Properties of Lattice and Continuum van der Waals Fluids at the Critical Point

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A suggestion by Fisher that the specific heats of lattice gases and continuum fluids near the critical point could be compared on the basis of specific heat measured in units of the volume per particle at close packing is examined for systems with hard cores and long-range attractive potentials (van der Waals systems). It is found that the discontinuity at the critical point in the specific heat so defined is indeed similar for lattice gases and continuum systems in one, two, and three dimensions, while the critical density varies widely. No explanation is offered. Numerical values of other critical constants are also given.

It was shown recently by Fisher that the specific-heat data of argon (and perhaps also oxygen) along the critical isochore are, in the vicinity of the critical point, in semiquantitative agreement with that computed theoretically for lattice gases with nearest-neighbor interactions. In order to achieve this agreement, Fisher compared the configurational specific-heat density \(C^*(T)\) = \(\rho C_{\text{conf}}(T)/\rho_{\text{max}}\) with the theoretical configurational specific heat per lattice site. Here \(C_{\text{conf}}(T)\) is the specific heat per particle, \(\rho\) is the number of molecules per unit volume (which is equal to \(\rho_0\) along the critical isochore), and \(\rho_{\text{max}}\) is the number density at close packing. For a lattice gas, as is well known, \(\rho_{\text{max}} = 2\rho_0\), \(\rho_{\text{max}}\) being equal to the number of lattice sites per unit volume. For argon Fisher estimated \(\rho_{\text{max}}\) by extrapolation of the "liquid" density to zero temperature obtaining roughly \(\rho_{\text{max}} \approx 3\rho_0\).

Fisher gave several arguments to justify choosing \(C^*(T)\), the "specific heat per particle volume" as the fundamental quantity most directly comparable in continuum fluids and lattice gases. In particular he pointed out that for a one-dimensional van der Waals system, for which \(\rho_{\text{max}}/\rho_0 = 3\) in the continuum and 2 in the lattice, the specific-heat discontinuities at the critical point \(\Delta C\) are \(3/2\kappa\) and \(3\kappa\), respectively, so that \(\Delta C^* = \frac{3}{2}\kappa\) in both cases. The question then arose immediately of whether this remarkable agreement between the continuum and lattice van der Waals systems was a pure coincidence for the one-dimensional case, or whether it holds also in higher dimensions.

where \(\rho_{\text{max}}/\rho_0\) \((\rho_{\text{max}}\) being the close packing density) is very different from 3. (For this system \(\rho_{\text{max}}\) is also the density of the fluid, or solid, phase at \(T = 0\).) The surprising answer that \(\Delta C^*\) is indeed \(\frac{3}{2}\kappa\), the lattice-gas value, in all dimensions is presented in Table I.

To obtain the correct generalized van der Waals equation in any dimension one considers a system whose interparticle potential \(v(r)\) consists of two parts: a "well-behaved" part \(q(r)\) and a "Kac potential" \(\gamma^* v(\gamma r)\),

\[
v(r) = q(r) + \gamma^* v(\gamma r),
\]

where \(v\) is the dimensionality of the space considered and we have written \(v\) as a function of \(r\), the vector displacement between two particles, so that our results apply also to lattice gases. It was then shown, for one dimension and special forms of \(q\) and \(v\), by Baker and by Kac, Uhlenbeck, and Hemmer, and for an arbitrary number of dimensions and quite general forms of the potential \(q\) and \(v\) by Lebowitz and Penrose, that in the limit \(\gamma \to 0\) (taken after the size of the system has been made infinite) the thermodynamic quantities are given by a generalized van der Waals–Maxwell theory, e.g.,

\[
\lim_{\gamma \to 0} p(T, \rho, \gamma) = p^*(T, \rho) + \frac{1}{2} \alpha \rho^2 (+\text{Maxwell's rule}),
\]

where \(p\) is the pressure, \(p^*(T, \rho)\) the pressure of the reference system for which \(\varphi = 0\), and

\[
\alpha = \int \varphi(y) \, dy.
\]

We shall be concerned here exclusively with the case where \(q(r)\) is a pure hard-core potential, which is either infinite or zero, so that the reference system has no configurational internal energy. We then have

\[
C_{\text{conf}} = 0, \text{ in one-phase region}
\]

\[
= -\frac{1}{2} \omega T \int [\rho_1 + \rho_2 - \rho_1 \rho_2 / \rho] / \rho^2 \, d\rho,
\]

in two-phase region,

where \(\rho_1\) and \(\rho_2\) are the densities of the two phases, the

Table I. Properties of lattice gases and continuum fluids with long-range interactions.

