

## Making a (colloidal) liquid: A van der Waals approach

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The relation between the nature of the phase diagram and the pair potential is investigated on the basis of a recently introduced van der Waals theory. Both simple fluids and colloidal dispersions that admit a simple fluid description are considered. A necessary and sufficient condition for the occurrence of a liquid phase is formulated and studied for four specific cases. The results compare favorably with data obtained from other sources.

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### I. INTRODUCTION

The relation between the phase diagram and the nature of the interparticle forces is the central theme of equilibrium statistical mechanics [1–3]. When the particles are spherical atoms interacting with pairwise additive central forces, this relation is fairly well understood [4,5]. Recent advances in the study of colloidal dispersions suggest that most of this knowledge can be applied to the study of colloidal dispersions by exploiting the analogy between a spherical colloidal particle and an atom [6–9]. Because of the complexity, compared to the atomic systems, of natural colloids, the use of this analogy usually requires consideration of carefully prepared monodisperse suspensions of synthetic spherical colloidal particles [10]. Henceforth we will consider only dispersions for which this analogy can be expected to hold and describe them as a simple fluid of colloidal particles. Even so, some important differences will remain because of the dramatic change in length scale and because the forces between the colloidal particles are mediated by the solvent and hence depend on the thermodynamic state of the suspension medium.

The interplay between the repulsive and attractive parts of the pair potential was already the central theme of the van der Waals theory for the equation of state of simple fluids [4,5]. Recently, a proposal has been made to extend this theory to the solid phase [11]. This is essential for the discussion of phase diagrams where the dense fluid phases always enter into competition with the solid phases. Although the combined van der Waals theory for the fluid and the solid phases used here is very simple and approximate, it is nevertheless sufficiently flexible to capture the essential features of the problem. For convenience, we first slightly rephrase and summarize the theory of [11] in Sec. II. Next we review its predictions for the particular case of purely hard-sphere interactions in Sec. III. In Sec. IV we formulate a necessary and sufficient condition for the attractive forces that guarantees the presence of a liquid phase in the phase diagram. This condition is analyzed for four specific cases in Sec. V and the results are compared with data available from other sources. Our conclusions are gathered in the final Sec. VI.

### II. THE van der WAALS APPROXIMATION

We consider a (atomic or colloidal) simple fluid composed of  $N$  spherical particles enclosed in a volume  $V$  at the equilibrium temperature  $T$  and interacting via a pair potential  $V(r)$  consisting of a hard-sphere (HS) repulsion and an as yet arbitrary attraction ( $A$ ),

$$V(r) = V_{HS}(r) + V_A(r), \quad (2.1)$$

with

$$V_{HS}(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma \end{cases}, \quad V_A(r) = \begin{cases} 0 & r < \sigma \\ -\epsilon\phi\left(\frac{r}{\sigma}\right) & r \geq \sigma \end{cases}$$

where  $r$  is the center-to-center distance,  $\sigma$  the HS diameter, and  $\epsilon$  the amplitude of the attractions described by the dimensionless potential  $\phi(x) \geq 0$ , with  $x = \frac{r}{\sigma}$ . Within the van der Waals (vdW) approximation, the (Helmholtz) free energy  $F$  of this system can be written (see [11]), similarly to (2.1), as the superposition of a repulsive (HS) and attractive ( $A$ ) contribution:

$$F(N, V, T) = F_{HS}(N, V, T) + F_A(N, V, T), \quad (2.2)$$

where  $F_{HS}$  is the free energy of the HS system and  $F_A$  represents the “cohesion energy” due to the attractions. In agreement with [11], we will approximate  $F_{HS}$  in terms of the free energy of an ideal system, say,  $F_{id}(N, V, T)$ , as

$$\begin{aligned} F_{HS}(N, V, T) &= F_{id}(N, \alpha V, T) \\ &= Nk_B T \left\{ \ln \left( \frac{\rho \Lambda^3}{\alpha} \right) - 1 \right\} \\ &= F_{id}(N, V, T) - Nk_B T \ln \alpha \\ &= F_{id}(N, V, T) + F_{HS}^{ex}(N, V, T), \end{aligned} \quad (2.3)$$

where  $k_B$  is Boltzmann’s constant,  $\Lambda = \frac{h}{(2\pi m k_B T)^{1/2}}$  the thermal de Broglie wavelength,  $\rho = \frac{N}{V}$  the number density, and  $\alpha = \alpha(\rho)$  the fraction of the total volume  $V$  that is freely accessible to the hard spheres, i.e.,  $\alpha V$  is the “free” volume and  $(1 - \alpha)V$  the “excluded” volume or co-volume. Moreover, for  $F_A$  we write

$$F_A(N, V, T) = \frac{N}{2} \int_V d\mathbf{r} V_A(r) \bar{\rho}(\mathbf{r}), \quad (2.4)$$

where  $\bar{\rho}(\mathbf{r})$  is the distribution of sites in the phase under consideration (see [11]). Note that by combining (2.2) and (2.4) we have  $F_{ex} = F - F_{id} = F_{HS}^{ex} + F_A$ , so that the excess (ex) free energy  $F_{ex}$  consists of an excess energy ( $E$ ) term entirely due to the attractions,  $F_A = E_A^{ex}$ , while the excess entropy ( $S$ ) term originates entirely from the HS potential,  $F_{HS}^{ex} = -TS_{HS}^{ex}$ , or  $F_{ex} = E_A^{ex} - TS_{HS}^{ex}$ .

For a fluid phase ( $F$ ) we have, according to [11],  $\alpha = (1 - \frac{\rho}{\rho_0})$  and  $\bar{\rho}(\mathbf{r}) = \rho$ , yielding for the reduced free energy per particle  $\frac{F(N,V,T)}{N\epsilon} = f(\rho, T)$

$$f_F(\rho, T) = t[\ln(\rho\Lambda^3) - 1] - t\ln\left(1 - \frac{\rho}{\rho_0}\right) - 2\pi\rho\sigma^3 \int_1^\infty dx x^2 \phi(x) \quad (2.5)$$

where  $t = \frac{k_B T}{\epsilon}$  is the reduced temperature and  $\rho_0$  is the maximum density for which the fluid phase can exist (see [11] and Sec. III below).

