Potts lattice-gas model for the solid-liquid interfacial tensions of simple fluids

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The q-state Potts lattice-gas model is used to model the solid-liquid interfaces of simple materials. The interfacial tension $\gamma_d$ is calculated using a mean-field approximation with a different value of the solid order parameter in each layer. An attempt to model the surfaces of Ar, Na, and Al leads to surface tensions $\frac{1}{4}$ to $\frac{1}{2}$ of the values inferred from nucleation data. Surface widths are of the order of three layers. The orientation dependence of $\gamma_d$ is found to be about 1%. Uniform liquids are found to exhibit considerable supercooling, but the solid phase can be superheated by at most 4%.

An interface is formed whenever two bulk phases are in equilibrium with each other. An essential property of an interface is the surface tension, which is defined to be the excess grand free energy per unit area due to the presence of the surface. Interfaces with very small surface tensions are easily generated; in such cases, it is energetically favorable for the system to decompose into many domains, as is seen, for example, in microemulsions. A particularly important interface is that between a solid and a liquid, which plays a crucial role in the process of crystal growth.

Most previous studies on solid-liquid interfaces have been carried out by numerical simulation. A more analytic, density-functional approach has recently been developed by Oxtoby and Haymet, who generalize the freezing theory of Ramakrishnan and Yussouf to solid-liquid interfaces and obtained surface tensions for the alkali metals Na and K. In this report, we present a theory for the solid-liquid interfacial tension within a somewhat stylized model, the Potts lattice-gas model. This model has been shown to be quite successful in describing wetting phenomena involving rare gases on substrates. An important virtue of the model is that it correctly predicts the occurrence of three bulk phases, which may be identified as solid, liquid, and gas, at appropriate temperatures and pressures. We calculate the solid-liquid interfacial tension for this model at the triple point within a mean-field approximation.

The model is specified by the Hamiltonian (nearest neighbors only)

$$ H = -\frac{1}{2} \sum_{n,i,a} J_{a0} n_i n_i' $$

where the occupation number $n_i$ is unity if site $i$ within layer $n$ is occupied by a Potts spin in a state $a$, and is zero otherwise. Thus $q$ and $\gamma$ are the basic parameters of the model, while all thermodynamic properties scale with $J$.

The mean-field approximation asserts that there are two order parameters for each layer:

$$ \langle n_{i,1} \rangle = m_{1,n} $$

$$ \langle n_{i,a} \rangle = m_{2,n}, \quad a \geq 1 $$

where $m_{1,n}$ represents the probability that a site in layer $n$ is occupied by a preferred state, say $a=1$, while $m_{2,n}$ denotes the corresponding probability for one of the other $q-1$ Potts states. The probability that a given site in the $n$th layer is empty is thus $1 - m_{1,n} - (q-1)m_{2,n}$. The density of the system (i.e., the average occupation of a site in the $n$th layer, is $d_n = m_{1,n} + (q-1)m_{2,n}$).

The mean-field approximation is a straightforward extension of the usual mean-field approximation for an Ising lattice gas, generalized to a $q$-state model and allowing for different order parameters in each layer. In general, there are twice as many coupled equations as there are layers; the coefficients of these equations depend on the type of lattice and orientation of the surface. For example, on an fcc (111) surface with nearest-neighbor interactions, we find

$$ m_{1,n} = \exp[\beta \mu + 3\beta J(\bar{m}_{1,n} + q(q-1)\bar{m}_{2,n})] / Z $$

$$ m_{2,n} = \exp[\beta \mu + 3\beta J(q(1+q-2)\bar{m}_{2,n})] / Z $$

$$ Z = 1 + \exp[\beta \mu + 2\beta J(\bar{m}_{1,n} + q(q-1)\bar{m}_{2,n}) ] + (q-1)\exp[\beta \mu + 3\beta J(\bar{m}_{1,n} + 1+q(q-2)\bar{m}_{2,n}) ] $$

$$ \bar{m}_{1,n} = 2m_{1,n} + m_{1,n+1} + m_{1,n-1} $$

$$ \bar{m}_{2,n} = 2m_{2,n} + m_{2,n+1} + m_{2,n-1} $$

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where $\mu$ is the chemical potential and $\beta = 1/k_B T$, $T$ being the absolute temperature.

In a uniform bulk system, the two order parameters become independent of layer. There are three bulk phases: gas, liquid, and solid. The symmetry-broken phase $m_1 \neq m_2$ corresponds to the solid; $m_1 = m_2$ is the fluid, with gas and liquid differentiated by their density. In order to determine the parameters $\gamma$ and $q$ for a given system, we need two conditions. To model a specific real system, for example, we may require that the model reproduce the experimental ratio of specific volumes $v_l/v_s$ of the solid and liquid passes at melting, and the entropy change at the triple point. Figure 1 shows the phase diagram corresponding to the rare gases, for which $\gamma = 0.49$ and $q = 7$, as determined in this way. The phase diagram has a triple point $T_3$ and a liquid-gas critical point $T_c$. The solid-liquid phase boundary is nearly perpendicular to the temperature axis, indicating that the density change on melting is very small. The coupling constant $J$ is obtained by fitting the model value of $T_3$ to the measured triple-point temperature.

