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A Meniscus Where Three Phases Coexist at Equilibrium: Microscopic Derivation of the Herring Relations

Joël De Coninck,[1] Philippe de Gottal,[1] and Frédéric Menu[1]

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The geometrical characteristics of a meniscus between two phases are studied. In particular, the behavior of the contact angles as a function of the temperature is derived for SOS-type models. A microscopic derivation of the Herring relations is given within a continuuous Gaussian model.

KEY WORDS: Wetting phenomena; Herring relations; Antonov's rule; SOS-type models.

1. INTRODUCTION

Let us consider three coexisting phases in two dimensions for simplicity. Two situations may occur: one may observe a meniscus or a film of, say, B between A and C. The equilibrium conditions for a meniscus of substance B between two other coexisting phases A and C relate the contact angles θ_1 and θ_2 as defined in Fig. 1 to the various surface tensions and their derivatives; these are the Herring relations,[1]

$$\begin{aligned}
&\sigma_{AB}(\theta_1)\cos\theta_1+\sigma_{BC}(\theta_2)\cos\theta_2\\
&\qquad -\sin\theta_1\,\sigma'_{AB}(\theta_1)-\sin\theta_2\,\sigma'_{BC}(\theta_2)=\sigma_{AC}(0)\\
&\sigma_{AB}(\theta_1)\sin\theta_1-\sigma_{BC}(\theta_2)\sin\theta_2\\
&\qquad +\sigma'_{AB}(\theta_1)\cos\theta_1-\sigma'_{BC}(\theta_2)\cos\theta_2=\sigma'_{AC}(0)
\end{aligned}\tag{1}$$

where $\sigma_{xy}(\cdot)$ denotes the surface tension of the interface between x and y, and $\sigma'_{xy}(\cdot)$ denotes its derivative with respect to the contact angle. The

[1] Faculté des Sciences, Université de l'État, 7000 Mons, Belgium.

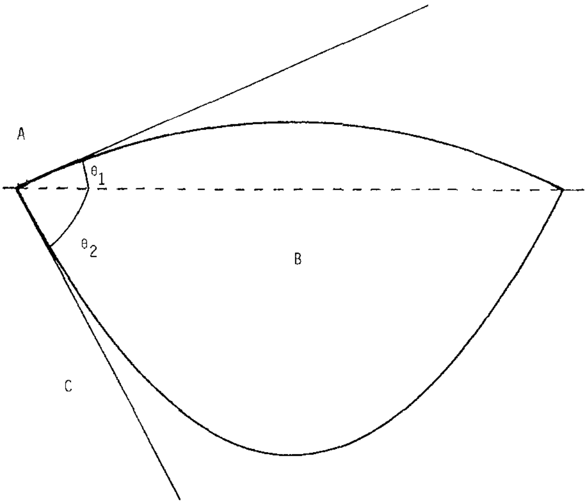


Fig. 1. A meniscus with the two contact angles θ_1 and θ_2.

wetting transition corresponds to the appearance of a film characterized by $\theta_1 = \theta_2 = 0$. The temperature at which this transition occurs is called the wetting temperature and is the solution of Antonov's equation

$$\sigma_{AB}(0) + \sigma_{BC}(0) = \sigma_{AC}(0), \qquad (T = T_w)$$

for substances such that $\sigma(\theta) = \sigma(-\theta)$.

To describe on a microscopic basis such transitions, one needs a model for which the coexistence of several phases is possible within a certain range of temperature. One may therefore consider this problem for several models: Potts, Blume–Capel, etc. The appearance of the film within such models has already been studied.[2-5] However, at least to our knowledge, the geometrical characteristics of the meniscus have not yet been considered.

The simplest way to get preliminary results along this line is to study a meniscus within SOS-type models. The corresponding results are expected to be valid at low temperatures. The advantage of this approximation is that we may exactly compute the surface tensions involved in the problem. This therefore leads directly to some predictions about the behavior of θ_1 and θ_2 as functions of the temperature T (Section 2). In order to get these results, we obviously need to assume the validity of relations (1). The aim of Section 3 is to give a microscopic derivation of relations (1) for a continuous Gaussian model.

