Bertrand, Bonn, and Meunier Reply: In a recent Letter [1], we studied the wetting of hexane on brine and reported the following: (i) a sequence of two wetting transitions, the first one, at a temperature $T_{w,1}$, being first order and the second one, at $T_{w,c}$ being critical; (ii) that the effect of the addition of sodium chloride (NaCl) on the two transition temperatures is a shift towards lower temperature that is the same for both transitions. $T_{w,c}$ being controlled by the Hamaker constant W [1], we concluded that $T_{w,1}$ appeared to also be connected to W.

Indekeu comments on the generality of this last conclusion [2]. We show here that the connection between W and $T_{w,1}$ can, however, be understood theoretically. W represents the net effect of the intermolecular van der Waals interactions as an effective interaction between the two interfaces bounding the wetting film. The van der Waals interactions intervene in two ways in the Cahn-Landau theory used by Indekeu [2]. First, the bulk equation of state of the hexane [3] takes into account the cohesive van der Waals interactions between the adsorbate molecules. Second, the adhesive interactions between the substrate and the adsorbate are included in a surface contact energy that is obtained from surface pressure measurements of alkanes on water and consequently contains both short-range and van der Waals interactions [3].

The difference in work of adhesion per unit area $\Delta\sigma$ between the wetting of hexane on pure water and the wetting of hexane on brine can be calculated directly from the long-range van der Waals interactions by considering the existence, near the interface between brine and hexane, of a layer of water depleted of NaCl [4]. Similar to the calculation of the Hamaker constant, we integrate the van der Waals interactions now over a four-layered structure (air/hexane/depleted water/brine), leading to [5]

$$\Delta\sigma = \frac{k_B T}{16\pi\delta^2} D_0 + \frac{\hbar\omega_{\mathrm{UV}}}{16\pi^2\delta^2} D,$$

where D_0 is a function of the static dielectric constants, and D of the refractive indices of the four media [5]; k_B is Boltzmann's constant, $\hbar$ is Planck's constant, and ω_{UV} is a typical absorption frequency. Note that apart from the depletion layer thickness the same parameters determine the Hamaker constant. The depletion layer thickness δ was calculated by Onsager and Samaras [4] within Debye-Hückel theory to be of the order of 2 Å for the NaCl concentrations considered here. Treating the depleted layer as a slab of this thickness, using a Cahn-Landau phase portrait, we can convert $\Delta\sigma$ directly into a shift in first-order wetting transition temperature [3]. Figure 1 shows the excellent agreement between the measured and the calculated first-order wetting temperatures. If we also take into account the dependence of δ on the salt concentration, the agreement is still very good, at least for low salinities. That the agreement deteriorates for higher salinities is possibly due to a breakdown of Debye-Hückel theory for high electrolyte concentrations [5].

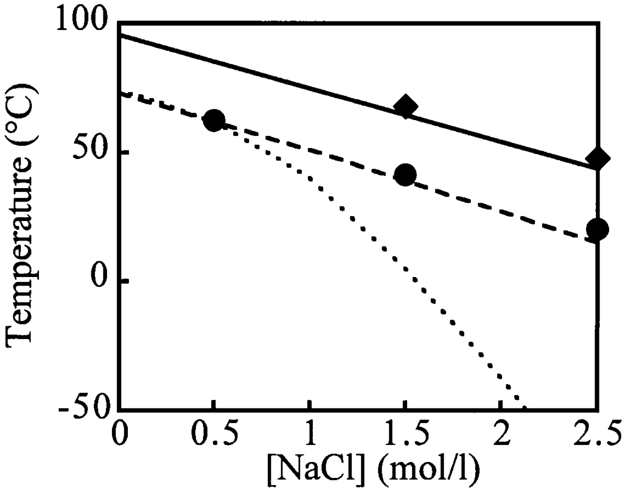

FIG. 1. Experimental first-order (circles) and critical (diamonds) wetting transition temperatures [1]. The solid line shows the calculated $T_{w,c}$ from W; the dotted and the dashed lines show our calculations for $T_{w,1}$ with and without taking into account the dependence of δ on salinity, respectively.

As this calculation involves only the long-range van der Waals forces, we have thus demonstrated a direct connection between W and $T_{w,1}$. This remains an important issue, since first-order wetting temperatures are notoriously hard to predict, whereas a Hamaker constant is calculated relatively easily. More generally, because the Cahn-Landau theory includes the long-range van der Waals forces in both the cohesive and the adhesive contributions to the surface free energy, the Hamaker constant and the first-order wetting temperature are coupled.

LPS de l'ENS is CNRS UMR 8550, associated with University P6 and P7. This work was supported by the EC under Joule and TMR programs.

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Received 14 April 2000
PACS numbers: 68.45.Gd

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0031-9007/00/85(19)/4189(1)$15.00