Liquid-gas spinodal and the interfacial properties from the lattice gas-fluid isomorphism approach

Kulinskii V. L.

Department for Theoretical Physics, Odessa National University, Dvoryanskaya 2, 65026 Odessa, Ukraine

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Outline

1. Global isomorphism of the lattice gas and the fluid
   - Projective isomorphism

2. Surface tension

3. Spinodal of the fluid
Empirical facts

- Global cubic character of the binodal of simple liquids;
Empirical facts

- Global cubic character of the binodal of simple liquids;
- Law of Rectilinear Diameter (LRD);
Empirical facts

- Global cubic character of the binodal of simple liquids;
- Law of Rectilinear Diameter (LRD);
- Batchinsky law (Zeno-Line)
PCS and Global cubic character of the binodal

\[ \frac{\rho_l}{\rho_c} = 1 + \frac{3}{4} \left( 1 - \frac{T}{T_c} \right) + \frac{7}{4} \left( 1 - \frac{T}{T_c} \right)^{\frac{1}{3}} \]

\[ \frac{\rho_g}{\rho_c} = 1 + \frac{3}{4} \left( 1 - \frac{T}{T_c} \right) - \frac{7}{4} \left( 1 - \frac{T}{T_c} \right)^{\frac{1}{3}} \]
LRD: Cailletet&Mathias, 1886

Law of Rectilinear Diameter

\[ n_d = \frac{n_l + n_g}{2n_c} = 1 + A \frac{T_c - T}{T_c}. \]
LRD: present time

Liquid–vapor coexistence curves for model potentials
Okumura & Yonezawa, JCP v.113 (2000)

FIG. 8. The liquid–vapor coexistence curves and the diameters in the scaled temperature $T_s = T^*/T_c^*$ – density $\rho_s = \rho^*/\rho_c^*$ plane.
Zeno-Line

\[ Z = \frac{P}{nT} = 1 \]
Z = P/(n T) = 1

\[ Z = \frac{P}{n T} = 1 - \frac{2\pi n}{3 T} \int r^3 \frac{\partial \Phi(r)}{\partial r} g_2(r; n, T) \, dr , \]

\( g_2 \) - pair correlation function.
Zeno-Line

\[ Z = 1 \Rightarrow \int r^3 \frac{\partial \Phi(r)}{\partial r} g_2(r; n, T) \, dr = 0 \]

Condition:

\[ g_2(r; n, T) = 0 \]

defines “ideal-gas” states (line \( n = 0 \) included trivially)
Zeno-Line

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Condition:

\[ g_2(r; n, T) = 0 \]

defines “ideal-gas“ states (line \( n = 0 \) included trivially)

Complete configurational order

\( n = n_B - \text{dense packing} \Rightarrow g_2 = 0 \)
Batchinsky law

\[ P(n, T) = \frac{nT}{1 - nb} - an^2 \]
Zeno-Line

\[ P(n, T) = \frac{n T}{1 - n b} - a n^2 \]

\[ \frac{P(n, T)}{n T} = \frac{1}{1 - n b} - a \frac{n}{T} = 0 \]
Batchinsky law

\[
\frac{P(n, T)}{nT} = \frac{1}{1 - nb} - a \frac{n}{T} = 0
\]

\[
\frac{P(n, T)}{nT} = 1 \Rightarrow \frac{n}{n_B} + \frac{T}{T_B} = 1, \quad n_B = 1/b, T_B = a/b
\]
For each $\alpha \leq \alpha_0$, there exists $B_0(\alpha)$ such that $E_{\text{max}} = E_{\text{min}}$ and, therefore, $\frac{d^2E}{dr^2} = 0$. (33)

On the graph $(\alpha, E)$ the relation $E_{\text{max}} = E_{\text{min}}$ determines the analog of the Zeno line.

Let us now represent the Zeno line on the graph $(\rho, T)$. Figure 1: $T$–$\rho$ diagram for gases corresponding to simple liquids, $T_r = T/T_{c\text{r}}$, $\rho_r = \rho/\rho_{c\text{r}}$. The $Z = P/V NT = 1$ line (Zeno–line) on the phase diagram. For states with $Z > 1$ (hard fluids) repulsive forces dominate. For states where $Z < 1$ (soft fluids) attractive forces dominate.

Further, for a fixed $\rho$, which is proportional to $\alpha$, we obtain the asymptotic behavior $E(r) = r^2 \Phi(r) - \rho r^4 B^2 - r^2$, as $B \to \infty$, where $B$ is the impact parameter, and also the ratio of the difference of the maximal and minimal points of $E(r)$ to the maximal point. By our correspondence principle, this ratio corresponds to the compressibility factor $Z = E_{\text{max}} - E_{\text{min}}/E_{\text{max}}$ and, as $B \to \infty$, for a given $\rho$, we obtain the minimum value of $Z$ on the graph $(\rho, T)$. The Zeno line has already been obtained by the rule given above.

