Microscopic expressions for the surface and line tension

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Abstract. We consider the change in grand potential of a fluid under a deformation of its containing vessel. Thermodynamically, the change is expressed in terms of the pressure, the surface tension and the line tension of the fluid. As the change can also be expressed in the fluid's microscopic properties, one obtains microscopic expressions for thermodynamic quantities. We consider two types of such expressions, the first one relating the pressure, surface and line tension to the density at the hard walls of the vessel, the second one relating them to the pressure tensor. Moreover, we can generalize these two types of expressions to a single expression which contains them both. Besides the distinction between surface and line tension, we consider two models of the wall: a 'hard wall' and a 'structured, soft wall'. It is shown that the expressions for the surface and the line tension are similar for all types of walls.

1. Introduction

The behaviour of fluids near a wall has attracted considerable interest in recent years. Especially the question whether a fluid wets a wall or not, has been the subject of many investigations (for a review see, e.g., [1]). This question refers to the equilibrium state of the wall–fluid interface which is characterized by the surface tension, describing the contribution of the wall–fluid interface to the grand potential of whole system. It forms the basis of many theoretical descriptions of the interface and can be measured experimentally. There exist formal expressions relating it to microscopic properties of the interface. As these properties are accessible in a simulation, the surface tension can also be evaluated in a simulation [2].

In reality, two thermodynamic phases meet at a wall–fluid interface: the fluid and the solid which forms the wall. The atoms of the solid form a lattice, oscillating around their lattice positions. In this perspective, a solid–fluid interface is similar to a liquid–vapour interface and the same molecular expressions apply. The description of the interface is greatly simplified if the solid atoms are frozen in at their lattice positions. This simplification alters the physics of the interface only marginally in many cases. Such a rigid lattice is no longer a part of the thermodynamic system but serves as a boundary condition for the fluid. The boundary condition appears as an external potential acting on the fluid particles and preventing them from escaping from the system. Microscopic expressions have to be adapted for such an inert wall.

This paper is addressed to the derivation of formal expressions for the surface tension and related quantities of an interface between a fluid and an inert wall. As a model for the wall we will consider two cases.

(a) The simplest model is a wall which is only a restriction on the positions of the fluid particles. The restriction is represented by an external potential which is zero at one side of the wall and infinite at the other side. This representation of a wall will be denoted as a 'hard wall'.

(b) A closer inert representation of a real wall is an external potential field which varies smoothly with the distance from the wall and the position along the wall. The latter variation models the lattice structure of the wall. Since a lattice is periodic, the external potential is taken to be periodic along the wall also. This model of the wall is denoted as a 'structured, soft wall'.

An example of a relation between a thermodynamic quantity and a microscopic quantity of a fluid is the connection between the density at a hard wall and the fluid's pressure. Approaching a hard wall from inside the fluid, the density of the fluid changes discontinuously from a finite value to zero in the wall. The finite, limiting value of the density is called the density at the hard wall, n_0. It is related to the pressure p of the fluid by [3]

$$p = k_B T n_0 \tag{1.1}$$

where k_B denotes Boltzmann's constant and T the temperature of the system. We call relations of this type between a thermodynamic quantity and the density of the fluid at a wall 'density expressions'.

In this example, the pressure is related to a surface property of the fluid. An example of a different kind is the classical relation [4] between the pressure and the pair correlation function of the bulk fluid, n_{2B}

$$p = k_B T n_B - \frac{2\pi}{3} \int_0^\infty dr\, r^3 \phi'(r) n_{2B}(r) \tag{1.2}$$

where n_B denotes the density of the bulk fluid, $\phi(r)$ the interparticle potential for two particles at a distance r and $\phi'(r)$ its derivative with respect to r. In this form, the relation holds for a three-dimensional fluid with central, pairwise additive interactions which is the type of fluid we will restrict ourselves to throughout this article. Relations such as (1.2), expressing a thermodynamic variable in essentially an integral over the pair correlation function, are called 'virial expressions'. Virial expressions can often be formulated in terms of a 'pressure tensor'. As an example, the virial expression for the surface tension of a hard wall, γ_h, located in the plane $z = 0$ with the fluid at $z > 0$, has the form [5]