For a (crystalline) solid phase ( $S$ ) of lattice sites  $\{\mathbf{r}_j\}$  we have, according to [11],  $\alpha = [1 - (\frac{\rho}{\rho_{cp}})^{\frac{1}{3}}]^3$  and  $\bar{\rho}(\mathbf{r}) = \sum_j \delta(\mathbf{r} - \mathbf{r}_j)$ , yielding within the nearest neighbor approximation [11]

$$f_S(\rho, T) = t[\ln(\rho\Lambda^3) - 1] - t\ln\left[1 - \left(\frac{\rho}{\rho_{cp}}\right)^{\frac{1}{3}}\right]^3 - \frac{n_1}{2}\phi\left[\left(\frac{\rho_{cp}}{\rho}\right)^{\frac{1}{3}}\right], \quad (2.6)$$

where  $\rho_{cp}$  is the maximum density for which the solid phase can exist, i.e., the density at (crystal) close packing (cp), while  $n_1$  is the number of nearest neighbors or the coordination number of the given crystal structure.

For the study of the phase diagram we also need to know the pressure  $p$  and the chemical potential  $\mu$ . These are given in terms of  $f$  by the usual thermodynamic relations

$$p = \epsilon\rho^2 \frac{\partial f}{\partial \rho}, \quad \mu = \epsilon \frac{\partial}{\partial \rho}(\rho f). \quad (2.7)$$

Using (2.5) and (2.6) we obtain for the pressure in the fluid phase [12]

$$p_F = \epsilon\rho \left\{ \frac{t}{1 - \frac{\rho}{\rho_0}} - 2\pi\rho\sigma^3 \int_1^\infty dx x^2 \frac{\partial}{\partial \rho}[\rho\phi(x)] \right\} \quad (2.8)$$

and in the solid phase [12]

$$p_S = \epsilon\rho \left( \frac{t}{1 - (\frac{\rho}{\rho_{cp}})^{\frac{1}{3}}} - \frac{n_1}{2}\rho \frac{\partial}{\partial \rho} \left\{ \phi \left[ \left(\frac{\rho_{cp}}{\rho}\right)^{\frac{1}{3}} \right] \right\} \right), \quad (2.9)$$

while the chemical potential can be obtained from [cf. (2.7)]

$$\mu = \epsilon f + \frac{p}{\rho} \quad (2.10)$$

using (2.5)–(2.9).

### III. THE HARD-SPHERE TRANSITION

It is well known from simulations [13], theory [14], and experiments with HS colloids [15] that a system of HS does exhibit an order-disorder transition between a fluid phase ( $F$ ) and a crystalline solid ( $S$ ). It is thus natural to inquire, first of all, how well the vdW theory for the  $F$  and  $S$  phases put forward in Sec. II can describe this transition. In the particular case of a purely HS system, i.e.,  $\phi(x) \equiv 0$ , the free-energy difference between a phase (1) = ( $F$  or  $S$ ) and a phase (2) = ( $F$  or  $S$ ) is seen from (2.5) and (2.6) to be determined by the ratio of their free volumes  $V_{(1)} = \alpha_{(1)}V$  and  $V_{(2)} = \alpha_{(2)}V$ , with  $\alpha_{(F)} = (1 - \frac{\rho}{\rho_0})$  and  $\alpha_{(S)} = [1 - (\frac{\rho}{\rho_{cp}})^{\frac{1}{3}}]^3$ , according to

$$f_{(1)}(\rho, T) - f_{(2)}(\rho, T) = t \ln \frac{\alpha_{(2)}}{\alpha_{(1)}}, \quad \phi(x) \equiv 0 \quad (3.1)$$

so that phase (1) will be the stable phase (for all  $T$ ), i.e.,  $f_{(1)} < f_{(2)}$  for all values of  $\rho$  for which phase (1) has the largest free volume, i.e.,  $\alpha_{(1)}(\rho) > \alpha_{(2)}(\rho)$ . Hence, within a HS system no fluid ( $F_1$ )-fluid ( $F_2$ ) transition can occur because all fluid phases of the same density will have the same free volume, i.e.,  $\rho_0^{(1)} \equiv \rho_0^{(2)}$ . Similarly, no solid ( $S_1$ )-solid ( $S_2$ ) transition can occur because if  $\alpha_{(1)} > \alpha_{(2)}$ , i.e.,  $\rho_{cp}^{(1)} > \rho_{cp}^{(2)}$ , for one density then this will remain so for all densities. Hence, the stable  $S$  phase is always the one with the largest possible  $\rho_{cp}$  value. This corresponds to any compact crystal structure for which we have

$$\rho_{cp}\sigma^3 = \sqrt{2}, \quad \phi_{cp} = \frac{\pi}{3\sqrt{2}}, \quad (3.2)$$

where  $\phi = \frac{\pi}{6}\rho\sigma^3$  denotes the corresponding HS packing or volume fraction. Moreover, for low densities we have  $\alpha_{(F)} > \alpha_{(S)}$ , whereas for high densities we have  $\alpha_{(S)} > \alpha_{(F)}$ , whatever the value of  $\rho_0 \leq \rho_{cp}$ . The present vdW theory predicts hence always a  $F$ - $S$  transition entropically driven by free-volume considerations. This scenario is in qualitative agreement with the experimental observations of a HS-transition between a fluid phase and a compact crystal composed of a random stacking of compact lattice planes [15].

Within the present vdW theory the precise location of the HS  $F$ - $S$  transition is monitored by the value of  $\frac{\rho_0}{\rho_{cp}} \equiv \frac{\phi_0}{\phi_{cp}}$ ,  $\phi_0$  being the largest value of the packing fraction  $\phi$  for which the fluid phase can exist. In many approximate theories, e.g., the Percus-Yevick theory [4], one has that  $\phi_0$  equals one. This, however, is unphysical, since spheres are not space filling. Physically, the value of  $\phi_0$  is certainly bounded from above by  $\phi_{cp}$  of (3.2). At the other extreme,  $\phi_0$  will also be bounded from below by  $\frac{1}{4}$ , which is the value of  $\phi_0$  for which the low density (second order) virial expansion is recovered from (2.8). Hence, physically,  $\frac{1}{4} < \phi_0 < \phi_{cp}$ , and as a rule of thumb we will henceforth put  $\phi_0$  equal to

$$\phi_0 = \frac{1}{2}(\phi_{cp} + \frac{1}{4}) = 0.4952\dots, \quad (3.3)$$

i.e., the HS fluid will become unstable halfway between

the lower and upper-bound value of  $\phi$ . Physically, (3.3) is acceptable because  $\phi_0$  is expected to lie well below the value of  $\phi$  corresponding to a random close packed (rcp) configuration,  $\phi_{rcp} \simeq 0.64$ , which corresponds to the upper limit of stability of the HS glass ( $G$ ) phase [16]. Although the  $G$  phase is not strictly speaking an equilibrium phase, it can be incorporated into the present vdW theory by adopting the following value for its free volume [16]:

$$\alpha_{(G)} = \left[ 1 - \left( \frac{\rho}{\rho_{rcp}} \right)^{\frac{1}{3}} \right]^3, \quad \phi_{rcp} = \frac{\pi}{6} \sigma^3 \rho_{rcp} \simeq 0.64. \quad (3.4)$$