The value of the compressibility factor $Z$ is already plotted along the $y$-axis. We must now establish the correspondence with the temperature scale. To do this, consider the ordinate axis, i.e., the case $\rho = 0$. The point $0.8\epsilon$, where $\epsilon$ is the depth of the well of the Lennard-Jones potential corresponds to the Boyle temperature.

For $\rho = 0$, let us find the point $\tilde{Z} = E_{\text{min}}/E_{\text{max}}$ equal to $Z_{c\text{r}} = 0.29$. This point corresponds to $3/2 E_{\text{max}}$, which, in turn, corresponds to the critical temperature $4/3$. The ratio of this point to $4/3$ is due to the fact that the value $E_{\text{max}}$ corresponds to the bottom of the well (after turning the wells upside down as mentioned above). It means that dimers lost $2/3$ of their degrees of freedom when due to viscosity they fell on the bottom of the well. This follows from the fact that circular motion takes place on the bottom of a vessel. Hence, the initial energy of dimers was in $3/2$ times larger. Since there is no a similar lost for $T_{B\text{r}}$, for $Z = Z_{c\text{r}}$, we have relation $T_{c\text{r}}/T_{B\text{r}} = 3/2(2/3)^{E_{\text{max}}(Z)/0.8E)$. According to the newest data [1] for Kr, Xe, N$_2$, O$_2$ and ethane the value of $T_{c\text{r}}/T_{B\text{r}}$ is equal to 0.39; compare Table 1.

Figure: Simple fluid phase diagram (methane), $T_r = T/T_{c\text{r}}$, $\tilde{n} = n/n_{c\text{r}}$, $Z = P/(n T) = 1$ – Zeno-Line. States $Z > 1$ “hard fluid“, $Z < 1$ “soft fluid“ (Ben-Amotz&Herschbach, 1990).
Characteristic properties (E. Apfelbaum and V. Vorob’ev)

- ZL is the tangent to the binodal in $n = n_B$, $T \to 0$
- “Median“

$$\frac{n}{n_B/2} + \frac{T}{T_B} = 1$$

at “low“ temperatures is close to the (rectilinear) diameter
Simplest fluid - Ising model (lattice gas)

\[ H = -J \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i, \quad n_i = 0, 1 \]
Simplest fluid - Ising model (lattice gas)

\[ H = -J \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i, \quad n_i = 0, 1 \]
Simplest fluid - Ising model (lattice gas)

\[ H = -J \sum_{ij} n_i n_j - \mu \sum_i n_i , \quad n_i = 0, 1 \]

Order parameter \( x = \langle n_i \rangle \) - lattice density.
... Thus I conceived the idea that there is no essential difference between the gaseous and the liquid state of matter - that the factors which, apart from the motion of the molecules, act to determine the pressure must be regarded as quantitatively different when the density changes and perhaps also when the temperature changes, but that they must be the very factors which exercise their influence throughout. And so the idea of continuity occurred to me ...
Liquid vs. Gas

Ising model

III II I

CP $T_c$

Fluid

$\rho$ $\rho_{Trp}$

$T_{Trp}$ $T$

$\rho_{Trp}$ $\rho$

CP
Figure: Correspondence between the linear elements of the phase diagrams. Zeno-Line and Zeno-median are shown. The latter coincides with the rectilinear diameter.
Figure: Correspondence between the linear elements of the phase diagrams. Zeno-line, generally, is not linear and we introduce the linear element $T/T_* + n/n_* = 1$.
Correspondence between linear elements
Correspondence between linear elements

critical isotherm \( t_c = 1 \iff T = T_c \)
Correspondence between linear elements

- **Critical isotherm**: \( t_c = 1 \Leftrightarrow T = T_c \)
- **Zeno-median**: \( x = 1/2 \Leftrightarrow \frac{2n}{n_*} + \frac{T}{T_*} = 1 \)
Correspondence between linear elements

\[
\text{critical isotherm } \quad t_c = 1 \Leftrightarrow \quad T = T_c
\]

\[
\text{rectilinear diameter } \quad x = 1/2 \Leftrightarrow \quad \frac{2n}{n^*} + \frac{T}{T^*} = 1,
\]
Correspondence between linear elements

- **critical isotherm** \( t_c = 1 \Leftrightarrow T = T_c \)
- **rectilinear diameter** \( x = 1/2 \Leftrightarrow \frac{2n}{n^*} + \frac{T}{T^*} = 1 \)
- **Zeno-Line** \( x = 1 \Leftrightarrow \frac{n}{n^*} + \frac{T}{T^*} = 1 \)
Correspondence between linear elements

critical isotherm \( t_c = 1 \iff T = T_c \)

rectilinear diameter \( x = 1/2 \iff \frac{2n}{n_\ast} + \frac{T}{T_\ast} = 1 \),

Zeno-Line \( x = 1 \iff \frac{n}{n_\ast} + \frac{T}{T_\ast} = 1 \).