$$\gamma_h = -k_B T \int_0^\infty dz\, (n(z) - n_B)$$
$$+ \frac{1}{2} \int_0^\infty dz_1 \int_{-\infty}^\infty dr_{12} \frac{\frac{1}{2}(x_{12}^2 + y_{12}^2)}{r_{12}} \phi'(r_{12})(n_2(z_1, z_2, r_{12}) - n_{2B}(r_{12})) \tag{1.3}$$

with $r_{12} = r_1 - r_2$, and n_2 is the pair correlation function. In terms of a pressure tensor, the relation is [5]

$$\gamma_h = -\int_0^\infty dz(p^T(z) - p) \tag{1.4}$$

where $p^T(z)$ denotes the component of a pressure tensor tangential to the hard wall at a distance z. The pressure tensor is defined in terms of the density and the pair correlation function (see below). Substitution of this definition transforms (1.4) back

into (1.3). Relations between thermodynamic variables and a pressure tensor are especially useful in simulations of fluids where the tensor can be measured explicitly [6]. We call such relations 'pressure expressions'.

Formal relations between thermodynamic and microscopic quantities such as (1.1)–(1.4) can be derived from a deformation of a vessel which contains the fluid and at the same time provides the wall-fluid interface. The deformation results in a change in the grand potential of the fluid which is thermodynamically expressed in terms of quantities like the pressure and surface tension. On the other hand, it is possible to express the change directly in microscopic quantities of the fluid. The equivalence of the two expressions leads to microscopic expressions for the thermodynamic quantities. This technique has been employed in various cases. A systematic evaluation of the deformation method has not been given and it is the purpose of this paper. We were confronted with this problem when we simulated fluids contained by structured, inert walls which require a delicate treatment of the microscopic expressions.

We will employ two microscopic expressions for the change in grand potential. The first expresses the change in grand potential in, essentially, the density at the hard walls. The expression gives rise to density expressions of the type (1.1). The second expresses the change in terms of a pressure tensor from which pressure expressions of the type (1.4) can be derived. In this paper, we will consider deformations of the vessel which result in an increase of the area of the vessel as well as an increase of the length of the edges. Therefore, the change in grand potential involves both the surface and the line tension and density and pressure expressions will be derived for both these quantities.

The deformation is applied to the two models of a wall we mentioned above. At first, a vessel of hard walls is considered and secondly, one of the hard walls is replaced by a structured, soft wall. We thus obtain density and pressure expressions for the surface tension of a hard wall and the line tension of an edge formed by two hard walls. In the case of the soft wall, we restrict ourselves to the surface tension since already at this level, a rigorous treatment of the effect of the structure turns out to be complicated.

The article is further organized in the following way. We introduce the concept of the pressure tensor and the two routes to the change in grand potential in section 2. Before we start the actual calculation, we give some comments on the definition of the surface and line tension in section 3. The first route to the change in grand potential is then exploited in section 4, which derives the density expressions. The second route is exploited in sections 5 and 6, in which the pressure expressions are presented. Section 5 treats the hard wall and the edge formed by two hard walls and section 6 treats the case of the structured soft wall. Finally, conclusions are drawn in section 7.

2. The pressure tensor and the change in grand potential

The concept of a pressure tensor has long been present in phenomenological descriptions of inhomogeneous fluids [4]. The concept has been formalized by Schofield and Henderson [7], who gave a microscopic definition of the tensor which they could link rigorously to the change in grand potential of a fluid. For a simple fluid, the microscopic definition is

$$\mathbf{p}(r) = k_{\mathrm{B}} T n(r) \mathbf{I} - \frac{1}{2} \int_{-\infty}^{\infty} \mathrm{d}r_1 \, \mathrm{d}r_2 \, \frac{r_{12}}{r_{12}} \, \phi'(r_{12}) n_2(r_1, r_2) \int_{C_{12}} \mathrm{d}l \, \delta(l - r) \quad (2.1)$$

where I denotes the unit tensor and C_{12} is a contour from r_2 to r_1. This contour can be chosen arbitrarily and therefore the pressure tensor is not defined uniquely. The most obvious choice for the contour is a straight line from r_2 to r_1, a choice which is referred to as the Irving and Kirkwood [8] (IK) tensor. An alternative choice has been investigated by Harasima [9] who took the contour to be a straight path from r_1 to (x_2, y_2, z_1) followed by a straight path to r_2. Clearly, each expression of a physical quantity in terms of a pressure tensor, like (1.4), must be independent of the choice of the tensor. It can furthermore be shown that the divergence of all tensors (2.1) satisfies

$$\nabla \cdot \mathbf{p}(r) = -n(r)\nabla \phi^{\text{ext}}(r) \tag{2.2}$$

where $\phi^{\text{ext}}(r)$ denotes the external potential acting on the fluid.

