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Extended cluster variation calculations for the plane quadratic lattice gas

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Abstract. A numerical procedure to perform the extended cluster variation calculations is reported. This procedure was applied to the 3×3-site cluster variation approximation for the plane quadratic lattice gas with first-neighbour exclusion and second-neighbour finite interaction. All known results concerning the phase diagram of this model are summarised.

The finite cluster variation method, first proposed by Kikuchi (1951), has proved itself to be a powerful tool to obtain a qualitatively correct description of the thermodynamics of the lattice gas systems. Described in detail by Hijmans and De Boer (1955), Kikuchi and Brush (1967), Woodbury (1967) and Shulepov and Aksenenko (1981), to which we refer to avoid detailed discussion, it consists of the following stages.

(i) The basic cluster is decided and its subclusters are constructed; these figures determine the expression for the thermodynamic potential, usually the free energy function $f = E/kTN - S/kN$, with energy E and entropy S per N lattice sites.

(ii) All possible configurations of the basic cluster and the subclusters are enumerated, a fraction variable (FV) being assigned to each configuration.

(iii) The set of compatibility equations between the FVs is constructed by partial summing over the 'extra' lattice sites of larger clusters. The normalisation equations are to be added to this set.

(iv) The set of equations defined in (iii) is solved, i.e. the subset of independent FVs is defined, in terms of which all extra FVs can be expressed.

(v) The free energy function expressed in terms of the independent FVs is minimised with respect to these independent variables to derive a set of simultaneous equations.

(vi) The equations defined in (v) are solved for some fixed values of the external parameters, usually the density and the temperature. This solution describes the equilibrium state of the system.

Among these stages, (iv), (v) and (vi) become rather cumbersome, especially for large basic clusters. To perform stages (v) and (vi) Kaye and Burley (1974a, b) used the constrained optimisation of the free energy procedure; Kikuchi (1974) proposed the natural iteration method, which does not require differentiation nor matrix inversion. Here we report another computational procedure which performs stages (iv)–(vi) automatically. The first three stages can also be automatised, but in this work they were performed by hand.

Provided that the set of equations (iii) is given, stage (iv) can be performed using the Gaussian elimination algorithm. At every successive step the current equation is

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used to eliminate one variable from all the preceding and following equations; this variable is marked to be defined by this equation. Some equations can turn into identities, in which case they are to be excluded from the set.

When all equations are processed, we obtain the expressions for the extra FVs in terms of the 'independent' ones. Introducing them into the expression for the free energy function, one obtains the matrices of coefficients a_i, b_{ij}, c_j, with the rows (say) corresponding to summands of the type $a_i(\Sigma_j b_{ij} v_j)\ln(\Sigma_j b_{ij} v_j)$ for the entropy and $\Sigma_j c_j v_j$ for the energy; the column entries are for the independent variables v_j and the density. Then the first and second derivatives of the free energy function with respect to the independent variables can be easily calculated, so Newton's method can be applied to perform stage (vi).

To test the program we considered the 3×3-site cluster approximation for the ordered phases of the plane quadratic lattice gas with first-neighbour exclusion and second-neighbour interaction ε. For the definition of phases see Aksenenko and Shulepov (1982). The calculations were performed for phase $\sqrt{2}\times\sqrt{2}$ (26 independent variables), phase 2×1 (33 independent variables) and the low-temperature limit of this phase, i.e. the first- and second-neighbour exclusion (18 independent variables). The

Table 1. The coordinates of characteristic points shown in figure 1, with ρ, Γ and z denoting the density, grand potential and the activity respectively. For the cluster variation calculations the size of the basic cluster is specified, e.g. 2×1.