\[
n/n_\ast = \frac{x}{1 + at}, \quad T/T_\ast = \frac{at}{1 + at}, \quad a = \frac{T_c}{T_B - T_c}.
\]
Figure 5. Dependence of the temperature and density along the phase coexistence curves on parameters reduced to the Zeno-line parameters for the different model systems and substances: (line 1) \( Z = 1 \) line, (line 2) critical points line, (line 3) Lennard-Jones numerical modeling of ref 11, (line 4) according to the van der Waals equation. The symbols correspond to the different substances. We have added the average diameter for Hg, water, and substances satisfying the corresponding states law.
Universal Triangle of States and Liquid Branch of the Binodal

Similarly to earlier work, let us present the binodals of all model systems and real substances considered above on the density-temperature plane using the coordinates reduced to the Zeno-line parameters, \( F' \) and \( T' \). In these coordinates, the Zeno-line is a straight line, universal for all substances.

\[
T_c = T_* \frac{z}{1+z}, \quad n_c = \frac{n_*}{2(1+a)}.
\]

Line of the critical points for the substances with \( z \) fixed:

\[
\frac{n_c}{n_B} + \frac{T_c}{T_B} = \frac{2z + 1}{2(1+z)}
\]
Global isomorphism

\[ n = n_* \frac{x}{1 + a t}, \quad T = T_* \frac{a t}{1 + a t}, \]
\[ x = \frac{n}{n_*} \left(1 - \frac{T}{T_*}\right), \quad t = \frac{1}{a} \frac{T}{T_*} \left(1 - \frac{T}{T_*}\right) \]
Global isomorphism

\[ n = n_* \frac{x}{1 + a t}, \]
\[ x = \frac{n}{n_*} \left( 1 - \frac{T}{T_*} \right), \]
\[ T = T_* \frac{a t}{1 + a t}, \]
\[ t = \frac{1}{a} \frac{T/T_*}{1 - T/T_*}, \]
\[ a = \frac{T_c}{T_* - T_c} \]

- thermodynamic similarity class parameter. For 3D LJ \( a = 1/2 \).
Global isomorphism

\[
n = n_\ast \frac{x}{1 + at}, \quad T = T_\ast \frac{at}{1 + at},
\]

\[
x = \frac{n}{n_\ast} \left( 1 - \frac{T}{T_\ast} \right), \quad t = \frac{1}{a} \frac{T/T_\ast}{1 - T/T_\ast}
\]

\[
a = \frac{T_c}{T_\ast - T_c}
\]

- thermodynamic similarity class parameter. For 3D LJ \( a = 1/2 \).

\[
T/T_\ast + n/n_\ast = 1 \iff x = 1
\]

\[
T_\ast \ - \ Boyle \ temperature \ in \ vdw \ approximation,
\]

\[
T^*_v = T^\text{vdW}_B = a_{vdw}/b \ and:
\]

\[
n_\ast = T_\ast \frac{B_2'(T_\ast)}{B_3(T_\ast)}
\]
Ising model (lattice gas) binodal maps onto the binodal of the fluid

\[ n(t) = n_* \frac{x(t)}{1 + a t}, \quad T(t) = T_* \frac{a t}{1 + a t} \]
Global isomorphism of the lattice gas and the fluid
Surface tension
Spinodal of the fluid

Mapping between binodals of the lattice gas and the fluid

Figure: Binodal of 2D Ising model (Onsager exact solution).

\[ x(t) = \frac{1}{2} \pm f(t)^{1/8}, \quad f(t) = 1 - \frac{1}{\sinh^4 \left( \frac{2J}{t} \right)} \]
Figure: Binodal of 2D Lennard-Jones fluid \( a = 1/3 \), \( T_* = 2.03 \approx T_B^{(vdW)} = 2 \) and \( n_* = 0.971 \) \((n_*^{(theor)} = 0.91)\) and the simulations data (Smith & Frenkel).
Figure: Binodal of 3D L-J fluid (blue) obtained via mapping (with $a = 1/2$) of the binodal of 3D Ising model (numerical data). Red line is the Guggenheim cubic law.
Scaling nature of $z$

Scaling symmetry

Different liquids differ by $T_c$ and $n_c$ because of different scales for energy interaction and the molecular sizes. The lattice gas hamiltonian obeys the scaling symmetry:

$$t_c \rightarrow \lambda^2 t_c, \quad x_c \rightarrow \lambda^{-1} x_c$$
Scaling nature of $z$

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$$n_c/n_\ast = \frac{1}{2(1+a)}, \ T_c/T_\ast = \frac{a}{1+a}$$
Scaling nature of $z$

Scaling symmetry

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$$t_c \to \lambda^2 t_c, \quad x_c \to \lambda^{-1} x_c$$

$$n_c/n_* = \frac{1}{2(1+a)}, \quad T_c/T_* = \frac{a}{1+a}$$

$$\frac{d \ln \left( \frac{T_c}{T_*} \right)}{d \ln \left( \frac{n_c}{n_*} \right)} = -\frac{1}{a}$$
The attractive part of the potential in d dimensions has the form $\Phi_{\text{attr}}(r) \sim r^{-(d+\varepsilon)}$, $\varepsilon > 0$. The energy of interaction is:

$$E_{\text{int}} = \frac{1}{2} \sum_{i,j} \Phi_{\text{attr}}(|r_i - r_j|) = \frac{V}{2} \int \Phi_{\text{attr}}(r_{12}) n(r_1) n(r_2) \, dr_{12}$$

$$n_c \sim \frac{1}{r_c^d}, \quad T_c \sim \Phi(r_c) \sim \frac{1}{n_c^{1+\varepsilon/d}}$$

naive scaling:
The attractive part of the potential in $d$ dimensions has the form $\Phi_{\text{attr}}(r) \sim r^{-(d+\varepsilon)}$, $\varepsilon > 0$. The energy of interaction is:

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$$n_c \sim \frac{1}{r_c^d}, \quad T_c \sim \Phi(r_c) \sim \frac{1}{n_c^{1+\varepsilon/d}}$$

naive scaling:

$$n_c \rightarrow n_c(0) e^{-\lambda}, \quad T_c \rightarrow T_c(0) e^{(1+\varepsilon/d)\lambda}.$$
Consistency condition

naive scaling:

\[- \frac{1}{a} = \frac{d \ln \left( \frac{T_c}{T_*} \right)}{d \ln \left( \frac{n_c}{n_*} \right)} = - \left( 1 + \frac{\varepsilon}{d} \right) \Rightarrow a = \frac{1}{1 + \frac{\varepsilon}{d}}.\]
Consistency condition

naive scaling:

\[-\frac{1}{a} = \frac{d \ln \left( \frac{T_c}{T_*} \right)}{d \ln \left( \frac{n_c}{n_*} \right)} = - \left( 1 + \frac{\varepsilon}{d} \right) \implies a = \frac{1}{1 + \frac{\varepsilon}{d}}.\]

For LJ-systems with $\Phi_{\text{attr}} \propto r^{-6}$ in $d$ dimensions $z = \frac{d}{6}$:

\[
d = 2 : a = \frac{1}{3}, \quad d = 3 : a = \frac{1}{2}.
\]
Global isomorphism of the lattice gas and the fluid

Surface tension

Spinodal of the fluid

Projective isomorphism

CP in d-dimensions

\[
\frac{T_c}{T_*} = \frac{1}{2 + \frac{\varepsilon}{d}}, \quad \frac{n_c}{n_*} = \frac{1 + \frac{\varepsilon}{d}}{2 \left(2 + \frac{\varepsilon}{d}\right)}.
\]

\[
T_* = \frac{4d}{6 - d}, \quad a_{\text{vdW}} = 2^{d-1} \frac{4d}{6 - d}, \quad b = 2^{d-1},
\]

hard core volume is normalized so that \(n_* = 1\).
Comparison with the simulations

<table>
<thead>
<tr>
<th>LJ “6-12“ fluid</th>
<th>2D</th>
<th>3D</th>
<th>4D</th>
<th>5D</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$</td>
<td>0.5</td>
<td>1.33</td>
<td>3.2</td>
<td>9.1</td>
</tr>
<tr>
<td>$T_c^{(num)}$</td>
<td>0.515</td>
<td>1.312</td>
<td>3.404</td>
<td>8.8 (?)</td>
</tr>
<tr>
<td>$n_c$</td>
<td>0.375</td>
<td>0.33</td>
<td>0.3</td>
<td>0.27</td>
</tr>
<tr>
<td>$n_c^{(num)}$</td>
<td>0.355</td>
<td>0.316</td>
<td>0.34</td>
<td>-</td>
</tr>
</tbody>
</table>
Global isomorphism of the lattice gas and the fluid SURFACE TENSION SPINODAL OF THE FLUID

Binodal as function of a
Binodal as function of $z$

\[ T/T_* \]

\[ n/n_* \]

\( a \to \infty \) Flory $\theta$-point?
Global isomorphism of the lattice gas and the fluid

Surface tension

Spinodal of the fluid

Projective isomorphism

"particle-hole" symmetry

Kulinskii V. L. Global isomorphism
Global isomorphism of the lattice gas and the fluid
Surface tension
Spinodal of the fluid

**Correspondence of thermodynamic states**

\[
\frac{n}{n^*} = \frac{x}{1 + a t}, \quad \frac{T}{T^*} = \frac{a t}{1 + a t}.
\]

Kulinskii V. L.  Global isomorphism
Connection between lattice and fluid

**Proposition**

Projective form of the lattice-fluid transformation is the consequence of the projective nature of the thermodynamic limit:

\[
\begin{pmatrix}
U \\
S \\
V \\
N
\end{pmatrix}
= \hat{L}
\begin{pmatrix}
U \\
S \\
N \\
N
\end{pmatrix}
\]
Connection between lattice and fluid

**Proposition**

Projective form of the lattice-fluid transformation is the consequence of the projective nature of the thermodynamic limit:

\[
\text{FLUID} \begin{pmatrix}
U \\
S \\
V \\
N
\end{pmatrix} = \hat{L} \begin{pmatrix}
U \\
S \\
N
\end{pmatrix} \quad \text{Ising Model}
\]
Relation between bulk thermodynamic potentials

\[
\frac{n}{n_*} = \frac{x}{1 + at}, \quad n = \frac{\partial J}{\partial \mu} \bigg|_T, \quad x = \frac{\partial \mathcal{G}}{\partial h} \bigg|_t
\]

we get relation between grand potentials:
Global isomorphism of the lattice gas and the fluid
Surface tension
Spinodal of the fluid

