

Classical Liquid–Gas Interface in Thermal Equilibrium

Jerome K. Percus¹

Received June 2, 1994

The Kac–Siegert transcription of a nonuniform classical fluid is described. It is applied to the energetics and spatial structure of a liquid–gas interface via direct and extended mean-field treatments and put in the context of Gaussian random field studies.

KEY WORDS: Nonuniform fluid; Kac–Siegert transformation; liquid–gas interface; Gaussian random field.

1. INTRODUCTION

It is delightfully easy to write something suitable in honor of Oliver Penrose's coming of age, since Oliver has made his own so many aspects of statistical physics. I will choose the area surrounding van der Waals' equation of state, which itself was finally made honest by Oliver and Joel Lebowitz.⁽¹⁾ To do so, they had to make very explicit the quenching of fluctuations inherent in van der Waals' approach,⁽²⁾ and one wonders which *should* be included, and to what end.

One of the difficulties in treating thermodynamics from a microscopic viewpoint is that particle density $\hat{\rho}(r) = \sum \delta(r - r_j)$, the seemingly unavoidable microscopic descriptor, is a horrible function, always zero except when it is infinite, and restricted by loads of sum rules: $\int_V \hat{\rho}(r) dr = \text{integer}$ for any subvolume V . Of course, this does not mean that one cannot write down exact solutions for some nontrivial systems—it just means

This paper is based on a presentation at the 71st Statistical Mechanics Meeting, May 1994.

¹ Courant Institute of Mathematical Sciences and Physics Department, New York University, New York, New York 10012.

that a per-configuration description of any approximation tends to be embarrassing. Van der Waals treated this problem for molecular fluids by imagining in essence that one knew how to solve an innocuous reference system in which only short-range pair exclusion forces acted between particles, and then asked how the addition of longer-range pair attractions served to organize the system. I want to describe the spatial structure of the liquid-gas interface of a simple fluid from this viewpoint, being aware of the physical hallmark of the structure: it looks like a membrane, feels like a membrane, and is thermally excited like a membrane.

The key to the approach I have in mind is the representation, due to Kac and Siegert,⁽³⁾ of a (negative-definite) tail interaction potential $-\phi(r-r')$ by an ensemble of external potentials. The result is that if $\Omega_0[\mu]$ is the grand potential of the reference system in a local chemical potential field $\mu(r) = \mu - u(r)$, with $u(r)$ the external potential, then

$$\exp -\beta\Omega[\mu] = \langle \exp -\beta\Omega_0[\mu - \phi_D - v] \rangle_v \quad (1)$$

where $\phi_D = \phi(0)$, β is reciprocal temperature, and the ensemble average is over the Gaussian random field v :

$$\langle F[v] \rangle_v = \int F[v] \exp\left(-\frac{1}{2}\beta v^T \phi^{-1} v - \frac{1}{2} \text{Tr} \ln 2\pi\phi/\beta\right) Dv \quad (2)$$

$\phi^{-1}(r-r')$ is the matrix inverse to $\phi(r-r')$. The nastiness of $\hat{\rho}(r)$ is hidden inside Ω_0 , and if the reference system correlation range is negligible on the scale of spatial density variation, we can replace (1) by

$$\exp -\beta\Omega[\mu] = \left\langle \exp \beta \int P_0(\mu(r) - \phi_D - v(r)) dr \right\rangle_v \quad (3)$$

where $P_0(\mu)$ is the reference system equation of state. In this event, the mean density $\mu(r) = -\delta\Omega/\delta\mu(r)$ becomes

$$n(r) = \left\langle n_0(\mu(r) - \phi_D - v(r)) \exp \beta \left(\Omega[\mu] + \int P_0(\mu(r) - \phi_D - v(r)) dr \right) \right\rangle_v \quad (4)$$

where $n_0(\mu)$ is the thermodynamic n - μ relation for the reference.

The first try at evaluating an expectation such as (4) is usually by mean-field approximation (demonstrably exact⁽⁴⁾ in one scaling limit). One assumes that the v distribution is concentrated at the maximal \bar{v} of the full kernel of (3), and on eliminating \bar{v} one readily finds that

$$\mu(r) = \mu_0(n(r)) + \phi_D - \phi n(r) \quad (5)$$

leading as well to the intrinsic Helmholtz free energy

$$\bar{F}(n) = \int f_0(n(r)) dr + \int \phi(0) n(r) dr - \frac{1}{2} \iint n(r) n(r') \phi(r - r') dr dr' \quad (6)$$

A Taylor expansion of $n(r')$ about $n(r)$ to second order recovers the van der Waals form

$$\bar{F}[n] = \int [f_0(n(r)) + \phi(0) n(r) - bn(r)^2] dr + \frac{1}{2}c \int |\nabla n(r)|^2 dr \quad (7)$$

Now an interface is generated precisely when $f(n) = f_0(n) + \phi(0) n - bn^2$ is not convex, and the corresponding $P(n) = P_0(n) - bn^2$ has the familiar van der Waals loop. But uniform $n(r)$ does not minimize (7). The simplest model to see what does happen uses the reference

$$\mu_0(n) = \{-\infty, \infty, 0\} \quad \text{for} \quad \{n \leq 0, n \geq \rho, 0 < n < \rho\} \quad (8)$$

that is either vacuum or incompressible at density ρ , and chooses $\phi(0) = b\rho$. The corresponding profile equation is

$$\mu(r) = b(\rho - 2n(r)) - c\nabla^2 n(r) \quad (9)$$

for $0 \leq n(r) \leq \rho$, with continuous ∇n when $n(r)$ arrives at 0 or ρ . Thus, e.g., a gravitational field $\mu(r) = -gx$ produces a planar interface profile of the form

$$n(x) = \frac{\rho}{2} + \frac{g}{2b} x + A \sin\left(\frac{2b}{c}\right)^{1/2} x \quad (10)$$

