficulty associated with a general theory of liquid thermodynamics, it has been common practice to use empirical rules to estimate thermodynamic quantities. Empirical rules, such as Richard's Rule of Melting or Trouton's rule of Vaporization, are practical but lack physical insight and granularity. In this work, we use physical arguments to arrive at a model for the entropy of melting of monatomic liquids that offers material-dependent corrections but reduces to the simpler rules in its limit. Such a model is needed to offer scientists and engineers insights into reaction kinetics, macroscopic thermodynamic cycles, and material design for phase change-based thermal storage material among other applications. The derivation of our model is motivated by Stillinger and Weber's work in the early 1980s [1,2], which used molecular dynamic simulation (MDS) to introduce and characterize a multi-minimum potential energy surface (PES) of liquid systems. These studies determined that the PES of a liquid system is rough, *i.e.*, contains many shallow local minima. The corresponding dynamics associated with a rough PES include (1) lattice vibrations, which are solid-like, except they generally exhibit anharmonicity due to large displacements from meta-stable equilibrium: (2) large scale diffusion (*slow*) transition), which is gas like and describes the hopping motion of the atom from one equilibrium lattice point to another as described by Frenkel [3]: (3) small scale diffusion (*fast*) transition) corresponding to the local re-distribution of equilibrium positions by traversing small energy barriers on the PES [4,5].

Trachenko, Brazhkin, and coworkers [3,6–8] recently re-introduced J. Frenkel's picture of liquid dynamics [9]. A simplified version of this picture describes the microscopic view of atoms in liquids as vibrating around equilibrium points at short time scales and hopping to neighboring equilibrium points at larger time scales. By considering large scale diffusion (s), this "phonon theory of liquids" model accurately predicted the decrease in heat capacity at constant volume (C_v) as a function of temperature (T) by accounting for the loss of transverse phonons with frequencies less than the Frenkel frequency (ω_F). However, this theory is not able to predict the absolute entropy of liquids, only the relative entropy changes in the liquid state, so it cannot be used to determine the entropy of melting.

Thus, there exists a need to develop a model that can predict the entropy of melting rather than determining it from experimental data and/or empirical rules. In this manuscript, we propose a simple model that employs the Debye approximation to offer a physical explanation for Richard's melting rule [10], and material-dependent corrections for more accurate calculations. We then employ the phonon theory of liquids to account for the temperature dependence of that correction and show how it can provide material-dependent corrections to Trouton's rule of Vaporization [11].

We begin by considering the solid-like local vibrations of a particle about its instantaneous equilibrium point for times less than the Maxwell relaxation time ($t < \tau_m$). In general, liquid particles vibrate in a potential well described by both harmonic and higher order (anharmonic) terms that act to soften the spring constant at larger displacements. The anharmonicity associated with lattice vibrations in liquids is not well understood, but it has been shown that it can be neglected for calculating the total entropy near melting [12] , so for now we will assume the particle vibrates in a harmonic potential. Anharmonicity is later included as a correction factor for T > T_m where T_m is the melting temperature.