Projective isomorphism

Relation between bulk thermodynamic potentials

\[ \frac{n}{n_*} = \frac{x}{1 + at}, \quad n = \frac{\partial J}{\partial \mu} \bigg|_T, \quad x = \frac{\partial \xi}{\partial h} \bigg|_t \]

we get relation between grand potentials:

\[ J(\mu, T, V) = P(\mu, T), \quad V = \xi \left( h(\mu, T), t(T), N \right) \]
Relation between bulk thermodynamic potentials

\[
n / n_* = \frac{x}{1 + a t}, \quad n = \left. \frac{\partial J}{\partial \mu} \right|_T, \quad x = \left. \frac{\partial \mathcal{G}}{\partial h} \right|_t
\]

we get relation between grand potentials:

\[
J(\mu, T, V) = P(\mu, T) V = \mathcal{G}(h, t, N) = N g(h, t)
\]

\[
\mu - \mu_0(T) = \frac{h}{1 + a t}
\]

\(\mu_0(T)\) - chem. potential along coexistence curve
The surface tension of 2D Ising model is determined by the next eigenvalue of the transfer matrix $\Lambda_1 < \Lambda_{\text{max}}$:

$$\Sigma_{m\times n}^{(\text{lat})} = \Lambda_{\text{max}}^m + \Lambda_1^m + \ldots$$
The surface tension of 2D Ising model is determined by the next eigenvalue of the transfer matrix $\Lambda_1 < \Lambda_{\text{max}}$:

$$\Sigma_{\text{m} \times \text{n}}^{(\text{lat})} = \Lambda_{\text{max}}^m + \Lambda_1^m + \ldots$$

$$V T \ln \Xi_V(\mu, T) = V P + \sigma A = N g + s A = N t \ln \Sigma_N(h, t)$$
Surface tension of 2D Ising model

\[ \sigma(t) = 2 + t \ln \left( \tanh \frac{1}{t} \right) = 4 \left( 1 - \frac{t}{t_c} \right) + \ldots \]
Surface tension of 2D LJ fluid

\[ \sigma_{\text{LJ}}(T) = \mathcal{S}(t(T)) = \frac{16}{3} \left(1 - \frac{T}{T_c}\right) + \ldots , \]
Global isomorphism of the lattice gas and the fluid

Surface tension

Spinodal of the fluid

Surface tension of 2D LJ fluid

\[ T_{c}^{(th)} = 0.5 \]

\[ T_{c} = 0.533 \]

simulation (X.C.Zeng, JCP (1996))

\[ \frac{T}{T_c} \]

\[ \frac{T}{T_c} \]
Surface tension of 2D LJ fluid

\[ T_{c}^{(th)} = 0.5 \]
\[ T_c = 0.533 \]

Simulation (X.C. Zeng, JCP (1996))

Theory
General Equation for the Surface Tension of the Lattice Gas

George W. Woodbury, Jr.*
Department of Chemistry, University of Montana, Missoula, Montana 59801
(Received 30 December 1968)

A general expression for the surface tension of a lattice gas is derived. The equation is \( \gamma A/kT = \langle \eta \rangle_e - \langle \eta \rangle_l \), where \( \gamma \) is the surface tension, \( A \) is the surface area, \( \eta \) is related to the eigenvector corresponding to the gas phase, and \( \langle \cdot \rangle_e \) and \( \langle \cdot \rangle_l \) are averages performed in the bulk gas and bulk liquid phase, respectively. The derivation, which incorporates rigorously defined local thermodynamic functions, is similar in some ways to the Cahn–Hilliard development. Numerical results are obtained by applying the Bragg–Williams approximation to the general equation.
General Equation for the Surface Tension of the Lattice Gas

George W. Woodbury, Jr.*

Department of Chemistry, University of Montana, Missoula, Montana 59801
(Received 30 December 1968)

A general expression for the surface tension of a lattice gas is derived. The equation is \( \gamma A/kT = \langle \eta \rangle_g - \langle \eta \rangle_l \), where \( \gamma \) is the surface tension, \( A \) is the surface area, \( \eta \) is related to the eigenvector corresponding to the gas phase, and \( \langle \cdot \rangle_g \) and \( \langle \cdot \rangle_l \) are averages performed in the bulk gas and bulk liquid phase, respectively. The derivation, which incorporates rigorously defined local thermodynamic functions, is similar in some ways to the Cahn–Hilliard development. Numerical results are obtained by applying the Bragg–Williams approximation to the general equation.