Since  $\rho_{rcp} < \rho_{cp}$ , we have,  $\alpha_{(S)} > \alpha_{(G)}$ , so that the glass phase is always metastable compared to the solid phase, but since  $\rho_0 < \rho_{rcp}$ , we find that for high enough densities the glass phase can become stable compared to the fluid phase, i.e.,  $\alpha_{(G)} > \alpha_{(F)}$  (see Fig. 1). The  $F$ - $S$  exchange of stability will occur [see (3.1)] when  $\alpha_{(F)} = \alpha_{(S)}$  and, similarly,  $\alpha_{(F)} = \alpha_{(G)}$  for the  $F$ - $G$  exchange of stability. Using the above expressions, we find for the values of  $\phi$ , say,  $\phi_{F-S}$  or  $\phi_{F-G}$ , for which the  $F$ - $S$  or  $F$ - $G$  exchange of stability occurs,

$$\phi_{F-S(G)} = \phi_{(r)cp} \left\{ \frac{\left[ 12 \left( \frac{\phi_{(r)cp}}{\phi_0} \right) - 3 \right]^{\frac{1}{2}} - 3}{2 \left( \frac{\phi_{(r)cp}}{\phi_0} - 1 \right)} \right\}^3. \quad (3.5)$$

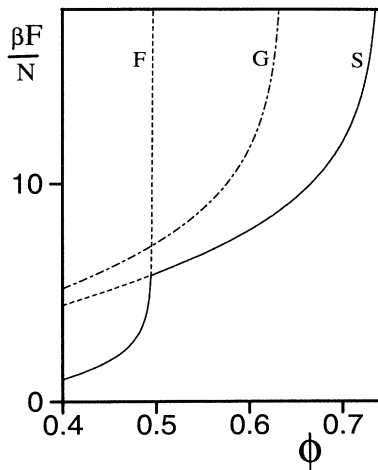


FIG. 1. The reduced ( $\beta = \frac{1}{k_B T}$ ) Helmholtz free energy ( $F$ ) per particle versus the number density  $\rho$  or packing fraction  $\phi = \frac{\pi}{6} \sigma^3 \rho$  for hard spheres of diameter  $\sigma$  as obtained from the present van der Waals theory. Only the high-density region is shown for the fluid ( $F$ ), glass ( $G$ ), and solid ( $S$ ) phases. The full lines correspond to the stable phases (lowest free energy), while the dashed lines indicate the metastable  $F$  and  $S$  phases. The  $G$  phase (dashed-dot curve) is always metastable relative to the  $S$  phase. If the  $S$  phase is suppressed (bypassed), the  $G$  phase is seen to become stable relative to the  $F$  phase for  $\phi > 0.4950$ , whereas the  $F$ - $S$  exchange of stability corresponds to  $\phi = 0.4942$ .

Adopting (3.3), we find from (3.5)  $\phi_{F-S} \simeq 0.4942$  and  $\phi_{F-G} \simeq 0.4950$ . The sequence  $\phi_{F-S} < \phi_{F-G}$ , i.e., the  $S$  phase becoming stable before the  $G$  phase, is again in qualitative agreement [17] with the findings of [15,16].

Notice that in [11] we did use  $\phi_0 = 0.5157$  instead of (3.3). This value of  $\phi_0$  was found by adjusting the vdW value of  $\phi_{F-S}$  given by (3.5) to the value of  $\phi_{F-S}$  found in the theory of Lutsko and Baus (see [14]), namely,  $\phi_{F-S} = 0.515$ . Here we prefer to use (3.3) because it keeps the present vdW-theory self-contained, whereas the presentation of [11] relied on the extraneous and much more sophisticated theory of Lutsko and Baus [14]. In Fig. 2 we show how the HS  $F$ - $S$  coexistence densities, obtained by solving  $p_{(F)} = p_{(S)}$  and  $\mu_{(F)} = \mu_{(S)}$  (see Sec. II), depend on the value of  $\phi_0$ . It is seen there that the difference of  $\phi_0$  value between (3.3) and  $\phi_0 = 0.5157$  as used in [11] has only a minor effect on the  $F$ - $S$  coexistence. In either case, we find that the experimental coexistence region corresponding to  $\phi_F = 0.494$  and  $\phi_S = 0.545$  is contained within the vdW prediction but that the latter is too large due to an overestimation of  $\phi_S$  by about 8% while the value of  $\phi_F$  is underestimated by about 2%. On this basis one can expect that the predictions of the present vdW theory will be quantitatively superior on the fluid side of the  $F$ - $S$  transition, whereas the solid side may indeed involve appreciable overestimations. We will nevertheless continue to use (3.3), since it yields a simple and self-contained vdW theory for the HS transition that is in full qualitative and even semi-quantitative agreement with the findings of [13–15].