To calculate an interfacial tension in this model, an interface is constructed by inserting layers between two bulk phases. Each layer is coupled to neighboring layers, and the two bulk-phase solutions are the boundary conditions. The total grand free energy $\Omega$ is then found, for the case of Eq. (4), from

$$\Omega = \sum_n \left[ \frac{3J}{2} [m_{1,n} m_{1,n} + (q - 1) [1 + \gamma(q - 2)] m_{2,n} m_{2,n} + \gamma(q - 1)(m_{1,n} m_{2,n} + m_{2,n} m_{1,n})] - \mu d_n \right] + kT[m_{1,n} \ln m_{1,n} + (q - 1)m_{2,n} \ln m_{2,n} + (1 - d_n) \ln (1 - d_n)], \tag{5}$$

and the excess grand free energy is $\Omega - \Omega_0$ where $\Omega_0$ is the grand free energy of the uniform liquid or solid. The surface tension $\gamma_s$ is then simply $n_a \Delta \Omega$ where $n_a$, the number density of sites per layer, depends on the lattice structure and the surface orientation. The resulting solid-liquid surface tensions for fcc (111) and fcc (100) rare-gas crystals with nearest-neighbor interactions are

$$\gamma_{s11}^{111} = 0.1935 v_l^{-2/3} T_3 \text{ erg/cm}^2,$$

$$\gamma_{s11}^{100} = 0.1950 v_l^{-2/3} T_3 \text{ erg/cm}^2,$$

where $v_l$ is the molar liquid volume at $T_3$ in cm$^3$ and $T_3$ is given in Kelvin. The results for the rare gases are shown in Table I. As is evident, the difference in surface tensions between different orientations is very small—of the order of 1%.

It is also of interest to consider the surface widths for this model. We define the 10-90 surface width $w$ as the number of layers over which the order parameter $m_1 - m_2$ rises from 10% to 90% of its ultimate value in the bulk state. For the rare gases, we find $w$ to be approximately four layers, which is comparable to the values found by Oxton and Haymet in their density-functional calculation.

Metals differ from insulators in several respects: (i) their pair potentials extend further in real space; (ii) the pair potentials are density dependent; (iii) there is a substantial structure-independent, volume-dependent energy to be considered.\textsuperscript{13} We have included effect (i) in our calculations, while effects (ii) and (iii) would require a "compressible Potts model" which is beyond the scope of the present work. A simple estimate of the lattice-gas interactions in metals is obtained as follows. First, the standard pairwise screened Coulomb interactions between the ions of a simple metal are computed using an empty-core pseudopotential and the Lindhard dielectric function with

<table>
<thead>
<tr>
<th></th>
<th>$T_3$ (K)</th>
<th>$\Delta S / N$</th>
<th>$V_l / V_s$</th>
<th>$v_l$ (cm$^3$)</th>
<th>$\gamma_{s11}^{111}$ (erg/cm$^2$)</th>
<th>$\gamma_{s11}^{100}$ (erg/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>83.8</td>
<td>1.69</td>
<td>1.14</td>
<td>28.14</td>
<td>1.75</td>
<td>1.76</td>
</tr>
<tr>
<td>Kr</td>
<td>116</td>
<td>1.69</td>
<td>1.151</td>
<td>34.13</td>
<td>2.13</td>
<td>2.15</td>
</tr>
<tr>
<td>Xe</td>
<td>161.3</td>
<td>1.71</td>
<td>1.151</td>
<td>42.68</td>
<td>2.55</td>
<td>2.57</td>
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</table>
a Hubbard-Geldart-Vosko correlation correction. The position of the first minimum in the potential is identified as the nearest-neighbor separation. Next-nearest-neighbor and further-neighbor coupling constants $J_2, J_3, \ldots$ are measured in units of the nearest-neighbor coupling $J$ and obtained by comparing the heights of the interionic potentials at the appropriate distances. The pair potentials for Na and Al as calculated in this manner are shown in Figs. 2 and 3. From these pair potentials we obtain the following sets of coupling constants

$$J_2 = 0.696J,$$
$$J_3 = 0.0513J,$$
$$J_4 = 0.0182J,$$

for Na;

$$J_2 = 0.521J,$$
$$J_3 = -0.0145J,$$
$$J_4 = 0.009J,$$
$$J_5 = 0.0335J,$$
$$J_6 = 0.0328J,$$

for Al.

As can be seen from these couplings, the effects of third-nearest-neighbor interactions and beyond are at most 10%. This effect is also found in the calculation of the liquid-solid surface tension, which is perturbed by at most 10% by inclusion of third and higher neighbors. Using the same criteria as for the rare gases, we find $\gamma = 0.55$ and $q = 6$ for Al, while $\gamma = 0.62$ and $q = 5$ for Na. In Table II we present the calculated tensions $\gamma_{sl}$ for Na and Al using the Hamiltonian (1) generalized to include interactions through second-nearest neighbors.