The tensor (2.1) can be used to describe the change in grand potential of a fluid when the container of the fluid is deformed. Schofield and Henderson discussed these deformations in the canonical ensemble, preserving the amount of particles in the system. It is, however, easy to show that the expression for the change in free energy that they obtain applies equally well to the change in grand potential. This thermodynamic potential has to be considered if the deformation is brought about in the grand canonical ensemble under constant chemical potential. Instead of considering the canonical partition function Z_N of a system of N particles

$$Z_N = \frac{1}{\Lambda^{3N} N!} \int_V dr_1, \ldots, dr_N \, e^{-\beta U_N} \tag{2.3}$$

where Λ denotes the thermic wavelength, U_N the energy of a configuration of N particles

$$U_N(r_1, \ldots, r_N) = \sum_{(i,j)} \phi(r_{ij}) + \sum_i \phi^{\text{ext}}(r_i) \tag{2.4}$$

one has to consider the grand canonical partition function Z_{gr} given by

$$Z_{\text{gr}} = 1 + \sum_{N=1}^{\infty} z^N Z_N \tag{2.5}$$

with z the activity, related to the chemical potential μ by

$$z = e^{\beta \mu}. \tag{2.6}$$

The grand potential is calculated from Z_{gr} as

$$\Omega = -k_B T \log Z_{\text{gr}}. \tag{2.7}$$

The integration volume V in (2.3) defines the position space in which the particles are allowed to move. If the external potential becomes strongly repulsive near the boundaries of V, the available position space is effectively defined by this potential since it prevents particles from intruding up to the boundaries. The volume is then bounded by soft walls and the precise location of the boundaries of V does not influence the physical behaviour of the system. If there is no external potential to prevent the particles from reaching the boundaries of V, the volume is bounded by hard walls. In this case, the boundaries of V, i.e. the position of the hard walls, cannot be changed without changing the physical behaviour of the system. In general, the volume can be bounded by a combination of soft and hard walls.

Schofield and Henderson considered the change in the partition function under an infinitesimal deformation of the integration volume V. The deformation is described

by an infinitesimally small displacement field $u(r)$ which shifts the boundaries of V from their original positions $\{r\}$ to new positions $\{r + u(r)\}$. We consider only cases in which ϕ^{ext} is not affected by the application of a displacement field, which implies that any soft wall remains in place and the deformation affects the hard walls only. The change in grand potential can, up to order u, be described by the one- and two-particle correlation function

$$\mathrm{d}\Omega = \int_V \mathrm{d}r(-k_B T \nabla \cdot u(r) + u(r) \cdot \nabla \phi^{\text{ext}}(r)) n(r)$$

$$+ \frac{1}{2} \int_V \mathrm{d}r_1\, \mathrm{d}r_2 (u(r_1) - u(r_2)) \frac{r_{12}}{r_{12}} \phi'(r_{12}) n_2(r_1, r_2). \tag{2.8}$$

However, it can equally well be described [7] by the pressure tensor (2.1)

$$\mathrm{d}\Omega = -\int_V \mathrm{d}r(\mathbf{p}(r) : \nabla u(r) - n(r)u(r) \cdot \nabla \phi^{\text{ext}}(r))$$

$$+ \int_{\partial V} \mathrm{d}S(\mathbf{p}(r) - k_B T n(r)\mathbf{I}) \cdot u(r). \tag{2.9}$$

The second integral is over the surface of V. If the surface is shielded by a soft wall, the density at the surface will be zero since particles never reach the boundary of V in that case. Therefore, for any reasonable choice of contour, the pressure tensor will also be zero at a soft wall, and thus soft walls do not contribute to the surface integral. At a hard wall, the pressure tensor $\mathbf{p}(r)$ becomes equal to $k_B T n(r)\mathbf{I}$ for a large class of contours. Each contour which does not intersect the wall belongs to this class. Note that the IK and the Harasima tensor both fulfil this condition (if the walls are in the xy, xz or yz plane). Therefore, for this class of tensors, hard walls also do not contribute to the surface integral which then does not contribute to $\mathrm{d}\Omega$ at all. So the change in grand potential is, up to first order in u, fully given by