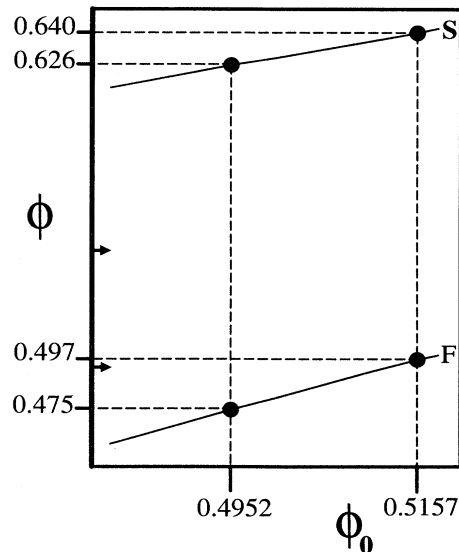


FIG. 2. The packing fraction  $\phi$  of the fluid ( $F$ ) and solid ( $S$ ) phases of a hard-sphere system at  $F$ - $S$  coexistence versus the packing fraction  $\phi_0$  at which the  $F$  phase becomes unstable in the present van der Waals theory. The dots correspond to the value (0.4952) of  $\phi_0$  used here [see (3.3)] and the value (0.5157) of  $\phi_0$  used in [11]. The arrows indicate the corresponding experimental values ( $\phi_F = 0.494$ ;  $\phi_S = 0.545$ ) of [13,15]. It is seen that while  $\phi_F$  is fairly well reproduced, the value of  $\phi_S$  is overestimated here by 8%.

#### IV. WHAT DOES IT TAKE TO MAKE A LIQUID?

In the presence of attractions, i.e., when  $\phi(x) \neq 0$ , the vdW free energies are not always monotonic and may exhibit a vdW loop for temperatures below some critical temperature as discussed within the present context in [11] for both the  $F$  and the  $S$  phases.

Here we will focus our attention on the critical point of the  $F$  phase only (see [11] for the  $S$  phase). The critical temperature  $T_c^{(F)}$  and the critical density  $\rho_c^{(F)}$  of the  $F$  phase can be found by solving the equations

$$\frac{\partial}{\partial \rho} p_F(\rho_c^{(F)}, T_c^{(F)}) = 0, \quad \frac{\partial^2}{\partial \rho^2} p_F(\rho_c^{(F)}, T_c^{(F)}) = 0 \quad (4.1)$$

or similar equations in terms of  $\mu_F$  (cf.  $\frac{\partial p}{\partial \rho} = \rho \frac{\partial \mu}{\partial \rho}$ ), where  $p_F(\rho, T)$  and  $\mu_F(\rho, T)$  denote the pressure and chemical potential of the  $F$  phase. Using, for instance, the simple expressions of Sec. II, one finds (see also [11])

$$\phi_c^{(F)} = \frac{1}{3}\phi_0, \quad t_c^{(F)} = \frac{8}{27}\Gamma \quad (4.2)$$

where  $\phi_c^{(F)} = \frac{\pi}{6}\sigma^3\rho_c^{(F)}$ ,  $t_c^{(F)} = \frac{k_B T_c^{(F)}}{\epsilon}$  denote the critical values of the packing fraction and reduced temperature, whereas  $\Gamma$  is given by

$$\Gamma = 12\phi_0 \int_1^\infty dx x^2 \phi(x) \quad (4.3)$$

at least for the case where  $\phi(x)$  does not depend on the density [12]. Hence, for  $T < T_c^{(F)}$  the  $F$  phase will phase separate into a dilute fluid phase ( $F_1$ ) or gas characterized by  $\phi$  values smaller than  $\phi_c^{(F)}$  and a dense fluid phase ( $F_2$ ) or liquid with  $\phi$  values larger than  $\phi_c^{(F)}$ . The presence of attractions,  $\phi(x) \neq 0$  or, better,  $\Gamma \neq 0$ , is therefore a necessary condition for a liquid phase ( $F_2$ ) to appear. It is, however, not a sufficient condition because this liquid could still be metastable with respect to the  $S$  phase, since the  $F$ - $S$  transition does not even require attractions to be present (see Sec. III). In other words, the  $F_1$ - $F_2$  transition can still be preempted by the  $F$ - $S$  transition. Let, therefore,  $\rho_F(T)$  denote the density of the  $F$  phase which, at a temperature  $T$ , coexists with the  $S$  phase of density  $\rho_S(T)$ . The necessary and sufficient condition for a stable liquid phase to appear in the phase diagram is then (see Fig.3)

$$\rho_c^{(F)} < \rho_F(T_c^{(F)}), \quad (4.4)$$

where  $\rho_c^{(F)}$  and  $T_c^{(F)}$  are given by (4.1) or (4.2) and  $\rho_F(T)$  and  $\rho_S(T)$  by

$$p_F(\rho_F, T) = p_S(\rho_S, T), \quad \mu_F(\rho_F, T) = \mu_S(\rho_S, T), \quad (4.5)$$

where  $p_{F(S)}$  and  $\mu_{F(S)}$  denote, respectively, the pressure and chemical potential of the  $F(S)$  phase (see Sec. II). Equation (4.4) states that the critical density of the fluid has to be smaller than the density of the fluid, which, at the critical temperature  $T_c^{(F)}$ , coexists with the solid. That Eq. (4.4) implies a condition on the potential can

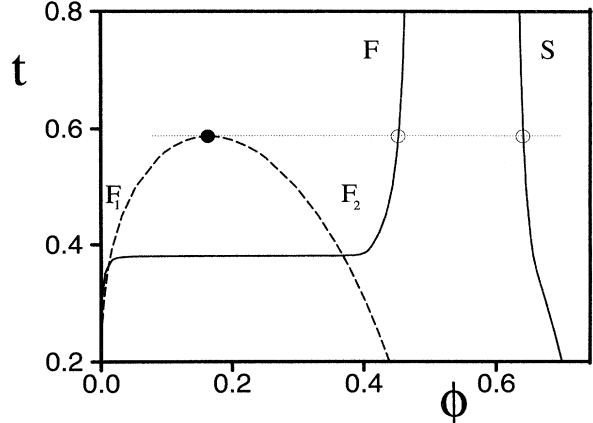


FIG. 3. The fluid ( $F_1$ )-fluid ( $F_2$ ) coexistence (dashed curve) and the fluid ( $F$ )-solid ( $S$ ) coexistence (full curves) in the temperature ( $t = \frac{k_B T}{\epsilon}$ ) density ( $\phi = \frac{\pi}{6}\sigma^3\rho$ ) plane for a subcritical potential. For such a potential the density of the fluid ( $F$ ) that coexists with the solid ( $S$ ) at the  $F_1$ - $F_2$  critical temperature (open dots) is larger than the critical density (full dot) [cf. (4.4)]. This corresponds to a situation where the dense fluid ( $F_2$ ) or liquid is stable relative to the  $F$ - $S$  transition. The case shown here corresponds to the results of the present vdW theory for inverse-power attractions [see (5.1)] of index  $n = 6$ .