<table>
<thead>
<tr>
<th>Lattice gas</th>
<th>Continuum</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\rho_{\text{max}}/\rho_0)</td>
<td>1</td>
</tr>
<tr>
<td>(\rho_0/\rho_{\text{max}})</td>
<td>0.5</td>
</tr>
<tr>
<td>(\Delta C^*/\kappa)</td>
<td>1.5</td>
</tr>
<tr>
<td>(\varphi(\rho)/\rho)</td>
<td>0.386</td>
</tr>
</tbody>
</table>

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two-phase region existing only for \( a \leq 0 \). The jump in \( C \) at \( T = T_c \) for \( \rho = \rho_c \) is then given by

\[
\Delta C = 3k \left[ \frac{\partial \beta \rho}{\partial \rho} \right]_{\rho_c} \left[ \rho_c \frac{\partial^2 \beta \rho}{\partial \rho^2} \right] \left|_{\rho_c} \right.,
\]

where \( \beta \rho = \rho / kT \) is a function of \( \rho \) alone.

Choosing, for lattices, \( q(r) \) to be a hard-core potential which prevents the multiple occupancy of a lattice site

\[
\begin{align*}
q(r) &= \infty, \quad r = 0, \\
&= 0, \quad r \neq 0,
\end{align*}
\]

we have \( p(T, \rho) = -kT \ln(1-\rho) \) in all dimensions and we obtain the results quoted before.

For the continuum fluid we shall again take \( q(r) \) to correspond to a hard-core interaction with diameter \( a \),

\[
\begin{align*}
q(r) &= \infty, \quad r < a, \\
&= 0, \quad r > a.
\end{align*}
\]

The thermodynamic properties of the reference system will now depend strongly on the dimensionality of the space being known exactly only in one dimension where \( p(T, \rho) = kT \rho / (1-\rho / \rho_{\text{max}}) \), from which follow the previously mentioned results. For two and three dimensions the best available equation of state, \( p(T, \rho) \), is the Padé approximation found by Ree and Hoover\(^*\) on the basis of the first six virial coefficients,

\[
\frac{\beta \rho}{\rho_{\text{max}}} = \frac{1 + 0.188103 + 0.152027 \rho}{1 - 1.663098 + 0.713358 \rho}, \quad \nu = 3;
\]

\[
\frac{\beta \rho}{\rho_{\text{max}}} = \frac{1 + 0.356780 + 0.021447 \rho}{1 - 1.757171 + 0.787808 \rho}, \quad \nu = 2,
\]

where

\[
\theta = \frac{\rho}{\rho_{\text{max}}},
\]

These equations of state agree to better than 1% with machine computations for densities in the "fluid range"; \( \rho_{\text{max}} / \rho \approx 1.312 \) for \( \nu = 2 \), \( \rho_{\text{max}} / \rho \approx 1.63 \) for \( \nu = 3 \). The critical density \( \rho_c \) of the gas-liquid transition due to the long-range attractive potential \( \gamma(r) \varphi(\gamma r) \) is found from the solution of the equation

\[
\frac{\beta \rho}{\rho} = \frac{d \beta \rho}{d \rho},
\]

and is independent of \( a \). The results for \( \Delta C^* \) as well as for the critical ratio \( \rho_c / \rho_c kT \) are presented in Table I. (For comparison, the critical ratio of argon is variously quoted as\(^*\) 0.291 or\(^\dagger\) 0.314 while machine computations for a system with a hard core and square well extending to 1.5 \( a \) yield\(^*\) a critical ratio of 0.306.)

The apparent insensitivity of \( \Delta C^* \), for van der Waals systems, to the dimensionality of space considered, (the lattice gas behaving in some way as a space for which \( \nu = 0 \)), is indeed remarkable. As seen from Eq. (5) \( \Delta C \) depends only on \( \beta \rho \), which is quite different for different \( \nu \)'s, leading to widely different values of \( \Delta C \) and of \( \rho_c / \rho_{\text{max}} \). Why then does \( \Delta C^* \) appear to remain essentially unchanged? (Conceivably it might even be exactly \( 1.5 k \) for all \( \nu \)') We have no ready explanation for this but it does seem to lend support to Fisher's idea that \( C^* \) is a more "natural" quantity for comparison between lattice and continuum systems in the vicinity of the critical point.

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\(^\text{1}\) J. de Boer, J. M. J. Van Leeuwen, and J. Groeneveld, Physica 30, 2284 (1964).

\(^*\) L. Verlet quoting B. J. Alder (private communication).