Figure 1. Phase diagrams of model colloid–polymer mixtures with size ratios (a) $q = \sigma_p/\sigma_c = 0.1$, (b) $q = 0.4$, (c) $q = 0.6$, and (d) $q = 0.8$ as functions of the colloid packing fraction η_c and the ideal polymer coil reservoir packing fraction η_p^r as obtained from simulations of the effective one-component Hamiltonian. F and S denote the stable fluid and solid (fcc) phase. F + S, F + F, and S + S denote, respectively, the stable fluid–solid, the (meta)stable fluid–fluid, and the metastable solid–solid coexistence region. The asterisks denote state-points at which pairwise correlation functions were calculated.

For $q \leqslant 0.4$, an enormous widening of the fluid–solid transition is observed when η_p^r increases sufficiently. This implies that the coexisting fluid and solid phase become progressively more dilute and dense, respectively, upon increasing η_p^r. This widening is consistent with earlier findings by Gast *et al* [3] in perturbation theory studies of the same pair potential model (see section 4.1). It has also been observed in experiments on colloid–polymer mixtures [5, 6] and in simulations of hard spheres and lattice polymers [10]. The shape of the coexistence curves implies that for small values of q the fluid phase only persists to very low values of η_c when η_p^r is sufficiently high. The calculations also reveal the existence of a fluid–fluid transition. However, for $q = 0.1$ and 0.4 we find this fluid–fluid coexistence is metastable with respect to the broad fluid–solid transition. For $q \geqslant 0.6$ the fluid–fluid coexistence becomes stable. Assuming a linear dependence on q of the difference between the polymer reservoir packing fraction at the triple point and at the critical point, we can estimate that the liquid phase becomes metastable for size ratios $q \leqslant 0.45$. This value of the size ratio