be seen by considering the limiting case  $\rho_c^{(F)} \rightarrow \rho_F(T_c^{(F)})$  determined by

$$p_F(\rho_c^{(F)}, T_c^{(F)}) = p_S(\rho_S, T_c^{(F)}), \\ \mu_F(\rho_c^{(F)}, T_c^{(F)}) = \mu_S(\rho_S, T_c^{(F)}), \quad (4.6)$$

which constitute a set of two equations for only one un-

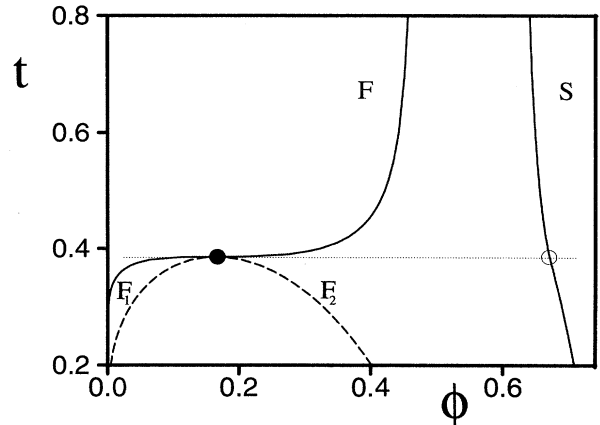


FIG. 4. The same as Fig. 3 but for a critical potential, i.e., a potential for which the ( $F_1$ - $F_2$ ) critical fluid satisfies, moreover, the  $F$ - $S$  coexistence. This corresponds to a situation where the dense ( $F_2$ ) fluid or liquid phase becomes marginally stable relative to the  $F$ - $S$  transition. The case shown here corresponds to the results of the present vdW theory for an inverse-power attraction [see (5.1)] with the critical index  $n = n_c^{(F)} \simeq 7.6$  [cf. (5.2)].

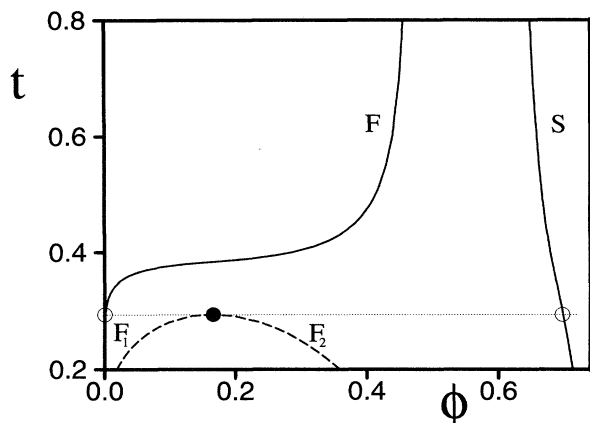


FIG. 5. The same as Fig. 3 but for a supercritical potential, i.e., one for which the  $(F_1-F_2)$  critical density exceeds the density of the fluid ( $F$ ) that coexists with the solid ( $S$ ) at the  $(F_1-F_2)$  critical temperature. In this case the dense ( $F_2$ ) fluid or liquid phase is always metastable relative to the  $F$ - $S$  transition. The case shown here corresponds to the results of the present vdW theory for an inverse-power attraction (5.1) of index  $n = 9$ , as suitable for fullerene molecules (see [19]).

known, namely,  $\rho_S(T_c^{(F)})$ . Eliminating (formally)  $\rho_S$  from (4.6), there remains a relation to be satisfied by the pair potential. This relation states then that the  $F_1$ - $F_2$  critical point satisfies the  $F$ - $S$  coexistence. Henceforth we will call any potential that satisfies (4.6) a “critical potential” with respect to the critical point of the fluid phase (see Fig. 4). A potential for which (4.4) holds will likewise be called a “subcritical potential,” whereas a “supercritical potential” is one for which (see Fig. 5)

$$\rho_F(T_c^{(F)}) < \rho_c^{(F)} \quad (4.7)$$

holds. The necessary and sufficient condition for a given potential to give rise to a (stable) liquid is hence that it be subcritical.

## V. FOUR CASE STUDIES

We will now analyze the condition (4.6) within the vdW theory of Sec. II for a few specific cases.

### A. Inverse-power potentials

Let us first reconsider the case of the inverse-power (IP) attractions already considered in [11]. For this case we have

$$\phi(x) = \frac{1}{x^n}, \quad x = \frac{r}{\sigma} \quad (5.1)$$

when adopting the amplitude of the attractions as temperature scale and the HS diameter  $\sigma$  as length scale [see (2.1)]. This family of potentials hence depends on a single parameter, the index  $n$ , which fixes its rate of decay. For  $n$  large (small) one usually speaks of a short (long)

ranged potential, although (5.1) is, strictly speaking, of infinite range for all  $n$ . Substituting (5.1) into (4.3) we find  $\Gamma = 12 \frac{\phi_0}{(n-3)}$ , provided  $n > 3$ . In [11] we constructed the phase diagrams for (5.1) and found empirically that a topological change did occur in the phase diagram for  $7 < n < 8$ . Here we use (5.1) in (4.6), which now becomes an equation for  $n$  (and  $\rho_S$ ) and find, but now with much less labor, that the critical IP-potential corresponds to  $n = n_c^{(F)}$  with

$$n_c^{(F)} \simeq 7.6, \quad (5.2)$$

while for  $n < n_c^{(F)}$  the IP potentials are subcritical. The necessary and sufficient condition to obtain a liquid phase with an IP attraction is therefore  $3 < n < 7.6$ . This is consistent with the current observation [2] that atomic systems with nonretarded ( $n = 6$ ) or retarded ( $n = 7$ ) London-vdW dispersion forces [3] do exhibit a liquid phase. In the case of molecular systems of the fullerene type (e.g.,  $C_{60}$ ) the atoms making up the fullerene molecule can be considered to be uniformly distributed over the surface of a sphere (at least for temperatures for which the molecules can freely rotate) and summing the London-vdW attractions between the atoms over the spherical surfaces leads then to an intermolecular potential of Girifalco type [18], which can, itself, be approximated by an IP attraction (5.1) with  $n \simeq 9$  (see, e.g., [19]). Since  $9 > n_c^{(F)}$  we then conclude, in agreement with [20], that the fullerenes should not exhibit a liquid phase, although this is still a somewhat controversial matter (see [21]).