Local representation of the surface tension

\[ \sigma = t \left( \langle \eta \rangle_{\text{gas}} - \langle \eta \rangle_{\text{liq}} \right) \]
Surface tension of lattice model

**Local representation of the surface tension**

\[ \sigma = t \left( \langle \eta \rangle_{\text{gas}} - \langle \eta \rangle_{\text{liq}} \right) \]

Bragg-Williams approximation \( \eta = \frac{1}{2} \sum_i p(s_i) \):
Surface tension of lattice model

Local representation of the surface tension

\[ \sigma = t \left( \langle \eta \rangle_{\text{gas}} - \langle \eta \rangle_{\text{liq}} \right) \]

Bragg-Williams approximation \( \eta = \frac{1}{2} \sum_i p(s_i) \):

\[ \sigma = \frac{t}{2a} \left( x_{\text{liq}} - x_{\text{gas}} \right) \ln \frac{x_{\text{liq}}}{x_{\text{gas}}} \]

a - lattice spacing
Surface tension of lattice model

Local representation of the surface tension

\[ \sigma = t \left( \langle \eta \rangle_{\text{gas}} - \langle \eta \rangle_{\text{liq}} \right) \]

Modified form:

\[ \sigma = \frac{t}{2^{\xi_{1-\eta}}} \left( x_{\text{liq}} - x_{\text{gas}} \right) \ln \frac{x_{\text{liq}}}{x_{\text{gas}}} \]
Surface tension of the lattice gas and the fluid

Surface tension

Spinodal of the fluid

Surface tension of lattice model

Local representation of the surface tension

\[ \sigma = t \left( \langle \eta \rangle_{\text{gas}} - \langle \eta \rangle_{\text{liq}} \right) \]

Modified form:

\[ \sigma = \frac{t}{2^{\xi_{1-\eta}}} \left( x_{\text{liq}} - x_{\text{gas}} \right) \ln \frac{x_{\text{liq}}}{x_{\text{gas}}} \sim \frac{\left( x_{\text{liq}} - x_{\text{gas}} \right)^2}{\xi_{1-\eta}} \]
Surface tension of lattice model

Local representation of the surface tension

\[ \sigma = t \left( \langle \eta \rangle_{\text{gas}} - \langle \eta \rangle_{\text{liq}} \right) \]

Modified form:

\[ \sigma = \frac{t}{2 \xi^{1-\eta}} \left( x_{\text{liq}} - x_{\text{gas}} \right) \ln \frac{x_{\text{liq}}}{x_{\text{gas}}} \sim \frac{(x_{\text{liq}} - x_{\text{gas}})^2}{\xi^{1-\eta}} \]

\( \xi(t) \) - effective thickness of the interface
Global isomorphism of the lattice gas and the fluid

Surface tension

Spinodal of the fluid

Test: 2D Ising model
Figure: Effective interfacial thickness, $\eta = 1/4$, $\nu = 1$. 
Surface tension of 3D fluid

\[ \sigma = \frac{t}{2 \xi^{1-\eta}} (x_{\text{liq}} - x_{\text{gas}}) \ln \frac{x_{\text{liq}}}{x_{\text{gas}}} \]
Surface tension of 3D fluid

\[ \sigma = \frac{t}{2\xi^{1-\eta}} (x_{\text{liq}} - x_{\text{gas}}) \ln \frac{x_{\text{liq}}}{x_{\text{gas}}} \sim \left( \frac{x_{\text{liq}} - x_{\text{gas}}}{\xi^{1-\eta}} \right)^2 \]
Surface tension of 3D fluid

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\[ \xi = \left( \frac{1}{t} - 1 \right)^{-\nu}, \eta \approx 0.03 - \text{Fisher’s critical exponent, } \nu \text{ taken as fitting parameter} \]
Global isomorphism of the lattice gas and the fluid

Surface tension

Spinodal of the fluid

Surface tension of 3D fluid

\[ x_{\text{liq, gas}}(T) = \frac{1}{2 (1 + a)} \frac{\rho_{\text{liq, gas}}}{1 - \frac{T}{T_c}} \frac{a}{1 + a}, \quad t(T) = \frac{t_c}{1 + a} \frac{T}{T_c} \frac{z}{1 + a} \]
Surface tension of 3D fluid

Surface tension of Argon and LJ fluid

Theory $\xi = (1/t-1)^\nu$ $\nu=0.628$

Argon (NIST)

LJ (simulation)
Surface tension of 3D fluid

Figure: Temperature dependence of the effective interfacial thickness
Surface tension of 3D fluid

Microscopic form (Kirkwood-Buff):

$$\sigma_\infty = \frac{1}{4} \int dz_1 \int d\vec{r} u'(r) (1 - 3 \cos^2 \theta) n_2(z_1, z_2, r),$$
Surface tension of 3D fluid

Microscopic form (Kirkwood-Buff):

\[ \sigma_\infty = \frac{1}{4} \int dz_1 \int d\mathbf{r} u'(r) \left( 1 - 3 \cos^2 \theta \right) n_2(z_1, z_2, r), \]