2. SEMIPHENOMENOLOGICAL APPROACH

Let us consider a meniscus. Within SOS-type models, the microscopic representation of the corresponding profiles will be given by random jumps distributed according to a certain probability measure. This measure is induced by the energetic cost of an interface and is therefore intimately connected to the corresponding Hamiltonian. One of the commonest is the Gaussian one, given by

$$H(h_0,\dots,h_N)=NJ_2+J_1\sum_i (h_{i+1}-h_i)^2$$

where J_1 and J_2 are the coupling constants which describe one interface, say AB. For the other two interfaces, we use the coupling constants J_1', J_2' for interface BC and J_1'', J_2'' for interface AC.

For such a model, it is known[6] that

$$\sigma_{AB}(\theta)=J_2\cos\theta+J_1\,\mathrm{tg}^2\,\theta\cos\theta-\frac{1}{2\beta}\cos\theta\log\left(\frac{\pi}{\beta J_1}\right)$$

where β is the inverse temperature.

Introducing this relation and the corresponding ones for $\sigma_{AC}(\theta)$ and $\sigma_{BC}(\theta)$ into (1), we get

$$\tan^2\theta_1=\frac{J_2+J_2'-J_2''}{J_1+J_1^2/J_1'}+\frac{1}{2(J_1+J_1^2/J_1')}\frac{1}{\beta}\log\frac{\beta J_1 J_1'}{\pi J_1''} \tag{2}$$

$$\tan\theta_2=\frac{J_1}{J_1'}\tan\theta_1 \tag{3}$$

and therefore

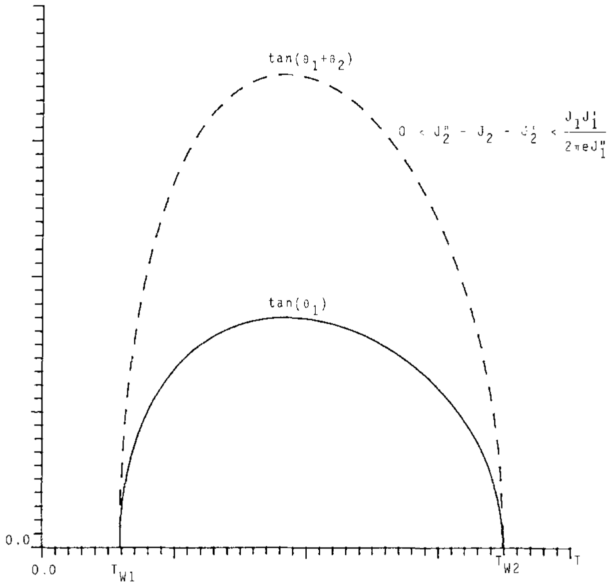
$$\tan(\theta_1+\theta_2)=\frac{[(J_1+J_1')^3/J_1J_1']^{1/2}\{J_2+J_2'-J_2''+[1/(2\beta)]\log(\beta J_1J_1'/\pi J_1'')\}^{1/2}}{J_1+J_1'+J_2+J_2'-J_2''+[1/(2\beta)]\log(\beta J_1J_1'/J_1''\pi)}$$

which as a function of the temperature behaves as indicated in Fig. 2.

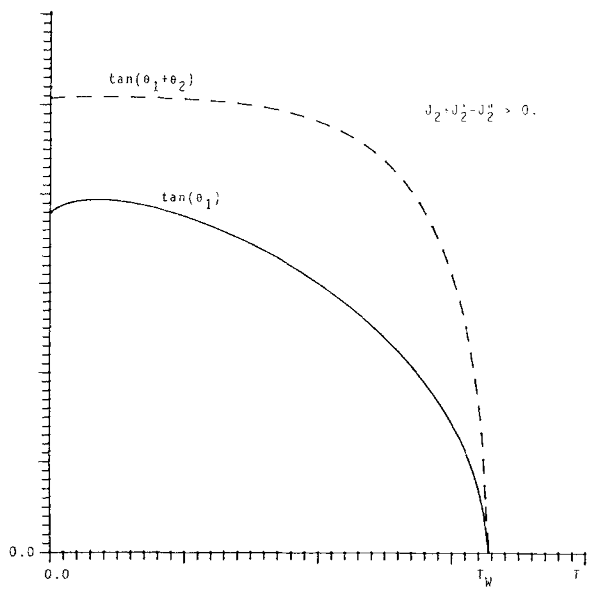
The study of the wetting transitions leads to different regimes:

(a) No wetting transition if

$$J_2''-J_2'-J_2>\frac{J_1J_1'}{2\pi eJ_1''}$$



(a)



(b)

Fig. 2. Plot of $\tan\theta_1$ and $\tan(\theta_1+\theta_2)$ as functions of the temperature for the continuous Gaussian model. (A) two wetting transitions, (B) one wetting transition.

(b) Two wetting transitions and therefore two wetting temperatures T_w if

$$0 < J_2'' - J_2 - J_2' < \frac{J_1 J_1'}{2\pi e J_1''}$$

(c) One wetting transition and therefore one wetting temperature T_w if

$$J_2'' - J_2 - J_2' < 0$$

Expanding (2) as a function of $T - T_w$, we get

$$\theta_1^2 \sim |T - T_w|$$

which is typical of a first-order transition. A similar behavior has been found for other continuous SOS-type models.

It should, however, be stressed that within the present context, a second-order transition may be found (e.g., restricted SOS model).

3. MICROSCOPIC APPROACH

In the preceding section, we derived the behavior of the contact angles θ_1 and θ_2 using the Herring relations (1). Let us now consider these relations from a microscopic point of view. The family of menisci with fixed volume V that we consider can be characterized by several random variables: we have the length N along the x axis, the upper part of the meniscus $h_1 \cdots h_{N+1}$, and the lower part $h_1' \cdots h_{N+1}'$ (Fig. 3).

Within the continuous Gaussian model, the corresponding probability measure is given by

$$\begin{aligned} d\mu(h_1 \cdots h_{N+1}, h_1' \cdots h_{N+1}', N) &= \Xi^{-1} \exp[\beta N \sigma_{AC}(0)] \\ &\times \exp\left\{-\beta \sum_1^{N+1} [J_2 + J_1(h_i - h_{i+1})^2] - \beta \sum_1^{N+1} [J_2' + J_1'(h_i' - h_{i+1}')^2]\right\} \\ &\times \delta\left(\sum_1^{N+1} (h_i - h_i') - V\right) \delta(h_1)\delta(h_1 - h_{N+1})\, \delta(h_1')\, \delta(h_1' - h_{N+1}') \\ &\times \prod_{i=1}^{N+1} 1_{\{h_i \geq h_i'\}}\, dh_i\, dh_i' \end{aligned} \tag{4}$$

where 1_A is a characteristic function which takes the value 1 if condition A is satisfied and 0 elsewhere, and Ξ is a normalization factor.

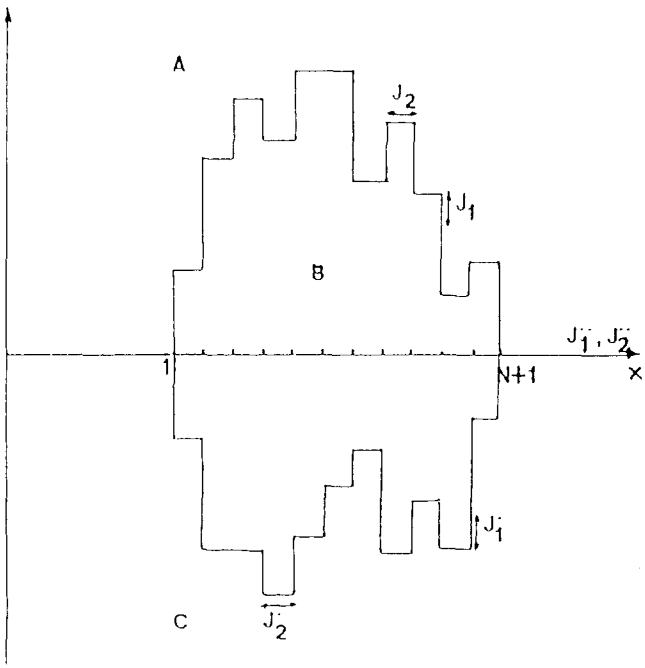


Fig. 3. Microscopic representation of a meniscus of length N.