### B. Yukawa potentials

A potential that by itself may not be very realistic but is often used to fit more realistic potentials (see, e.g., [22]) or to perform simulation studies (see, e.g., [23]) is the Yukawa potential:

$$\phi(x) = \frac{e^{-\kappa(x-1)}}{x}, \quad (5.3)$$

which, just like (5.1), depends on a single parameter,  $\kappa$ , controlling its decay rate. Substituting (5.3) into (4.3) yields  $\Gamma = 12\phi_0 \frac{(\kappa+1)}{\kappa^2}$ , provided  $\kappa > 0$ . Equation (4.6) becomes now an equation for  $\kappa$  (and  $\rho_S$ ) that defines the critical Yukawa potential as corresponding to  $\kappa = \kappa_c^{(F)}$ , with

$$\kappa_c^{(F)} \simeq 5.2, \quad (5.4)$$

so that the phase diagram of (5.3) will exhibit a liquid phase for  $0 < \kappa < 5.2$ . This is consistent with the simulations of [23] where a liquid was found for  $\kappa = 3.9$  but not for  $\kappa = 7$  and  $\kappa = 9$ . Similarly, in our previous theoretical study [22] based on a variational approach, we found a liquid phase for  $\kappa = 2.7$  but not for  $\kappa = 14$  and 398, again in agreement with (5.4). This should be contrasted with the recent much more sophisticated theoretical study of [24] and the mixed theory-simulation results of [23], both of which still predict a liquid for  $\kappa = 7$ .

### C. The Hamaker-vdW potential

Dispersions of spherical mesoscopic objects can often be described as simple fluids of colloidal particles (see [7–10]). In this case the sum over the London-vdW attractions between atoms distributed uniformly over the volume of a sphere leads to the following Hamaker-vdW potential between the colloidal particles [3,7,8,10]:

$$\phi(x) = \frac{A}{\epsilon} h(\gamma x), \quad (5.5)$$

where

$$h(x) = \frac{1}{x^2 - 1} + \frac{1}{x^2} + 2 \ln \left( 1 - \frac{1}{x^2} \right), \quad (5.6)$$

while the Hamaker constant  $A$  of (5.5) can usually be approximated by

$$\frac{A}{\epsilon} = m(1+t), \quad (5.7)$$

with  $m$  a dimensionless measure ( $m > 0$ ) of the difference (mismatch) in refractive index between the material making up the colloidal particle and the material making up the solvent, and  $t = \frac{k_B T}{\epsilon}$  the dimensionless temperature resulting from choosing the energy scale  $\epsilon$  to be proportional to the main ultraviolet electronic absorption frequency (see [7,8] for details). The dispersion can then be stabilized against the flocculation induced by the singularity of  $h(x)$  of (5.6) when  $x \rightarrow 1$  by using a steric stabilization mechanism which will lead to an effective HS diameter  $\sigma$  somewhat larger than the Hamaker-vdW diameter, say,  $\sigma_0$ , of the colloidal particle and, hence,  $\gamma = \frac{\sigma}{\sigma_0} > 1$  in (5.5).

The resulting potential (5.5–5.7) depends now on two dimensionless parameters,  $m$  and  $\gamma$ . Because of the temperature dependence of the Hamaker constant (5.7), we have, for (4.3),  $\Gamma = (1+t)\tilde{\Gamma}$ , with

$$\begin{aligned} \tilde{\Gamma} &= 12m\phi_0 \int_1^\infty dx x^2 h(\gamma x) \\ &= m\phi_0 \left[ 2 \ln \left( \frac{\gamma-1}{\gamma+1} \right) - 8\gamma - 8\gamma^3 \ln \left( 1 - \frac{1}{\gamma^2} \right) \right], \end{aligned} \quad (5.8)$$

while (4.2) becomes:

$$\phi_c^{(F)} = \frac{1}{3}\phi_0, \quad \frac{t_c^{(F)}}{1+t_c^{(F)}} = \frac{8}{27}\tilde{\Gamma} \quad (5.9)$$

or

$$t_c^{(F)} = \frac{\frac{8}{27}\tilde{\Gamma}}{\left(1 - \frac{8}{27}\tilde{\Gamma}\right)}, \quad (5.10)$$

so that the two parameters  $m$  and  $\gamma$  must satisfy the additional relation ( $t_c^{(F)} > 0$ )

$$2 \ln \left( \frac{\gamma-1}{\gamma+1} \right) - 8\gamma - 8\gamma^3 \ln \left( 1 - \frac{1}{\gamma^2} \right) < \frac{27}{8m\phi_0}, \quad (5.11)$$

which implies that for a given  $m$ ,  $\gamma$  must be large enough

to prevent flocculation. We have performed only a limited search but could find no solution to (4.6) for (5.5) with physical values of  $m$  and  $\gamma$ . This seems to imply that the present potential is always subcritical or, more precisely, if the system does not flocculate it will always admit a liquid phase for  $t < t_c^{(F)}$ .

### D. The depletion potential

When the colloidal dispersion is index matched [i.e.,  $m = 0$  in (5.7)] we can neglect the Hamaker-vdW attractions and the (uncharged) colloidal particles will behave essentially (see [7–10]) as the HS system of Sec. III. Assume now that we add to such a HS colloid a polymer that does not adsorb onto the colloidal particles. To a first approximation we can assimilate the polymer molecules to spherical particles with a diameter, say,  $\sigma_p$ , equal to the radius of gyration of the polymer. When this effective diameter  $\sigma_p$  of the polymer is much smaller than the diameter  $\sigma$  of the colloidal particles we may invoke the depletion picture [7,8,10,25]. In this picture the (colloid + polymer) mixture is described as an effective one-component system of colloidal HS interacting moreover with an effective, polymer induced, attraction. The interest of this situation stems from the fact that it provides us with an experimentally realizable system for which the attractions can be tuned by changing the length and/or concentration of the polymer for a given HS colloid [7,8,10]. Indeed, when the depletion picture holds, the effective attraction between the colloidal HS particles reads [7,8,10]

$$\phi(x) = \Pi_p \frac{\pi}{6} \frac{\sigma^3}{\epsilon} (1+\xi)^3 \omega \left( \frac{x}{1+\xi} \right), \quad (5.12)$$