Fluctuational (mesoscopic) form (Triezenberg-Zwanzig, 1972):

\[ \sigma_\infty = T \iint dz_1 dz_2 \frac{d n(z_1)}{d z_1} K_2(z_1, z_2) \frac{d n(z_2)}{d z_2} \]

\[ K_2(z_1, z_2) = \frac{1}{4} \int d^{d-1} \rho \rho^2 C_2(z_1, z_2; \rho) \]
Surface tension of 3D fluid

\[
\frac{1}{T} \left( \frac{\partial p}{\partial n} \right) _T = 1 - n \int C_2(n; r_{12}) \, dr_{12},
\]

\[
\left( \frac{\partial p}{\partial n} \right) _T \propto |\tau|^\gamma \quad T \to T_c.
\]

\[
C_2(n; r_{12}) \propto |\tau|^{2-\alpha+\gamma} \propto \frac{1}{\xi^{d+2-\eta}}
\]

\[
K_2 = \frac{1}{4} \int d^{d-1} \rho \rho^2 C_2(z_1, z_2; \rho) \propto \frac{\xi^{d+1}}{\xi^{d+2-\eta}} \propto \frac{1}{\xi^{1-\eta}}.
\]
Global isomorphism of the lattice gas and the fluid

Surface tension

Spinodal of the fluid

Surface tension of 3D fluid

Fluctuational (mesoscopic) form (Triezenberg-Zwanzig, 1972):

\[ \sigma_\infty = T \int \int dz_1 \, dz_2 \, \frac{d\, n(z_1)}{d\, z_1} \, K_2(z_1, z_2) \, \frac{d\, n(z_2)}{d\, z_2} \propto |\tau|^\mu \]

\[ K_2(z_1, z_2) = \frac{1}{4} \int d\rho \, \rho^2 \, C_2(z_1, z_2; \rho) \]
Surface tension of 3D fluid

Fluctuational (mesoscopic) form (Triezenberg-Zwanzig, 1972):

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\]

\[
K_2(z_1, z_2) = \frac{1}{4} \int d \rho \rho^2 C_2(z_1, z_2; \rho)
\]

\[
d \nu = 2 - \alpha, \quad 2 - \alpha = \beta + \gamma, \quad \gamma = \nu(2 - \eta)
\]
Surface tension of 3D fluid

Fluctuational (mesoscopic) form (Triezenberg-Zwanzig, 1972):

$$\sigma_\infty = T \int \int dz_1 dz_2 \frac{dn(z_1)}{dz_1} K_2(z_1, z_2) \frac{dn(z_2)}{dz_2} \propto |\tau|^\mu$$

$$K_2(z_1, z_2) = \frac{1}{4} \int d\rho \, \rho^2 C_2(z_1, z_2; \rho)$$

$$d\nu = 2 - \alpha, \quad 2 - \alpha = \beta + \gamma, \quad \gamma = \nu (2 - \eta), \quad \sigma \propto |\tau|^\mu$$

$$\sigma_\infty \sim \left( n_{\text{liq}} - n_{\text{gas}} \right)^2$$

$$\xi^{1-\eta}$$
Global isomorphism of the lattice gas and the fluid

**Surface tension**

Spinodal of the fluid

**Surface tension of 3D fluid**

Fluctuational (mesoscopic) form (Triezenberg-Zwanzig, 1972):

\[
\sigma_\infty = T \int \int dz_1 \, dz_2 \frac{dn(z_1)}{dz_1} K_2(z_1, z_2) \frac{dn(z_2)}{dz_2} \propto |\tau|^{(d-1)\nu}
\]

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K_2(z_1, z_2) = \frac{1}{4} \int d\rho \rho^2 C_2(z_1, z_2; \rho) \propto \frac{1}{\xi^{1-\eta}}
\]

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\]

\[
\sigma_\infty \sim \frac{(n_{\text{liq}} - n_{\text{gas}})^2}{\xi^{1-\eta}} \propto |\tau|^{2\beta + \nu(1-\eta)} = |\tau|^{(d-1)\nu}
\]
Tolman length

Definition

\[ \Delta p = \frac{2\sigma_\infty}{R} \left( 1 - \frac{\delta_T}{R} + \ldots \right) \Rightarrow \sigma \neq \sigma_\infty \left( 1 - 2 \frac{\delta_T}{R} + \ldots \right) \]
Global isomorphism of the lattice gas and the fluid

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Definition

$$\Delta p = \frac{2 \sigma_\infty}{R} \left( 1 - \frac{\delta_T}{R} + \ldots \right) \Rightarrow \sigma = \sigma_\infty \left( 1 - 2 \frac{\delta_T}{R} + \ldots \right)$$

Microscopic form $\delta_T$ (Bokhuis & Bedeaux, 1992)

$$\delta_T = -\frac{1}{8 \sigma_\infty} \int dz_1 \int d\vec{r}_{12} u'(r) r \left( 1 - 3 \cos^2 \theta \right) (z_1 + z_2) n_2(z_1, z_2, r).$$
Question

Does the fluctuational (mesoscopic) form similar to Tietzenberg-Zwanzig for $\sigma_\infty$ exist for $\delta_T$?
Tolman length

Square-gradient approx (Fisher&Wortis, PRB (1984))

\[
\delta_T = \frac{\int_{-\infty}^{+\infty} z \, n'(z) \, dz}{\int_{-\infty}^{+\infty} n'(z) \, dz} - \frac{\int_{-\infty}^{+\infty} z \, n'^2(z) \, dz}{\int_{-\infty}^{+\infty} n'^2(z) \, dz}
\]

\(n(z)\) is the equilibrium density profile.
Global isomorphism of the lattice gas and the fluid

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$n(z)$ is the equilibrium density profile.