$$\mathrm{d}\Omega = -\int_V \mathrm{d}r(\mathbf{p}(r) : \nabla u(r) - n(r)u(r) \cdot \nabla \phi^{\text{ext}}(r)) \tag{2.10}$$

if the pressure tensor at a hard wall ∂V_h reduces to

$$\mathbf{p}(r, \partial V_h) = k_B T n(r, \partial V_h)\mathbf{I}. \tag{2.11}$$

We will restrict ourselves to tensors satisfying (2.11) in the remaining part of this paper, which means that only reasonably simple contours will be considered, typical examples of which are the IK and the Harasima contour.

Equation (2.10) is what we referred to as the 'pressure route' to $\mathrm{d}\Omega$. The 'density route' to $\mathrm{d}\Omega$ is easily obtained from (2.9) if the combination $n\nabla \phi^{\text{ext}}$ is replaced by $-\nabla \cdot \mathbf{p}$, in accordance with (2.2). Partial integration of the resulting term gives

$$\mathrm{d}\Omega = -k_B T \int_{\partial V} \mathrm{d}S \cdot u(r)n(r) \tag{2.12}$$

which expresses $\mathrm{d}\Omega$ entirely in terms of the density at the wall. The equation shows that if the volume is bounded by soft walls everywhere, the grand potential does not change since the density vanishes at a soft wall. This must be so because in that case the boundaries of V can be distorted without changing the physical behaviour of the system. Equation (2.12) also shows that $\mathrm{d}\Omega$ does not depend on the value of u in the

interior of V. This reflects the fact that the deformation is determined by the value of u at the boundary of V only. In particular, Ω does not change if u vanishes at the boundary of V since in that case, the integration volume is not distorted at all. Equations (2.8), (2.10) and (2.12) denote three different but equally valid ways to express the change in grand potential under a deformation u of the boundaries of the fluid.

3. The definition of the surface and line tension

Consider a fluid in a three-dimensional, rectangular box which consists of hard walls. The grand potential of the fluid is defined by (2.3)-(2.7) with $\phi^{\text{ext}}(r) = 0$. As we mentioned in section 1, the surface tension γ_h of the hard walls and the line tension τ_{hh} of the edges of the box can be defined from the change in the grand potential under a well chosen deformation of the box. An alternative definition of these quantities is obtained from a decomposition of the grand potential in terms of the order of the volume V, the size of the surface A_h, and the length of the edges L_{hh} of the box

$$\Omega = \Omega_V + \Omega_S + \Omega_E. \tag{3.1}$$

Expansion (3.1) could become ambiguous if p and γ_h depend too strongly on the system size, e.g., approach their thermodynamic value inversely proportional to the linear size of the system. If, however, p and γ_h in a finite system are defined in terms of local quantities such as in (1.2) and (1.4), it is reasonable to assume that the influence of the size of the system is exponentially small. This assumption does probably not hold near criticality, where the distinction between pressure and surface tension should be carefully reanalysed, which is beyond the scope of this paper.

To be complete, we should have added a term of order 1 to (3.1) to include the contributions of the corners of the box to the grand potential. Such contributions, however, will not be studied in this article and therefore we neglect them. Ω_V, Ω_S and Ω_E define the pressure, surface tension and line tension

$$\Omega_V = -pV \tag{3.2}$$

$$\Omega_S = \gamma_h A_h \tag{3.3}$$

$$\Omega_E = \tau_{hh} L_{hh}. \tag{3.4}$$

The geometry of the box is the geometry of the integration volume in (2.3). Changes in the volume induce changes in the grand potential. Consequently, the proportionality factors p, γ_h and τ_{hh} are unambiguously defined.