where  $\xi = \frac{\sigma_p}{\sigma}$  is the polymer to colloid diameter ratio,  $\omega \left( \frac{x}{1+\xi} \right)$  is the normalized overlap volume of two depletion spheres,

$$\omega(x) = \begin{cases} 1 - \frac{3}{2}x + \frac{1}{2}x^3, & x \leq 1 \\ 0, & x > 1, \end{cases} \quad (5.13)$$

and  $\Pi_p$  is the (osmotic) pressure of the polymer in the given colloidal dispersion. As our energy scale  $\epsilon$  we will take

$$\epsilon = \Pi_p^* \frac{\pi}{6} \sigma_p^3, \quad (5.14)$$

where  $\Pi_p^*$  is the (osmotic) pressure of the polymer in the absence of colloidal particles, a variable that can be easily controlled experimentally. In many instances it has been assumed (see [7,8,10,26]) that van't Hoff's ideal gas law,  $\Pi_p^* = \rho_p^* k_B T$  and  $\Pi_p = \rho_p k_B T$ , holds well for polymers in solvents close to their theta point. In this case the reduced temperature becomes [see (5.14)]

$$t \equiv \frac{k_B T}{\epsilon} = \frac{1}{\phi_p^*}, \quad (5.15)$$

so that the control parameter of the phase transition is no longer the temperature but the polymer concentration

$\rho_p^*$  or polymer volume fraction  $\phi_p^* = \frac{\pi}{6} \sigma_p^3 \rho_p^*$ . In the spirit of this simple vdW theory we can relate  $\rho_p$  to  $\rho_p^*$  by an excluded volume argument,

$$\rho_p = \frac{\rho_p^*}{[1 - \phi(1 + \xi)^3]}, \quad (5.16)$$

where  $\phi(1 + \xi)^3 \equiv \frac{\pi}{6} \rho(\sigma + \sigma_p)^3$  is the fraction of the volume excluded to the polymer because of the presence of a depletion sphere of volume  $\frac{\pi}{6}(\sigma + \sigma_p)^3$  around each colloidal particle. From (5.16) it follows that the concentration  $\rho_p$  or volume fraction  $\phi_p = \frac{\pi}{6} \sigma_p^3 \rho_p$  of the polymer in the presence of the colloidal particles depends on the amount of polymer added ( $\phi_p^*$ ) and on the amount of colloid present ( $\phi$ ). As already observed elsewhere (see Lekkerkerker *et al.* [26]), this implies that any phase separation of the colloid will induce a partitioning of the polymer between the coexisting phases.

Returning to (4.1), we note that because of (5.16),  $\phi(x)$  now becomes density dependent so that (4.2) and (4.3) no longer hold [12]. We can, however, still solve (4.1) exactly, yielding now for the critical point

$$\phi_c^{(F)} = \frac{\phi_0}{3 - 2\phi_0(1 + \xi)^3}, \quad t_c^{(F)} = \frac{8}{27} \frac{\tilde{\Gamma}}{[1 - \phi_0(1 + \xi)^3]}, \quad (5.17)$$

with  $\tilde{\Gamma}$  given by

$$\begin{aligned} \tilde{\Gamma} &= 12\phi_0 \frac{(1 + \xi)^3}{\xi^3} \int_1^\infty dx x^2 \omega \left( \frac{x}{1 + \xi} \right) \\ &= \frac{\phi_0}{2\xi^3} \{ (1 + \xi)^6 - 8(1 + \xi)^3 + 9(1 + \xi)^2 - 2 \} \end{aligned} \quad (5.18)$$

and  $\tilde{\Gamma} > 0$  for  $\xi > 0$ . Since we must have  $\phi_c^{(F)} > 0$ ,  $t_c^{(F)} > 0$ , Eq. (5.17) implies, moreover, that  $\xi < 0.264$ . The present theory is therefore limited to  $0 < \xi < 0.264$ , which is consistent with the fact that the original depletion picture assumes  $\xi \ll 1$ . Turning now to (4.6) we find that the depletion potential (5.12)–(5.16) becomes critical for a size ratio  $\xi = \xi_c^{(F)}$ , with

$$\xi_c^{(F)} \simeq 0.262, \quad (5.19)$$

so that for  $t < t_c^{(F)}$  or, better, for  $\phi_p^* > \frac{1}{t_c^{(F)}}$ , the presence of polymer will induce a liquid phase whenever  $0.262 < \xi < 0.264$ . The depletion potential is thus almost always supercritical. Note, however, that the very small region where the potential is subcritical ( $0.262 < \xi < 0.264$ ) may result from the rough approximation used in (5.16). Using more elaborate expressions for (5.16), one will, however, lose the simplicity of the present vdW theory, since the critical point (4.1) can

then no longer be obtained in analytic form as in (5.17). In the related theoretical studies of [26], it was found that  $\xi_c^{(F)} \simeq 0.32$ , while the simulations of [27] did predict the still higher value  $\xi_c^{(F)} \simeq 0.45$ . In the experiments reported in [28] one did find no liquid for  $\xi = 0.08$ , while a liquid was found for  $\xi = 0.24$  and  $0.57$ , with  $\xi = 0.24$  being very close to, but slightly larger than,  $\xi_c^{(F)}$ .

When the depletion picture is applied to a binary mixture of very dissimilar HS colloids, as already done in [29], then the same critical value (5.19) will be found because the fact that the small colloid no longer obeys van't Hoff's ideal gas law will affect only the temperature scale. In view of this, the experimental results of [30] for  $\xi < 0.2$  could well have to be reinterpreted in terms of a  $F$ - $S$  coexistence, since for such a small  $\xi$  value the latter will preempt the  $F_1$ - $F_2$  transition predicted in [31]. To close, we would like to emphasize here that it would be very interesting to investigate, perhaps following the lines of [32], at what  $\xi$  value the effective one-component description based on the depletion picture breaks down and one has to use a genuine two-component description to study this type of (colloid + polymer) or (colloid + colloid) mixture.