Next, we address the large-scale, slow diffusion by describing the hopping motion of the atom from one lattice cage to another, resulting in a large and lasting change in the atoms neighbor list. The hopping rate is described by the Maxwell relaxation time [3] (also known as the Frenkel frequency), $\omega_F(T) = \frac{G}{\eta(T)}$, where G is the high strain rate shear modulus and $\eta(T)$ is the temperature-dependent shear viscosity [6]. At T_m , the viscosity of metallic liquids is very high; under these conditions, the hopping frequency is small compared to the Debye frequency, ω_D, and has been shown to be on the order of $\frac{\omega_D}{10}$ or less [3,6,13]. Thus, at T_m, we assume the dynamics are dominated by small-scale *fast* diffusion and lattice-like vibrations and we neglect large-scale diffusion in our model. We emphasize that for liquids with $\omega_D \approx \omega_F$ at melt, this assumption fails, as is the case for noble gasses where density changes are large upon melt [6]. When $T > T_m$, large-scale
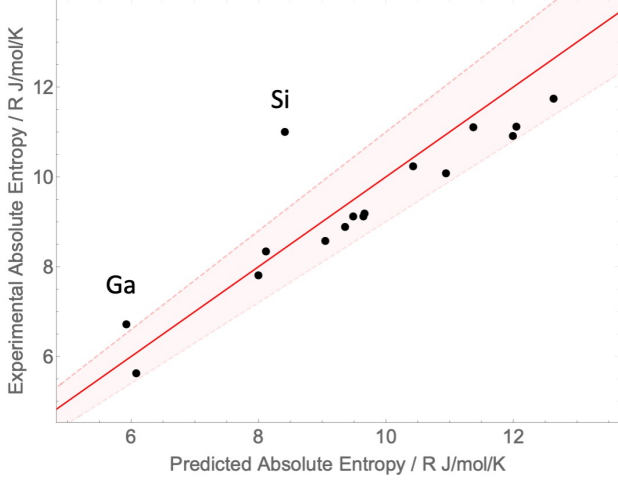
FIG 1: Predicted vs experimental liquid entropy at melt. The solid red line represents equivalence and the dashed lines represent 10% error. In order of increasing experimental entropy entropy, the dots represent Li, Ga, Na, Hg, Al, Mg, In, K, Zn, Cu, Rb, Ag, Si, Cs, Pb, and Au.

diffusion will be accounted for using the phonon theory of liquids.

Finally, we consider small-scale, fast diffusion, or the hopping of small energy barriers ($< k_BT$) corresponding to the particles' changing center of oscillation [4,14,15]. The particle's equation of motion can be written as $m\ddot{x}_p = -k\nabla U$ and expanded such that $m\ddot{x}_p = -k(x_p(t) - x_o(t))$ where $x_p(t)$ describes the position of the particle, and $x_o(t)$ describes the time-dependent position of the center of the particle's potential well. Describing the particle coordinate with respect to its displacement from the center of oscillation (Δx), $x_p(t) = x_o(t) + \Delta x(t)$, the equation of motion becomes $m(\ddot{x}_o + \Delta\ddot{x}) = -k\Delta x(t)$. Small-scale fast diffusion is responsible for changing x_o, giving it its time dependence [4,14,15].

The particle undergoes simple harmonic motion about its center of oscillation, so a harmonic trial solution is chosen such that $\Delta x(t) = Ae^{i\omega_{eff}t}$. The trial solution of $x_o(t)$ is more nuanced; molecular dynamics simulations have demonstrated that the center of oscillation also oscillates [4,14,15] with similar amplitude to the particle's vibration. The hopping of small barriers that give rise to this oscillation does not significantly alter the character of the system configuration. Indeed, Rabani et al. [5] were unable to distinguish between the small-scale diffusion and solid-like vibrations when observing the decay of neighbor list correlation functions. Provided that the small-scale diffusion energy barriers are small, they thus lumped these mechanisms together, both being local perturbations occurring within the domain of a particular particle's local minima. Our model is motivated by MDS that have shown rapid re-crossing of these
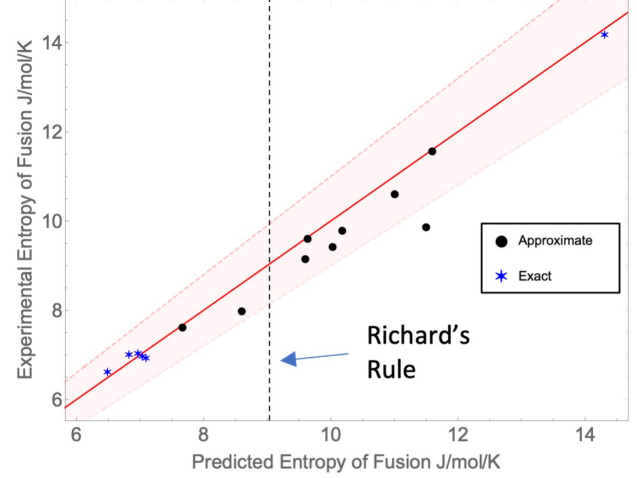