These notions may appear somewhat trivial but more care is needed when soft walls are involved. Consider the same box as before with one of the hard walls, taken to be in the plane $z = 0$, replaced by a soft wall. Contributions from the hard wall to the grand potential must now be distinguished from contributions from the soft wall

$$\Omega_S = \gamma_s A_s + \gamma_h A_h \tag{3.5}$$

with γ_s and A_s the surface tension and the area of the soft wall. Similarly, the contributions from the edges formed by two hard walls must be distinguished from the contributions from the edges formed by a hard and a soft wall

$$\Omega_E = \tau_{sh} L_{sh} + \tau_{hh} L_{hh} \tag{3.6}$$

with τ_{sh} and L_{sh} the line tension and length of the edges formed by a hard and a soft wall. Contrary to the previous case, the lower limit on the z-integrations in (2.3) can be shifted without affecting Z_N. The geometry of the box, however, does change under such a shift. If the lower boundary is shifted from $z = 0$ to $z = \delta z$, the geometric changes in the box are

$$\delta V = -A_s \,\delta z \qquad \delta A_s = 0 \qquad \delta A_h = -L_{sh}\,\delta z$$
$$\delta L_{sh} = 0 \qquad \delta L_{hh} = -4\delta z \qquad\qquad (3.7)$$

so

$$\delta \Omega_V = p \,\delta z \, A_s \qquad\qquad (3.8)$$

$$\delta \Omega_S = \delta \gamma_s \, A_s - \gamma_h \,\delta z \, L_{sh} \qquad\qquad (3.9)$$

$$\delta \Omega_E = \delta \tau_{sh} \, L_{sh} - 4 \,\tau_{hh} \,\delta z. \qquad\qquad (3.10)$$

Note that p, γ_h and τ_{hh} do not change because they were completely specified by the temperature and the chemical potential, which remain of course unaltered by the shift δz in the boundary of the box. Since Z_N does not change, the grand potential of the fluid does not change. Adding (3.8), (3.9) and (3.10) gives

$$\delta \Omega = (p\delta z + \delta \gamma_s)A_s + (\gamma_h \delta z - \delta \tau_{sh})L_{sh} + O(1) = 0. \qquad\qquad (3.11)$$

In (3.11) we have neglected the term $\tau_{hh}\delta z$ which is of the order 1. The two terms in (3.11) are of a different orders of magnitude and must vanish separately

$$\delta \gamma_s = -p \,\delta z \qquad\qquad (3.12)$$

$$\delta \tau_{sh} = \gamma_h \,\delta z. \qquad\qquad (3.13)$$

These equations demonstrate that the magnitude of γ_s and τ_{sh} depends on the location of the lower boundary $z = 0$ of the box. The dependence is trivial in the sense that, e.g., γ_s varies linearly with the position of the boundary with a coefficient which is not an intrinsic property of the surface but can be determined from the bulk state of the fluid alone. Note also that in, e.g., the study of surface phenomena at a fixed wall the absolute value of the surface tension is never of importance but only the difference in surface tension between competing interfaces. For instance, in the wetting problem, the coexisting liquid and vapour phases, competing to wet the wall, both have the same bulk pressure p and thus the difference in surface tension is independent of the location of the lower boundary $z = 0$. Although the dependence of γ_s and τ_{sh} on the location of the boundary forces one to treat the boundary carefully, they remain central parameters in the description of interfaces and contact lines.

4. Density expressions

Relations between thermodynamic and microscopic quantities of the fluid will be obtained from deformations of the box which contains the fluid. The box we will use throughout this paper has dimensions $0 \leq x, y, z \leq L$. The wall in the plane $z = 0$ is the wall of interest. It will be taken to be a hard wall in this section. The five remaining walls will always be taken to be hard walls. The box is deformed according to the displacement field

$$\mathbf{u}(\mathbf{r}) = \lambda\,(x - L, y - L, z). \qquad\qquad (4.1)$$

The parameter λ makes u infinitesimally small. This displacement field transforms the box from a cube with edge length L to a cube with edge $(1+\lambda)L$. To obtain density expressions, expression (2.12) for the change in grand potential is exploited, which expresses the change in the density at the walls

$$d\Omega = -k_B T \int_{\partial V} dS \cdot u(r) n(r). \tag{4.2}$$

The product $dS \cdot u$ vanishes at the planes $x = L$, $y = L$, and $z = 0$. Only the three remaining walls contribute to the integral (4.2).