A mean-field profile such as (1) gives little evidence of softening due to surface modes as the constraining field is weakened. But in fact, mean field may be quite suitable *within* each phase. Define the liquid domain of a given v configuration—not to be confused with a particle configuration—as that within which $\mu(r) - \phi_D - v(r) \geq 0$, the gas as that in which $\mu(r) - \phi_D - v(r) < 0$. Then with the reference system (8),

$$P_0(\mu) = \rho\mu\varepsilon(\mu) \quad (11)$$

The kernel of (3) is indeed Gaussian within each phase. And to within a generally irrelevant multiplier, the integral of a Gaussian is given exactly by mean field. Thus, if the interface geometry is defined by the (multivalued) function $z = \xi(x, y)$ through

$$v(r) = \mu(r) - \phi_D \quad \text{at} \quad r = (x, y, \xi(x, y)) \quad (12)$$

and enough normal derivatives of v are fixed so that the remaining degrees of freedom in the two phases no longer communicate, we can simply compute

$$\min_v -\alpha \int_D \rho(\mu(r) - \phi_D - v(r)) dr + \frac{1}{2} \int \int_D v(r) v(r') \phi^{-1}(r - r') dr dr' \quad (13)$$

($\alpha = 0$ or 1) over each phase domain D . For this purpose, it is necessary that ϕ^{-1} be of zero range, e.g., a polynomial in ∇^2 . Simplest is a first-order polynomial, but then ϕ is Yukawa and $\phi(0)$ diverges, requiring an infinite chemical potential renormalization.⁽⁵⁾ Next simplest is $\phi(r) = Ae^{-\gamma r}$, so that ϕ^{-1} is quadratic in ∇^2 . Then it suffices to fix the common values $s(x, y) = \partial v / \partial n$ (representing an inverse thickness) on the two sides of the interface, so that after "mean-field integration" of the accessible amplitude $v(r)$, only the interface grand potential $\Omega[\mu, \xi, s]$ remains, with

$$\Omega[\mu] = \iint \Omega[\mu, \xi, s] D\xi Ds \quad (14)$$

In practice, this procedure is only feasible when the surface curvature is small enough that it can be locally modeled as quadric, but then one does obtain a curvature-dependent surface free energy in which the internal structure is taken into account.

There is another fashion in which the mean-field concept can be used. If it is sufficient to focus on the vicinity of the geometric interface, which is itself a hybrid phase, one may approximate α in (13) by a local liquid fraction $\alpha(r)$. Hence $\{v(r)\}$ is literally a random Gaussian field, and the interfacial structure in each configuration is determined by the "level surface" (12). There are at least two consequences. On the one hand, the full machinery of Gaussian random fields is available to find the distribution of various geometric parameters⁽⁵⁾ associated with the v configuration. On the other hand, the very easily manipulated Gaussian model can be chosen as a variational ansatz, either in its general form or in the specific form associated with (13) and $\alpha(r)$. Then one uses the standard variational principle for $\Omega = -\frac{1}{\beta} \ln \int e^{-\beta H[v]} Dv$:

$$\Omega = \min_{\{\rho[v] Dv=1\}} \left\langle \frac{1}{\beta} \ln \rho[v] + H[v] \right\rangle_{\rho[v]} \quad (15)$$

In the present case,

$$\begin{aligned} H[v] &= -\rho \int [\mu(r) - \phi_D - v(r)] \varepsilon[\mu(r) - \phi_D - v(r)] dr + \frac{1}{2} v^T \phi^{-1} v \\ &\quad + (\frac{1}{2} \beta) \text{Tr} \ln 2\pi\phi/\beta \\ \ln \rho[v] &= -\frac{1}{2} \beta (v + \phi\alpha)^T \phi^{-1} (v + \phi\alpha) - \frac{1}{2} \text{Tr} \ln 2\pi\phi/\beta \end{aligned}$$

leading to the quite explicit

$$\Omega = \min_{\{\alpha\}} \frac{1}{2} \alpha^T \phi \alpha - [\beta/2\pi\phi(0)]^{1/2} \rho \int \int^{\mu(r) - \phi_D} (\mu(r) - \phi_D - v(r)) \exp - \beta[v + \phi\alpha(r)]^2/2\phi(0) dv dr$$

with

$$n(r) = [\beta/2\pi\phi(0)]^{1/2} \rho \int_{-\infty}^{\mu(r) - \phi_D} \exp - \beta[v + \phi\alpha(r)]^2/2\phi(0) dv \quad (16)$$

REFERENCES

1. J. L. Lebowitz and O. Penrose, *J. Math. Phys.* 7:98 (1966).
2. J. D. van der Waals, *Z. Phys. Chem.* 13:657 (1894).
3. M. Kac, In *Applied Probability*, L. A. MacColl, ed. (McGraw-Hill, New York, 1957);
A. J. F. Siegert, In *Statistical Physics* (Benjamin, New York, 1993).
4. M. K.-H. Kiessling and J. K. Percus, *J. Stat. Phys.*, to be published.
5. J. K. Percus, *Physica A* 172:1 (1991).
6. M. Teubner, *Europhys. Lett.* 14:403 (1991).