FIG 2: Predicted vs experimental entropy of fusion using equation 3. The blue asterisks denote exact predictions using liquid Debye frequencies from [20,21]. The black circles represent approximate predictions where the liquid and solid Debye frequencies were evaluated at their respective densities. In order of increasing predicted enthalpy of fusion, the dots represent Li, K, Cs, Na, Rb, In, Pb, Ag, Cu, Mg, Au, Zn, and Al. The solid red line is the 45° line, and the dashed lines represent 10% error.

small barriers on time scales associated with lattice vibrations. In these simulations, a particle's neighbor list correlation function returns to its initial state after $t \approx \frac{2\pi}{\omega_D}$ [5,14,16], thus we choose $x_o(t) = Ae^{i\omega_{eff}t}$ as an ansatz. Plugging this into the equation of motion yields $m(A + A)\omega_{eff}^2 = k(A)$. We note that k, the intermolecular spring constant, is governed by the nature of the intermolecular bond and is therefore fixed. The frequency of the oscillation then becomes

$$\omega_{eff} = \frac{1}{\sqrt{2}}\sqrt{\frac{k}{m}} = \frac{1}{\sqrt{2}}\omega_D^L \qquad (1)$$

Where ω_D^L is the Debye frequency characterizing the atomic vibration in the liquid phase. We remark that this result is equivalent to putting two springs with spring constants corresponding to the Debye frequency in series. Thus, we argue that the dynamics of the particle near melting can be simplified by modeling the small-scale diffusive translational motion as a harmonic spring in series with harmonic lattice-like vibration.

Using the Debye model, we can calculate the entropy associated with the effective Debye frequency at melt as $S_{T_m} =$
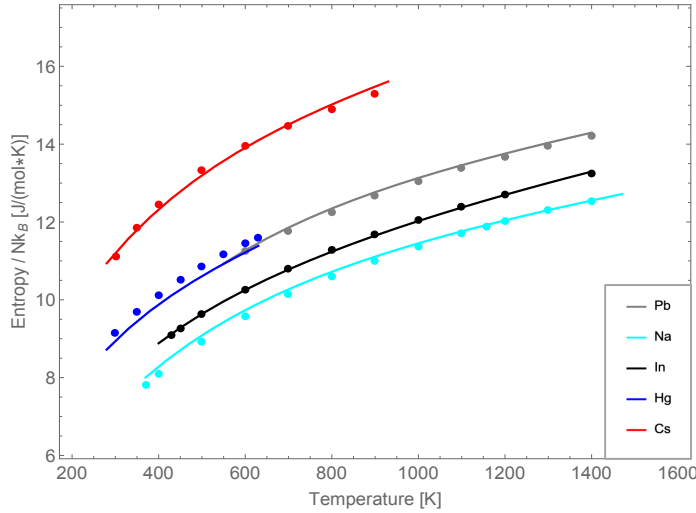
FIG. 4: Predicted vs experimental entropy of vaporization. The solid red line is the 45° line, and the dashed lines indicate 10% error. The black dashed horizontal line shows Trouton's Rule. In order of increasing predicted entropy, the dots represent Ga, Sn, Pb, In, Cs, Rb, Hg, Na, and K.

$$S_{T_m} = 4R + 3Rln\left(\frac{k_b T_m}{\hbar\omega_{eff}}\right) \qquad (2)$$

A comparison of the entropy at melt (equation 2 with ω_{eff} from equation 1) to experimental data from Selected Values of the Thermodynamic Properties of the Elements [18] for 16 monatomic liquids is plotted in Figure 1. Debye temperatures evaluated at the crystal melt and density were taken from [12], and we observe that with just this single input property equation 2 predicts entropy at melt to within 10% of experimental values for 14 of the 16 liquids. The notable outliers are silicon and gallium. Wallace identifies silicon, as well as Ge, Bi, Ga, and Sb, as "anomalous melting" elements because they are shown to undergo significant change in electronic structure from crystal to liquid [12,19], which impacts the Debye frequency and our model does not account for this.