The change in grand potential in this box with six hard walls is given by

$$d\Omega = -p\, dV + \gamma_h\, dA_h + \tau_{hh}\, dL_{hh}. \tag{4.3}$$

With displacement field (4.1), the changes are

$$dV = 3\lambda L^3 \qquad dA_h = 12\lambda L^2 \qquad dL_{hh} = 12\lambda L. \tag{4.4}$$

The thermodynamic expression (4.3) for $d\Omega$ has to be compared with the microscopic expression (4.2). The three walls that contribute to (4.2) give the same contribution. Take the wall $x = 0$ as an example:

$$d\Omega = -3k_B T\lambda L \int_0^L dy \int_0^L dz\, n(0, y, z). \tag{4.5}$$

Note that the thermodynamic expression (4.3) consists of different orders of L. The term of order L^3 determines p, the term of order L^2 determines γ_h and the term of order L determines τ_{hh}. We also decompose (4.5) in orders of L. The decomposition is obtained from a decomposition of the density. Define the density at the wall, n_w

$$n_w(y, z) = n(0, y, z). \tag{4.6}$$

This density has a constant value n_0 far away from the edges and corners at the wall $x = 0$. The density is distorted by the presence of neighbouring walls within some microscopic length ζ of the edges. The distortion near an edge, far away from a corner, is denoted Δn_h. The additional distortions near a corner are denoted Δn_{hh}. The decomposition of n_w has the form

$$n_w(y, z) = n_0 + \Delta n_h(y) + \Delta n_h(z) + \Delta n_{hh}(y, z) \tag{4.7}$$

where $\Delta n_h(y)$ denotes the correction near an edge formed with a wall in the xz plane, $\Delta n_h(z)$ the correction near an edge formed with a wall in the xy plane. A correction term vanishes if its argument, or one of its arguments, is chosen far away from the edges. We denote such positions, $\zeta \ll y$, $z < \frac{1}{2}L$, as y, z approaching infinity. Taking, e.g., y and z to infinity, (4.7) gives the definition of n_0

$$n_0 = n_w(\infty, \infty). \tag{4.8}$$

Taking only y to infinity, (4.7) gives the definition of $\Delta n_h(z)$

$$\Delta n_h(z) = n_w(\infty, z) - n_0 \tag{4.9}$$

while Δn_{hh} is defined by (4.7) itself. Substitution of decomposition (4.7) into (4.5) gives

$$d\Omega = -\lambda k_B T 3L \left(\int_0^L dy\, dz\, n_0 + 2 \int_0^\infty dy \int_0^L dz\, \Delta n_h(y) + 2 \int_0^\infty dz \int_0^L dy\, \Delta n_h(z) \right.$$

$$\left. + 4 \int_0^\infty dy \int_0^\infty dz\, \Delta n_{hh}(y, z) \right). \tag{4.10}$$

The factor of 2 in front of the integral over Δn_h accounts for the fact that there are two walls in both the xz and xy plane bordering on the wall at $x = 0$. The factor of 4 in front of the integral over Δn_hh accounts for the fact that there are four corners at this wall. The symmetry between the walls implies that the integral over $\Delta n_\text{h}(y)$ gives the same contribution to $d\Omega$ as the integral over $\Delta n_\text{h}(z)$. Decomposition (4.10) is the decomposition of $d\Omega$ in orders of L

$$d\Omega = -\lambda k_\text{B} T 3 L \left(L^2 n_0 + 4L \int_0^\infty dz\, \Delta n_\text{h}(z) + 4 \int_0^\infty dy\, dz\, \Delta n_\text{hh}(y, z) \right) \tag{4.11}$$

comparison with (4.3) shows that

$$p = k_\text{B} T n_0 \tag{4.12}$$

$$\gamma_\text{h} = -k_\text{B} T \int_0^\infty dz\, \Delta n_\text{h}(z) \tag{4.13}$$

$$\tau_\text{hh} = -k_\text{B} T \int_0^\infty dy \int_0^\infty dz\, \Delta n_\text{hh}(y, z) \tag{4.14}$$

which are the desired density expressions. The first of these was already quoted in (1.1). It is seen to be the first of a hierarchy of three which relate the pressure, surface tension and line tension to the density at a hard wall.

These density expressions do not only exist in the case of corners and edges formed by hard walls. It can be shown in the same manner that the molecular expressions (4.13) and (4.14) also apply when the hard wall at $z = 0$ is replaced by a 'structureless soft wall'. This is a representation of a wall as an external field which varies smoothly with the distance from the wall but which does not vary along the wall. In the structureless, soft wall case, γ_h in (4.13) should be replaced by γ_s, the surface tension of a structureless soft wall, and τ_hh in (4.14) by τ_sh, the line tension of an edge formed by a hard and a structureless soft wall. We will stipulate in section 6 that density expressions also hold in case when the wall at $z = 0$ is a structured soft wall, but that they are more complicated.