Among this family of menisci, the most probable one should in principle be characterized by contact angles which obey the Herring relations. This is precisely the object of the following result.

Theorem. Among the family of menisci distributed according to (4), the most probable one has contact angles θ_1 and θ_2 which satisfy the Herring relations (1).

Proof. Let us first fix the length N and let

$$h_i' = h_i + x_i, \qquad 1 \leqslant i \leqslant N+1$$

We then have instead of (45) a Gaussian measure which couples the x_i to the h_i with the constraints $x_i \geqslant 0$ for all i. The introduction of the step variables ($k_i = \beta J_i$; $k_i' = \beta J_i'$)

$$\chi_i = (h_{i+1} - h_i)(k_1 + k_1')^{1/2} \qquad \text{with} \quad i = 1, \ldots, N$$

$$\chi_{N+1} = -h_{N+1}(k_1 + k_1')^{1/2}$$

$$\chi_{i+(N+1)} = (x_{i+1} - x_i)\sqrt{k_1} \qquad \text{with} \quad i = 1, \ldots, N$$

$$\chi_{2N+2} = -x_{N+1}\sqrt{k_1}$$

leads to

$$d\mu(\chi_1,\ldots,\chi_{2N+2},N)$$

$$= \Xi^{-1}\{k_1'(k_1+k_1')\}^{(N+1)/2}\exp\{-[k_2+k_2'-\sigma_{AC}(0)]N\}$$

$$\times \exp\left[\sum_1^{2N+2}\chi_i^2 - 2\left(\frac{k_1'}{k_1+k_1'}\right)^{1/2}\sum_1^{N+1}\chi_i\chi_{i+N+1}\right]$$

$$\times \delta\left(\sum_1^{N+1}\chi_i\right)\delta(\chi_{N+1})\,\delta(\chi_{2N+2})\,\delta\left(\sum_{N+2}^{2N+2}\chi_i\right)\delta\left(\sum_1^{N-1}\frac{i}{\sqrt{k_1'}}\chi_{i+(N+1)}+V\right)$$

$$\times \prod_{i=1}^{2N-2} d\chi_i$$

It remains to use the standard diagonalization procedure of Berlin and Kac[7] to obtain, defining

$$\eta_i = \left\{2\left[1-\left(\frac{k_1'}{k_1+k_1'}\right)^{1/2}(-1)^{i+1}\right]\right\}^{-1/2}\sum_1^{2N+2}V_{ij}\chi_j$$

$$V_{ij} = \frac{1}{(2N+2)^{1/2}}\left\{\cos\left[\frac{\pi}{N+1}(j-1)(i-1)\right]\right.$$

$$\left. + \sin\left[\frac{\pi}{N+1}(j-1)(i-1)\right]\right\}$$

$$d\mu = \Xi^{-1}2^{-(N+1)}(\exp\{-[k_2+k_2'-\sigma_{AC}(0)]N\})(k_1k_1')^{-(N+1)/2}$$

$$\times \prod_{i=1}^{2N+2}\exp(-\eta_i^2/2)\,d\eta_i\,\delta\left(\sum_1^{2N+2}A_j\eta_j\right)\delta\left(\sum_1^{2N+2}B_j\eta_j\right)$$

$$\times \delta\left(\sum_1^{2N+2}C_j\eta_j\right)\delta\left(\sum_1^{2N+2}D_j\eta_j\right)\delta\left(\sum_1^{2N+2}E_j\eta_j+V\right)$$

where

$$A_j = \left\{2\left[1-\left(\frac{k_1'}{k_1+k_1'}\right)^{1/2}(-1)^{j+1}\right]\right\}^{-1/2}\sum_{i=1}^{N+1}V_{ji}$$