In addition, equation 2 can be combined with the Debye model for crystals to calculate the entropy and enthalpy of fusion:

$$\Delta S_M = 3Rln\left(\frac{\omega^S_{D,T_m}}{\omega^L_{eff}}\right) = 3Rln\left(\frac{\sqrt{2}\omega^S_{D,T_m}}{\omega^L_{D,T_m}}\right) \qquad (3)$$

where ω^S_{D,T_m} is the Debye frequency in the solid state and ω^L_{D,T_m} is the Debye frequency in the liquid state at melt. It has been shown [20]) that for many metals $\omega^L_{D,T_m} \approx \omega^S_{D,T_m}$. In this case, equation 3 reduces to $\Delta S \approx 1.1R$ which is the empirical value used in Richard's Melting Rule [10].
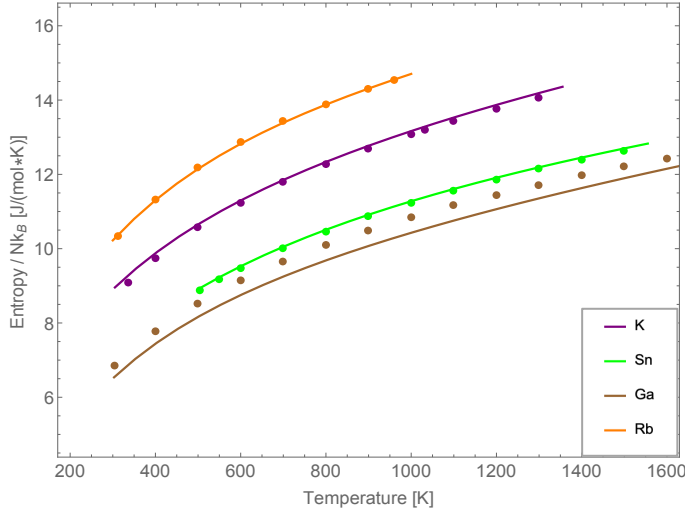

FIG 3: Theory and experimental entropies of various monatomic liquids versus temperature. Experimental entropy values were taken from Selected Values of the Thermodynamic Properties of the Elements[18] at a pressure of 1 atm. Solid lines represent theory, whereas dots represent experimental data. Input parameters and their sources are provided in SI section 4.

