strength U as

$$F = E - TS; \qquad \mathrm{d}F = -S\,\mathrm{d}T + D\,\mathrm{d}U. \tag{3.21}$$

These expressions are not directly useful in the context of QMC simulations. As pointed out in Sec. 1.3, the free energy cannot be estimated using QMC since the importance sampling technique by construction samples the partition sum only up to an unknown prefactor. Since E can be measured within QMC (and T is an external parameter), this argument and (3.21) also imply the inability of QMC to measure S directly. However, using

$$\left.\frac{\partial \beta F}{\partial \beta}\right|_U = F + \beta \left.\frac{\partial F}{\partial \beta}\right|_U = F - T \left.\frac{\partial F}{\partial T}\right|_U = F + TS = E \tag{3.22}$$

with $\beta = 1/T$, the differential may be rewritten as

$$\mathrm{d}(\beta F(\beta, U)) = E(\beta, U)\,\mathrm{d}\beta + \beta D(\beta, U)\,\mathrm{d}U\,, \tag{3.23}$$

i.e., expressed in terms of observables which we have determined in Sec. 3.5. Provided that both the metallic and the insulating solution can be continuously followed (in general on different paths[35] in the (U,β) plane) up to a point (U_1,β_1) in the crossover region where they coincide, then by integrating equation (3.23) one can calculate $\beta F_{\mathrm{m/i}}(\beta, U) - \beta_1 F(\beta_1, U_1)$ within the coexistence region and, in principle, determine the transition line.[36] In practice, however, it is likely that along these different paths different systematic errors will contribute to the free energy estimates for metal and insulator, respectively. Consequently, the resulting estimate for the transition line may be systematically biased.

Systematic errors can be kept to a minimum in a scheme where differences in observables (between metal and insulator) are only computed locally, i.e., for fixed U and β. This may be achieved by rewriting equation (3.23) for metal/insulator

$$\mathrm{d}\big(\beta F_{\mathrm{m/i}}(\beta, U)\big) = E_{\mathrm{m/i}}(\beta, U)\,\mathrm{d}\beta + \beta D_{\mathrm{m/i}}(\beta, U)\,\mathrm{d}U \tag{3.24}$$

and taking the difference

$$\mathrm{d}\big(\beta \Delta F(\beta, U)\big) = \Delta E(\beta, U)\,\mathrm{d}\beta + \beta \Delta D(\beta, U)\,\mathrm{d}U\,. \tag{3.25}$$

Here, $\Delta F(\beta, U) = F_{\mathrm{m}}(\beta, U) - F_{\mathrm{i}}(\beta, U)$; corresponding differences for the energy and double occupancy are denoted by ΔE and ΔD, respectively. Since the transition line $U_{\mathrm{c}}(\beta)$ is smooth and determined by $\Delta F(\beta, U_{\mathrm{c}}(\beta)) = 0$, all derivatives of ΔF also vanish along the line $U_{\mathrm{c}}(\beta)$. This is true, in particular, for the differential:

$$\mathrm{d}(\beta \Delta F(\beta, U))|_{U=U_{\mathrm{c}}(\beta)} = 0. \tag{3.26}$$

From (3.25) and (3.26) we get

$$0 = \Delta E(\beta, U_{\mathrm{c}}(\beta))\,\mathrm{d}\beta + \beta \Delta D(\beta, U_{\mathrm{c}}(\beta))\,\mathrm{d}U_{\mathrm{c}} \tag{3.27}$$

[35]The necessity of using different paths for metallic and insulating solutions arises from the shift of the coexistence region with $\Delta\tau$ and from the larger numerical errors of each solution near its stability edge.

[36]Here and in the following, the indices m and i indicate metal and insulator, respectively.