$$B_j = \left\{2\,[1-\left(\frac{k_1'}{k_1+k_1'}\right)^{1/2}(-1)^{j+1}\right]\right\}^{-1/2}V_{j,N+1}$$

$$C_j = \left\{2\left[1-\left(\frac{k_1'}{k+k_1'}\right)^{1/2}(-1)^{j+1}\right]\right\}^{-1/2}V_{j,2N+2}$$

$$D_j = \left\{2\left[1-\left(\frac{k_1'}{k_1+k_1'}\right)^{1/2}(-1)^{j+1}\right]\right\}^{-1/2}\sum_{i=1}^{N+1}V_{j,i+(N+1)}$$

$$E_j = \left\{2\left[1-\left(\frac{k_1'}{k_1+k_1'}\right)^{1/2}(-1)^{j+1}\right]\right\}^{-1/2}\sum_{i=1}^{N+1}iV_{j,i+(N+1)}$$

Let us now compute the asymptotic value of the normalization factor

$$\Xi = \sum_{N \geqslant 2} e^{\beta \sigma_{AC}(0) N} Z_{N, V}$$

where

$$Z_{N, V} = (4k_1 k_1')^{(N+1)/2} e^{-(k_2 + k_2')N} \int_{-\infty}^{+\infty} \prod_{i=1}^{2N+2} d\eta_i \, e^{-\eta_i^2/2}$$

$$\times \delta\left(\sum_{j=1}^{2N+2} A_j \eta_j\right) \delta\left(\sum_{j=1}^{2N+2} B_j \eta_j\right) \delta\left(\sum_{j=1}^{2N+2} C_j \eta_j\right) \delta\left(\sum_{j=1}^{2N+2} D_j \eta_j\right)$$

$$\times \delta\left(\sum_j E_j \eta_j + V\right)$$

Using a Fourier representation of the Dirac measures, we have

$$Z_{N, V} = \exp\left[-\left(k_2 + k_2' + \frac{1}{2} \log \frac{k_1 k_1'}{\pi^2}\right) N + O(\log N)\right]$$

$$\times \int_{-\infty}^{+\infty} du \, dv \, dw \, ds \, dt$$

$$\times \exp(itV) \exp\left\{-\frac{1}{2}\left[\sum_1^{2N+2} (A_j u + B_j v + C_j w + D_j s + E_j t)\right]\right\} \quad (5)$$

The integration gives

$$Z_{N, V} = \exp\left[-\left(k_2 + k_2' + \frac{1}{2} \log \frac{k_1 k_1'}{\pi^2}\right) N + O(\log N) - \frac{1}{2} Q_{55} V^2\right]$$

where Q_{55} is the fifth row and the fifth column element of the covariance matrix Q in (5). The asymptotic evaluation of Q_{55} leads to

$$Z_{N, V} = \exp\left[-\left(k_2 + k_2' + \frac{1}{2} \log \frac{k_1 k_1'}{\pi^2}\right) N - 12 \frac{V^2}{N^3} \frac{k_1 k_1'}{k_1 + k_1'} + O(\log N)\right] \quad (6)$$

Let us now consider a meniscus as the union of two droplets ($h_i \geqslant 0$, $h_i' \leqslant 0$ for $i = 1, \ldots, N+1$). Within this approximation, one easily gets

$$Z_{N, V} = \int_0^V dV_+ \, dV_- \, \xi_{N, V_+} \xi_{N, V_-} \, \delta(V_+ + V_- - V) \quad (7)$$

where V_+ (resp. VB_-) is the volume of the upper (resp. lower) droplet and where $\xi_{N, V}$ is the partition function of a droplet of length N and volume V. Within the Gaussian continuous model, it is known[6] that

$$\xi_{N, V_+} = \exp\left[-k_2 N - 12 k_1 \frac{V_+^2}{N^3} - \frac{N}{2} \log \frac{k_1}{\pi} + O(\log N)\right]$$

An asymptotic evaluation of (7) leads directly to

$$Z_{N,V}=\exp\left[-(k_2+k_2')N-\frac{N}{2}\log\frac{k_1k_1'}{\pi^2}-\frac{12}{N^3}V^2\frac{k_1k_1'}{k_1+k_1'}+O(\log N)\right] \qquad (8)$$