## VI. CONCLUSIONS

We have formulated a necessary and sufficient condition for the occurrence of a liquid phase in the phase diagram of a simple fluid (see Sec. IV). Within the vdW theory of [11], summarized in Sec. II, this condition can be easily analyzed. Before doing so, we have shown in Sec. III that the HS theory underlying the present vdW theory is consistent with all the known facts. In Sec. V we have established on this basis the condition for the occurrence of a liquid phase in systems governed by four specific potentials of increasing complexity. In each case we have found a quantitative agreement between the results of this simple vdW theory and data from other sources. From this we conclude that although the present vdW theory is too crude to answer quantitatively questions of absolute stability of phases, it may well be reliable for investigating questions of relative stability such as the relative stability of the fluid ( $F_1$ )-fluid( $F_2$ ) transition with respect to the fluid ( $F$ )-solid( $S$ ) transition that was investigated here.

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- [1] D.L. Goodstein, *States of Matter* (Dover Publications, New York, 1985).  
 [2] D.A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).

- [3] J.N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic Press, London, 1992).  
 [4] J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids*, 1st ed. (Academic Press, London, 1976).

- [5] P.A. Egelstaff, *An Introduction to the Liquid State*, 2nd ed. (Clarendon Press, Oxford, 1992).
- [6] P. Pieranski, *Contemp. Phys.* **24**, 25 (1983).
- [7] P.N. Pusey, in *Liquids, Freezing and the Glass Transition*, edited by J.P. Hansen, D. Levesque, and J. Zinn-Justin (Elsevier, Amsterdam, 1991), Chap. 10.
- [8] W.B. Russel, D.A. Saville, and W.R. Schowalter, *Colloidal Dispersions*, 2nd ed. (Cambridge University Press, Cambridge, 1991).
- [9] H. Löwen, *Phys. Rep.* **237**, 249 (1994).
- [10] W.C.K. Poon and P.N. Pusey, in *Observation, Prediction and Simulation of Phase Transitions in Complex Fluids*, edited by M. Baus, L.F. Rull, and J.P. Ryckaert (Kluwer Academic Publishers, Dordrecht, 1995), p. 3.
- [11] A. Daanoun, C.F. Tejero, and M. Baus, *Phys. Rev. E* **50**, 2913 (1994).
- [12] Note that when  $\phi(x)$  is density dependent we have  $\frac{\partial}{\partial \rho}[\rho\phi(x)] = \phi(x) + \rho\frac{\partial}{\partial \rho}\phi(x)$ , although we did not indicate this  $\rho$  dependence explicitly.
- [13] W.W. Wood and J.D. Jacobson, *J. Chem. Phys.* **27**, 1207 (1957); B.J. Alder and T.E. Wainwright, *ibid.* **27**, 1208 (1957); W.G. Hoover and F.H. Ree, *ibid.* **49**, 3609 (1968); D. Frenkel and A.J.C. Ladd, *ibid.* **81**, 3188 (1984).
- [14] J.F. Lutsko and M. Baus, *Phys. Rev. A* **41**, 6647 (1990); M. Baus, *J. Phys. Condens. Matter* **2**, 2111 (1990); Y. Singh, *Phys. Rep.* **207**, 351 (1991).
- [15] P.N. Pusey and W. van Megen, *Nature* **320**, 340 (1986); P.N. Pusey, W. van Megen, P. Bartlett, B.A. Ackerson, J. G. Rarity, and S. M. Underwood, *Phys. Rev. Lett.* **63**, 2753 (1989); N. A. M. Verhaegh, J.S. van Duijneveld, A. van Blaaderen, and H.N.W. Lekkerkerker, *J. Chem. Phys.* **102**, 1416 (1995).
- [16] L.V. Woodcock, *Ann. N.Y. Acad. Sci.* **371**, 274 (1981).
- [17] Note that if the solid phase is suppressed (bypassed) the present theory would predict a  $F$ - $G$  coexistence between a fluid of  $\phi_F = 0.483$  (hence, metastable with respect to the  $F$ - $S$  transition) and a glass of  $\phi_G = 0.583$  while HS glass phases have indeed been observed in [15] for  $0.58 < \phi < \phi_{rcp}$ .
- [18] L.A. Girifalco, *J. Phys. Chem.* **96**, 858 (1992).
- [19] See Eq. (6) in V.I. Zubov, N.P. Tretrakov, J.N. Teixeira Rabelo, and J.F. Sanchez Ortiz, *Phys. Lett. A* **194**, 22 (1994).
- [20] M.H.J. Hagen, E. J. Meijer, G.C.A.M. Mooij, D. Frenkel, and H.N.W. Lekkerkerker, *Nature* **365**, 425 (1993).
- [21] A. Cheng, M.L. Klein, and C. Caccamo, *Phys. Rev. Lett.* **71**, 1200 (1993).
- [22] C.F. Tejero, A. Daanoun, H.N.W. Lekkerkerker, and M. Baus, *Phys. Rev. Lett.* **73**, 752 (1994).
- [23] M.H.J. Hagen and D. Frenkel, *J. Chem. Phys.* **101**, 4093 (1994).
- [24] L. Mederos and G. Navascues, *J. Chem. Phys.* **101**, 9841 (1994).
- [25] S. Asakura and F. Oosawa, *J. Chem. Phys.* **22**, 1225 (1954); A. Vrij, *Pure Appl. Chem.* **48**, 471 (1976).
- [26] A.P. Gast, C.K. Hall, and W.B. Russel, *J. Colloid. Interface Sci.* **96**, 251 (1983); H.N.W. Lekkerkerker, W.C.K. Poon, P.N. Pusey, A. Stroobants, and P. B. Warren, *Europhys. Lett.* **20**, 559 (1992).
- [27] E.J. Meijer and D. Frenkel, *J. Chem. Phys.* **100**, 6873 (1994).
- [28] S.M. Ilett, A. Orrock, W.C.K. Poon, and P.N. Pusey, *Phys. Rev. E* **51**, 1344 (1995).
- [29] H.N.W. Lekkerkerker and A. Stroobants, *Physica A* **195**, 387 (1993); W.C.K. Poon and P. B. Warren, *Europhys. Lett.* **28**, 513 (1994).
- [30] J.S. van Duijneveld, A.W. Heinen, and H.N.W. Lekkerkerker, *Europhys. Lett.* **21**, 369 (1993).
- [31] T. Biben and J.P. Hansen, *Phys. Rev. Lett.* **66**, 2215 (1991).
- [32] H. Xu and M. Baus, *J. Phys. Condens. Matter* **4**, L663 (1992); H. Xu and C. Barentin, *ibid.* **7**, L13 (1995).