There exist no direct experimental measurements of the solid-liquid interfacial tensions for the rare gases or for Na. Turnbull has estimated the surface tension of Al using nucleation data. Our result for Al is about one-third that of Turnbull. For Na, our result is half that of Oxtoby and Haymet, calculated from density-functional theory.

It is possible to use the same Potts lattice-gas model to calculate the liquid-gas surface tension for the same materials. For liquid-gas interfaces it is appropriate to use a different set of conditions to fix $\gamma$ and $q$. We have chosen to fit these parameters to the experimental values of the ratio $T_3/T_c$ and of $\Delta S_{ls}$, the entropy change between

<table>
<thead>
<tr>
<th>$T_m$ (K)</th>
<th>$\Delta S_N/k_B$</th>
<th>$V_l/V_s$</th>
<th>$n_i$ (units of $a_0^{-3}$)</th>
<th>$\gamma_{sl}^{(110)}$ (erg/cm$^2$)</th>
<th>$\gamma_{sl}^{(100)}$ (erg/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>371</td>
<td>0.85</td>
<td>1.025</td>
<td>0.0036</td>
<td>5.13</td>
</tr>
<tr>
<td>Al</td>
<td>933</td>
<td>1.39</td>
<td>1.06</td>
<td>0.00787</td>
<td>32.3</td>
</tr>
</tbody>
</table>

*Calculated by Oxtoby and Haymet.

*Estimated by Turnbull from nucleation data.
TABLE III. Liquid-gas surface tensions at the triple point.
The columns represent the experimental ratio of triple-point
temperature to critical temperature, the calculated and the ex-
perimental surface tensions.

<table>
<thead>
<tr>
<th>$T_1/T_c$</th>
<th>$\gamma_{sl}^{theo}$ (erg/cm$^2$)</th>
<th>$\gamma_{sl}^{exp}$ (erg/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.57</td>
<td>4.14</td>
</tr>
<tr>
<td>Na</td>
<td>0.13</td>
<td>75</td>
</tr>
<tr>
<td>Al</td>
<td>0.12</td>
<td>285</td>
</tr>
</tbody>
</table>

liquid and vapor at the triple point. Results for Na, Al, and Ar are shown in Table III. As is evident, the theory predicts a surface tension which is about one-third the experimental value in all three cases. For metals, we may understand this discrepancy as resulting from the omission of volume-dependent, structure-independent terms in the energy, which are known to be important in metallic fluids. For Ar, the causes of the discrepancy are less clear. Presumably, either the lattice-gas model is inadequate to treat a phase transition between two fluids in which the atomic positions are continuous variables, or else our choice of criteria with which to fix $\gamma$ and $q$ is not appropriate.

We may also make a brief comment about the superheating and supercooling limits of the present model, within the mean-field approximation. The superheating limit is identified as the highest temperature at which a solid-phase solution to the mean-field equations exists. For Na, the superheating limit is estimated to be $\sim 4\%$. However, there appears to be no supercooling limit—i.e., a liquidlike solution to the mean-field equations can be found at any temperature below the thermodynamic freezing point. These estimates are reasonable, since experimentally it is very difficult to superheat a solid but easy to supercool a liquid. However, no quantitative significance should be attached to our results, since we have not made a detailed numerical survey of mean-field solutions with boundary conditions appropriate to typical nucleation experiments.

It is reasonable to ask about the extent to which our results are affected by the mean-field approximation. This question has already been investigated in relation to the Potts model in other contexts (see Ref. 12). The conclusion is that mean-field theory gives results which are scarcely different from the more accurate ones provided by Monte Carlo simulations. Thus the discrepancy between our results and experiment is primarily due to the use of the Potts model, not to the mean-field approximation made on the model.

In conclusion, we have presented a theory for the solid-liquid interfacial tension $\gamma_{sl}$ within a Potts lattice-gas model. This calculation appears to be the first of $\gamma_{sl}$ in a statistical model with a realistic bulk-phase diagram. The theory gives the correct ratio of $\gamma_{sl}/\gamma_{lk}$ although both values are about $\frac{1}{3}$ of experimental values for both metals and nonmetals. We attribute these discrepancies to the probability that a lattice version of the fluid phases in the model is probably inadequate to treat quantitatively the properties of a real fluid. In the case of the metallic calculations, a second problem is undoubtedly the omission of volume-dependent terms in the Hamiltonian.

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12For a recent review, see C. Ebner (unpublished).

13See, for example, W. A. Harrison, Pseudopotentials in the Theory of Metals (Benjamin, New York, 1963).

14These choices are discussed in greater detail in a number of places. See, for example, a review by Stroud in Theory of Alloy Phase Formation, edited by L. H. Bennett (Metallurgical Society of AIME, Warrendale, 1980), pp. 84–126.