In general, we can therefore state that the deviations of the density at a hard wall near an edge formed by the hard wall and a second wall are related to the surface tension of that second wall. Similarly, the deviations of the density at a hard wall near a corner formed with two other walls are related to the line tension of the edge formed by the two other walls.

Finally, note that the density at a soft wall can also be related to thermodynamic quantities of the fluid. Such density expressions can be derived from a deformation which also shifts these walls. In that case, the displacement field does not only affect the boundaries of V but also the external potential which forms the soft wall. An extra term must be added to (2.12) to account for this shift, and density expressions can then be derived from the modified (2.12) in the way demonstrated here. As an example, one easily notices that the relation between the pressure and the density near a structureless, soft wall is given by

$$p = -\int_0^\infty dz\, n(z) \frac{\partial}{\partial z} \phi^\text{ext}(z) \tag{4.15}$$

since the RHS denotes the force per unit of area which the wall exerts on the fluid.

5. Pressure expressions for the surface and line tension: hard wall

In this section, we exploit route (2.10) to the change in grand potential which leads to relations between thermodynamic quantities and the pressure tensor of the fluid. The box and displacement field are the same as in section 4. The wall in the plane $z = 0$ is taken to be a hard wall in this section.

The thermodynamic expression for $d\Omega$ is given by (4.3) while on the other hand, equation (2.10) with $\phi^{ext}(r) = 0$, states

$$d\Omega = -\int_V dr \, \mathbf{p}(r) : \nabla u(r). \tag{5.1}$$

With displacement field (4.1), the tensor ∇u has the simple form

$$\nabla u(r) = \lambda \mathbf{I}. \tag{5.2}$$

Our strategy is the same as in the previous section: we split the microscopic expression (5.1) in orders of L. On comparison with (4.3), the term of order L^2 gives the microscopic definition of γ_h, the term of order L the definition of τ_{hh}. The decomposition of (5.1) in orders of L is obtained from a decomposition of the pressure tensor.

This decomposition is similar to the decomposition of n_w of the previous section. The tensor is translationally invariant and isotropic in the bulk fluid

$$\mathbf{p}_B = p\mathbf{I} \tag{5.3}$$

where p denotes, as usual, the bulk pressure. Near the walls, within some microscopic length ζ, $\mathbf{p}$ deviates from $\mathbf{p}_B$. The deviation near a wall, far away from edges and corners, is denoted as $\Delta\mathbf{p}_h$. The additional deviations near an edge are denoted as $\Delta\mathbf{p}_{hh}$. The influence of the corners is denoted as $\Delta\mathbf{p}_{hhh}$. The decomposition of $\mathbf{p}$ in the corner $x, y, z \geq 0$ has the form

$$\mathbf{p}(r) = \mathbf{p}_B + \Delta\mathbf{p}_h(x) + \Delta\mathbf{p}_h(y) + \Delta\mathbf{p}_h(z) + \Delta\mathbf{p}_{hh}(x, y) + \Delta\mathbf{p}_{hh}(x, z)$$
$$+ \Delta\mathbf{p}_{hh}(y, z) + \Delta\mathbf{p}_{hhh}(x, y, z). \tag{5.4}$$

The correction terms $\Delta\mathbf{p}$ vanish if one of their arguments is taken far away from the walls. We denote such positions, $\zeta \ll x, y, z < \frac{1}{2}L$, as x, y, z approach infinity. With x, y and z in this limit, (5.4) becomes the definition of $\mathbf{p}_B$

$$\mathbf{p}_B = \mathbf{p}(\infty, \infty, \infty). \tag{5.5}$$

Taking x and y to infinity, one obtains the definition of $\Delta\mathbf{p}_h$

$$\Delta\mathbf{p}_h(z) = \mathbf{p}(\infty, \infty, z) - \mathbf{p}_B. \tag{5.6}$$

Taking only x to infinity, one obtains the definition of $\Delta\mathbf{p}_{hh}$

$$\Delta\mathbf{p}_{hh}(y, z) = \mathbf{p}(\infty, y, z) - \mathbf{p}_B - \Delta\mathbf{p}_h(y) - \Delta\mathbf{p}_h(z). \tag{5.7}$$