$4RD\left(\frac{\theta_{D,eff}}{T_m}\right) - 3Rln\left(1 - e^{\frac{\theta_{D,eff}}{T_m}}\right)$, where $\theta_{D,eff}$ is the effective Debye temperature corresponding to ω_{eff} in Eq. 1 and D is the Debye function. We emphasize that the Debye model is used for its simplicity, and note that the Debye approximation is a simplification of the real density of states of monatomic liquids, which in reality exhibits a much flatter transverse phonon dispersion for small wavevectors at high temperatures [17]. Because we are modeling the liquid state, we can use the high temperature Debye expansion to obtain the entropy of the liquid at melt:
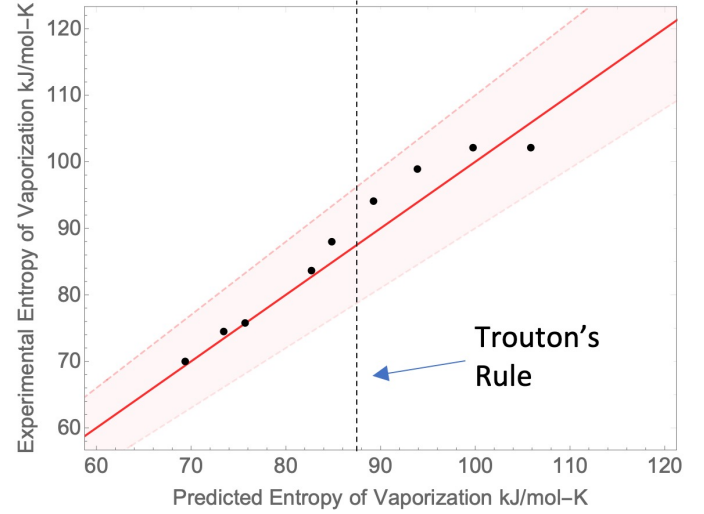
The true value for ΔS of metals ranges from 0.8R-1.5R. Equation 3 converges to a single value (1.1R) when we assume $\omega_{D,T_m}^L \approx \omega_{D,T_m}^S$. In reality, ω_{D,T_m}^L differs from that ω_{D,T_m}^S because of the density changes on melt, and the nature of the liquid dynamics change from that of the solid. The true liquid Debye frequencies for Ar, Cs, Rb, K, Li, and Na were determined in [20,21], and were used to evaluate equation 3 without approximation. Figure 2 compares the exact predictions of equation 3 with experimental values (identified by blue asterisks), The exact predictions give a root mean squared error of 1.64%, showing excellent agreement with experimental entropy of fusion values. When the exact value of ω_{D,T_m}^L is not available, equation 3 can be evaluated using the quasiharmonic phonon approximation, whereby the change in Debye frequency can be related to the change in density from the solid to the liquid state. For small density changes, this can be approximated as $\theta_D(\rho) \approx \theta(\rho_o)\left(\frac{\rho}{\rho_o}\right)^\gamma$, where ρ_o is the density at which the original Debye temperature was evaluated, ρ is the density at which the new Debye temperature is to be evaluated, and γ is the grüneisen parameter Debye frequencies evaluated at liquid state densities are tabulated in [20] and were used to evaluate equation 3. The approximate results are shown in figure 2, identified by black circles, and excluding the elements for which exact predictions were made (Ar, Cs, Rb, K, Li), the approximate predictions give an RMSE of 6.35%, compared to a 19.1% RMSE given by Richard's rule. Thus, equation 3 provides an excellent material dependent correction to Richard's rule of melting. The results for enthalpy of fusion ΔH_m, given by $\Delta H_M = T_M \Delta S_M$ are shown in the SI.

We note that the viscosity of Ar is low at melt such that $\omega_{F,T_m} \approx \omega_{D,T_m}$, so large scale diffusive dynamics should become important. However, although our model neglects the large-scale diffusion, it still predicts the entropy of fusion of Ar with less than 1% error, suggesting that the large scale diffusion does not strongly influence the entropy at melt in this case. More accurate values for ω_{D,T_m}^L , which can be computed from Molecular Dynamics [20], are needed to test this model against a larger set of the known 0.8R-1.5R entropy jump seen in metals.

Our model for the entropy at melt does not explain thermodynamic properties at higher temperatures. To do this, one can incorporate prior models for the temperature dependent heat capacity of liquids [22,23]. To illustrate this, we use the results of Trachenko, Brazhkin, and coworkers' phonon theory of liquid thermodynamics to predict the thermodynamic properties at $T > T_m$ under constant pressure. We must include the entropy increase due to expansion and anharmonicity, and the entropy decrease associated with the loss of transverse phonons, which account for the effect of large-scale diffusion. This can be written as $S(T) = S_{T_m} + \int_{T_m}^T \frac{C_p}{T} dT$,   where $C_p = 3R + C_{exp} + C_{anharmonic} - C_{loss}$.[20] Expansion heat capacity is expressed as $C_{exp} = MB\alpha_V^2 T$ where M is the molar volume, B is the fluid's bulk modulus and α_V is the fluid's volumetric thermal expansion coefficient. The anharmonic heat capacity can be approximated as