	2×1[a]	*PY*[b]	*BL*[c]	*BL*[d]	2×2[e]	2×3[f]	*CE*[g]	3×3[h]	Exact or best known
ρ_T	0.25	0.275		0.2857	0.3170	0.33		0.3411	0.368[i]
Γ_T	0.5232			0.6121	0.6931	0.725		0.7451	0.792[i]
z_T	1.6875	2.0		2.25	2.8729			3.3346	3.7962[i]
τ_{TC}	1.9516	2.933	3.834	2.969	3.0340			4.3630	5.054[j]
ρ_{TC}	0.1601	0.158	0.1667	0.1685	0.1947			0.1993	0.2763[k]
Γ_{TC}	0.2142	0.142	0.1150		0.1549			0.0848	
z_{TC}	0.2894	0.121	0.0741	0.0904	0.1242			0.0571	
τ_L	0.1408		[m]	0.0940	0.0605	[m]		0.0357	0.038[j]
ρ_L	0.2202			0.2618	0.2366			0.2452	0.25[j]
z_L				21.226				505.0	
ρ_S	0[l]		[m]	0.2249	0.1910	[m]	0.2018	0.2218	0.240[j]
Γ_S				0.9242	0.6931		0.7878	1.0157	
z_S				22.54	11.090		17.22	48.88	109.9[j]

[a] Burley (1961), Aksenenko and Shulepov (1982).
[b] Percus–Yevick approximation, Robledo and Farquhar (1976), Shulepov (1983).
[c] Branched lattice approximation, Aksenenko and Shulepov (1978).
[d] Branched lattice approximation, Aksenenko and Shulepov (1982).
[e] Kaye and Burley (1974a), Aksenenko and Shulepov (1982).
[f] Kaye and Burley (1974a).
[g] Expansion in irreducible clusters, Bellemans and Nigam (1967).
[h] This work.
[i] Series expansions, Gaunt and Fisher (1965), Baxter *et al* (1980).
[j] Exact finite method—phenomenological scaling, Kinzel and Schick (1981).
[k] Exact result $\rho_{TC}=(5-\sqrt{5})/10$, Huse (1982), Baxter and Pearce (1983).
[l] Non-physical result $\rho_S=0$.
[m] Phase 2×1 does not exist in these approximations.

last two cases were of particular interest since this phase can be shown not to exist in the 2×3-site cluster approximation, and our previous studies (1982) in the 2×2-site cluster approximation indicated the existence of a first-order transition between the disordered phase and the 2×1 phase.

We tabulated the thermodynamic functions along the isotherms using the initial approximations either constructed from the solution for the 2×2-site cluster (Aksenenko and Shulepov 1982) on the first few steps of the tabulation, or using the polynomial extrapolation on the subsequent steps. The convergence was rather rapid: it took not more than five iterations to achieve an accuracy of order 10^{-8}.

We found it useful for reference purposes to cummarise in table 1 all known results concerning the phase diagram of the model considered. Figure 1 explains the notation used in the table. It is interesting to note that the values of the characteristic parameters being extrapolated against the inverse number of cluster sites converge rather well to their most accurate known values. Contrary to our previous calculations (1982), no first-order transition loop was detected near the high-density branch of the curve separating the disordered phase and the 2×1 phase.

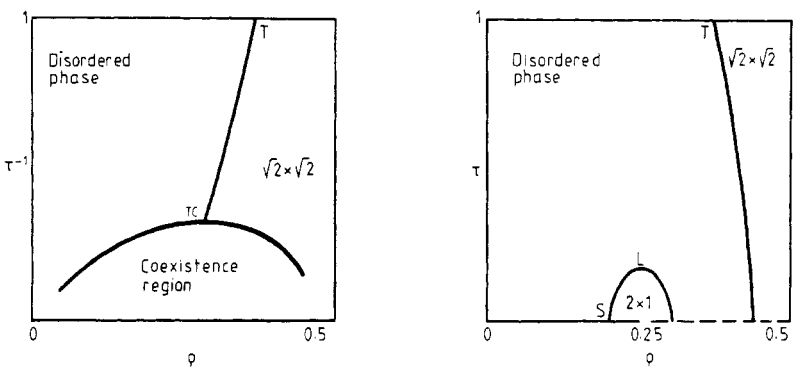

Figure 1. Phase diagram of the plane quadratic lattice gas with first-neighbour exclusion and second-neighbour attraction (left) and repulsion (right). Shown are three phases of the system; $\tau = \exp(-\varepsilon/kT)$, ρ is the density, TC the tricritical point, L the limiting separation point between the disordered phase and the 2×1 phase, and T and S the transition points for $\tau = 1$ and $\tau = 0$ respectively.

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