Anisimov’s expression, PRL (2007)

$$\delta_T \simeq \frac{n_d - 1}{n_{\text{liq}} - n_{\text{gas}}} \xi$$
Tolman length

Square-gradient approx (Fisher&Wortis, PRB (1984))

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\delta_T = \frac{\int_{-\infty}^{+\infty} z n'(z) \, dz}{\int_{-\infty}^{+\infty} n'(z) \, dz} - \frac{\int_{-\infty}^{+\infty} z n'^2(z) \, dz}{\int_{-\infty}^{+\infty} n'^2(z) \, dz}
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Anisimov's expression, PRL (2007)

\[
\delta_T \simeq \frac{n_d - 1}{n_{liq} - n_{gas}} \xi
\]

Symmetry

If there is "particle-hole" symmetry (Ising model) then \(\delta_T \equiv 0\).
TZ-like form for the Tolman length

We start with B&B expression:

$$\delta_T = -\frac{1}{8\sigma_\infty} \int dz_1 \int d\vec{r}_{12} (z_1 + z_2) u'(r) r (1 - 3 \cos^2 \theta) n_2(z_1, z_2, r)$$
TZ-like form for the Tolman length

\[ \delta_T = -\frac{1}{8\sigma_\infty} \int dz_1 \int d\vec{r}_{12} (2z_1 + z_{12}) u'(r) r (1 - 3 \cos^2 \theta) n_2(z_1, z_2, r) = \]
proceed with:

$$\delta_T = -\frac{1}{8\sigma_\infty} \int dz_1 \int d\vec{r}_{12} \left( 2z_1 + z_{12} \right) u'(r) r \left( 1 - 3 \cos^2 \theta \right) n_2(z_1, z_2, r) =$$

$$-\frac{1}{4\sigma_\infty} \int dz_1 \, dz_2 \, z_1 \, n'(z_1) K_2(1, 2) n'(z_2)$$
TZ-like form for the Tolman length

\[ \delta_T = -\frac{1}{8 \sigma_{\infty}} \int dz_1 \int d\vec{r}_{12} (2z_1 + z_{12}) u'(r) r \left(1 - 3 \cos^2 \theta\right) n_2(z_1, z_2, r) = \]

\[ = -\frac{1}{4 \sigma_{\infty}} \int dz_1 dz_2 z_1 n'(z_1) K_2(1, 2) n'(z_2) \]

\[ - \frac{1}{4 \sigma_{\infty}} \int dZ d\vec{r} z \left( x \frac{\partial u}{\partial x} - z \frac{\partial u}{\partial z} \right) n_2(\vec{R}, \vec{R} + \vec{r}) \]
Global isomorphism of the lattice gas and the fluid
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Square Gradient approximation = local approximation for $K_2(1, 2)$, so the first term goes to:

$$-rac{1}{4\sigma_\infty} \int dz_1 \, dz_2 \, z_1 \, n'(z_1) \, K_2(1, 2) \, n'(z_2) \Rightarrow - \frac{\int_+ \infty \, z \, n'^2(z) \, dz}{\int_- \infty \, n'^2(z) \, dz}$$
Square Gradient approximation = local approximation for \( K_2(1, 2) \), so the first term goes to:

\[
-\frac{1}{4\sigma_\infty} \int dz_1 \, dz_2 \, z_1 \, n'(z_1) \, K_2(1, 2) \, n'(z_2) \Rightarrow -\frac{+\infty}{-\infty} \int \frac{z \, n'^2(z)}{-\infty} \, dz + \frac{+\infty}{-\infty} \int \frac{n'^2(z)}{-\infty} \, dz
\]

the second:

\[
-\frac{1}{4\sigma_\infty} \int dZ \, d\vec{r} \, z \left( x \frac{\partial u}{\partial x} - z \frac{\partial u}{\partial z} \right) \, n_2 \left( \vec{R}, \vec{R} + \vec{r} \right) \Rightarrow \frac{+\infty}{-\infty} \int \frac{z \, n'(z)}{-\infty} \, dz + \frac{+\infty}{-\infty} \int \frac{n'(z)}{-\infty} \, dz + \ldots?
\]
Spinodal

Figure: Binodal and spinodal for LJ fluid (Imre et al., JCP (2008))
Corollary of the Global Isomorphism

The law of rectilinear diameter holds also for the spinodal
Corollary of the Global Isomorphism

The law of rectilinear diameter holds also for the spinodal

\[ \frac{n}{n_c} \]

\[ \frac{T}{T_c} \]

Conclusions and future routes

- There is the 1-1 correspondence between equilibrium states of simple LJ-fluid and those of lattice gas (Ising model);
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- Is it possible to connect the transport coefficients of the fluid and the lattice gas?
Thank you for attention!