$C_{anharmonic} = 3R\alpha_V T$.[10,21] The heat capacity associated with the large-scale diffusion, or the loss of transverse phonons is $C_{loss} = \frac{d}{dT}\left[RT\left(\frac{\omega_F(T)}{\omega_D}\right)^3\right]$.[10] Therefore $S(T)$ can then be written as:

$$S(T) = S_{T_m} + 3R\ln\left(\frac{T}{T_m}\right) + MB\alpha_V^2(T - T_m)$$
$$+3R\alpha_V(T - T_m) - R\int_{T_m}^T\left\{\frac{1}{T}\frac{d}{dT}\left[RT\left(\frac{\omega_F(T)}{\omega_D}\right)^3\right]\right\}dT \quad (4)$$

with S_{T_m} from the model described in this work. The phonon loss term (final term in equation 4) can be approximated as $S_{Loss}(T) = -R\left(\frac{\omega_F(T)}{\omega_D}\right)^3$ with less than 2% total error on S(T) (see supplementary information, (SI) section 1). All other thermodynamic properties of interest can be determined using appropriate thermodynamic relations with (4). For $S(T)$ at constant volume, the expansion term (3rd term) in Eqn. 4 should be neglected. Details on calculation of ω_F, including differences from values used by Trachenko and Brazhkin [6], are provided in the SI. Comparison of equation 4 to experimental entropy data as a function of temperature is plotted in Figure 3. Besides gallium, which also has a significant change in electronic structure like silicon [12], there is excellent agreement between experiment and model. Constant pressure and constant volume heat capacities evaluated as $C_{P,V} = T\left(\frac{\partial S}{\partial T}\right)_{V,P}$ are compared to experimental data in SI section 2 based on our calculation of ω_F.

To demonstrate that the previous results are valid even near the boiling point, we compare our combined model with experimental data for the entropy of vaporization (ΔS_V), which is typically given by the well-known Trouton' rule [11] that states $\Delta S_V \approx 88$ J/mol –K. We used experimental entropy data for the gas phase [18] and subtracted it from equation 4 evaluated at the boiling temperature to predict ΔS_V, as plotted in Fig. 4. Examination of Fig. 4 reveals that our model predicts ΔS_V very well (mean absolute error of 2.42 J/mol-K) whereas Trouton' rule, which is independent of material properties, gives a constant value. Thus, we have shown that equation 4 gives accurate thermodynamic values over the entire liquid range at atmospheric pressure.

In summary we have developed a simple analytical model to predict thermodynamic properties of monatomic liquids. It requires input of the Debye frequency in the liquid state for precise evaluation, or density-corrected Debye frequencies for approximate use. Data for ω_D^L is rare, and future efforts in determining ω_D^L are needed to more accurately test the model for such liquids. In addition, our model uses the Debye approximation, but future modelling efforts should focus on more realistic dispersion for transverse phonons, which in reality are far more complex [17]. Our model also assumes $\omega_F \ll \omega_D$ at melt so that large-scale diffusion is much slower than interatomic vibration, which may break down for low viscosity liquids. Moreover, we restricted our analysis to monatomic systems to

isolate the thermodynamic contributions from the inter-molecular interactions, and therefore make a simpler and more meaningful comparison to our model. Further work must be done to include the effects of intra-molecular interactions in order to test the model for multiatomic systems. This can be done by modeling intra-molecular degrees of freedom as Einstein oscillators, for example, or by combining equation 4 with group contribution methods for quick estimates of thermodynamic functions.

Supplementary Information
The supplementary Information discusses an approximation for the entropy loss associated with the loss of transverse phonons, compares constant pressure and constant volume heat capacity predictions to experimental data, tabulates the model input parameters, and includes an additional comparison to the enthalpy of fusion for the elements listed in Fig. 2.

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