Comparing (8) with (6), one has that, asymptotically, the partition function of a meniscus of volume V is equivalent to the partition function of the union of two droplets of appropriate volumes. One therefore deduces that the most probable meniscus is given by the union of the two most probable droplets. The shape of this meniscus is thus given by

$$\tilde{h}_i=\frac{6(i-1)(N-i+1)}{(N^2-1)N}V\frac{k_1'}{k_1+k_1'}$$

$$\tilde{h}_i'=\frac{6(i-1)(N-i+1)}{(N^2-1)N}V\frac{k_1}{k_2+k_1'}$$

Now that we know the profile of the meniscus for a fixed length N, let us consider the sum over N. We have

$$\Xi=\sum_{N\geqslant 2}e^{\beta N\sigma_{AC}(0)}Z_{N,V}$$

The term that maximizes this sum is asymptotically given for

$$N=N(V)=V^{1/2}\left(\frac{36k_1k_1'/(k_1+k_1')}{k_2+k_2'-k_2''+\frac{1}{2}\log(k_1k_1'/\pi k_1'')}\right)^{1/2}$$

This corresponds to the most probable length of the meniscus. It remains to derive the corresponding contact angles. This is obtained by a law of large numbers of the following form:

$$\tan\theta_1=\lim_{\substack{j\to\infty\\ 1\ll j\ll N(V)}}\frac{\tilde{h}_j}{j}$$

The results are

$$\tan\theta_1=\left[\frac{k_2+k_2'-\sigma_{AC}(0)+\frac{1}{2}\log(k_1k_1'/\pi^2)}{k_1+k_1^2/k_1'}\right]^{1/2}$$

$$\tan\theta_2=\frac{k_1}{k_1'}\tan\theta_1$$

These contact angles derived on a microscopic basis are identical to those derived from the Herring relations [cf. (2), (3)].

To achieve the proof, it remains to show that this concept of most probable profile from which we have derived the value of contact angles makes sense. This means that one has to control the fluctuations of the profile with respect to the most probable one. A standard procedure gives

$$\langle (N - \langle N \rangle)^2 \rangle \approx O(V^{1/2})$$

A reasoning analogous to the one developed in ref. 6 for one droplet leads to

$$\langle (h_i - \tilde{h}_i)^2 \rangle \approx O(N)$$

for a fixed length N.

These two results show indeed that the relative fluctuations can be kept small. This achieves the proof of the theorem.

4. CONCLUDING REMARKS

In this paper, we have verified the microscopic validity of the Herring relations within a Gaussian continuous model. It should be stressed that our model is a rather crude approximation since it considers the meniscus as a superposition of three interfaces between two media. The study of one meniscus as part of a three-phase system along this line remains an interesting open subject.

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REFERENCES

1. C. Herring, *Structure Properties of Solid Surfaces*, R. Gomer and C. S. Smith, eds. (University of Chicago Press, 1951).
2. W. Selke, Interfacial adsorption in multi-state models, in *Static Critical Phenomena in Inhomogeneous Systems*, A. Pekalsky and J. Sznajd, eds. (Lecture Notes in Physics No. 206, Springer, Berlin, 1984).
3. B. Derrida and M. Schick, Interfacial wetting in the q-state Potts model, *J. Phys. A: Math. Gen.* **19**:1439 (1986).
4. J. Bricmont and J. L. Lebowitz, Wetting in Potts and Blume–Capel models, *J. Stat. Phys.* **46**:1015 (1987).
5. J. De Coninck, A. Messager, S. Miracle-Sole, and J. Ruiz, A study of perfect wetting for Potts and Blume–Capel models with correlation inequalities, *J. Stat. Phys.* **52**:45 (1988).
6. J. De Coninck and F. Dunlop, Partial to complete wetting: A microscopic derivation of the Young relation, *J. Stat. Phys.* **47**:827 (1987).
7. T. H. Berlin and M. Kac, The spherical model of a ferromagnet, *Phys. Rev.* **85**:821 (1952).