The definition of $\Delta\mathbf{p}_{hhh}$ is (5.4) itself. The decomposition (5.4) of the pressure tensor is inserted in (5.1). This integral splits in an integral involving $\mathbf{p}_B$, six integrals involving $\Delta\mathbf{p}_h$ (resulting from the deviations of $\mathbf{p}$ near the walls), twelve integrals involving $\Delta\mathbf{p}_{hh}$ (from the deviations near the edges) and eight integrals involving $\Delta\mathbf{p}_{hhh}$ (from the deviations near the corners). The six integrals involving $\Delta\mathbf{p}_h$ give the same contribution to $d\Omega$ by symmetry. We take the deviations near the wall $z = 0$ as exemplary. Similarly, we take the deviations near the edge formed by the wall at $z = 0$ and $y = 0$ as exemplary

for the twelve edges. The corner formed by these two walls and the wall at $x = 0$ is taken as exemplary for the eight corners. The decomposition of (5.1) has the form

$$d\Omega = -\lambda \left(\int_0^L dx \int_0^L dy \int_0^L dz \, \mathbf{p}_B : \mathbf{1} + 6 \int_0^L dx \int_0^L dy \int_0^\infty dz \, \Delta\mathbf{p}_h(z) : \mathbf{1} \right.$$

$$+ 12 \int_0^L dx \int_0^\infty dy \int_0^\infty dz \, \Delta\mathbf{p}_{hh}(y, z) : \mathbf{1}$$

$$\left. + 8 \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \, \Delta\mathbf{p}_{hhh}(x, y, z) : \mathbf{1} \right) \tag{5.8}$$

$$\equiv d\Omega_B + d\Omega_h + d\Omega_{hh} + d\Omega_{hhh} \tag{5.9}$$

(5.9) is the expansion of $d\Omega$ in orders of L. With the definition of $\mathbf{p}_B$, (5.3), the first term is easily calculated

$$d\Omega_B = -\lambda p L^3. \tag{5.10}$$

Compared with the term of order L^3 in (4.3), (5.10) shows that the constant p which defines $\mathbf{p}_B$ is indeed equal to the pressure of the fluid. The second term, $d\Omega_h$, is

$$d\Omega_h = -6\lambda L^2 \int_0^\infty dz (\Delta p_h^{xx}(z) + \Delta p_h^{yy}(z) + \Delta p_h^{zz}(z)) \tag{5.11}$$

which is of the order L^2. The third term, $d\Omega_{hh}$, is

$$d\Omega_{hh} = -12\lambda L \int_0^\infty dy \int_0^\infty dz (\Delta p_{hh}^{xx}(y, z) + \Delta p_{hh}^{yy}(y, z) + \Delta p_{hh}^{zz}(y, z)) \tag{5.12}$$

which is of order L. The last term, $d\Omega_{hhh}$, is

$$d\Omega_{hhh} = -8\lambda \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz (\Delta p_{hhh}^{xx}(x, y, z) + \Delta p_{hhh}^{yy}(x, y, z)$$

$$+ \Delta p_{hhh}^{zz}(x, y, z)) \tag{5.13}$$

which is of the order L^0. First, we will discuss the term $d\Omega_h$ to extract the definition of γ_h.

Comparison of $d\Omega_h$ with the term of order L^2 in the thermodynamic expression for $d\Omega$, (4.3), gives for the microscopic definition of γ_h

$$\gamma_h = \frac{1}{2} \int_0^\infty dz (\Delta p_h^{xx}(z) + \Delta p_h^{yy}(z) + \Delta p_h^{zz}(z)). \tag{5.14}$$

This expression can be simplified. It can be shown that the term Δp_h^{zz} vanishes (see (A1.1) in appendix 1) while $\Delta p_h^{xx}(z) = \Delta p_h^{yy}(z)$ by symmetry. We define

$$\Delta p_h^{xx}(z) = \Delta p_h^{yy}(z) \equiv \Delta p_h^T(z) \tag{5.15}$$

and (5.14) simplifies to

$$\gamma_h = -\int_0^\infty dz \, \Delta p_h^T(z). \tag{5.16}$$

In terms of p^T and p it has the form

$$\gamma_h = -\int_0^\infty dz (p^T(\infty, \infty, z) - p). \tag{5.17}$$

This form is the usual expression [4] for γ_h. It was already mentioned, in a slightly different notation, in (1.4). Before we proceed to the term of order L in $d\Omega$, we will derive an extension of (5.16) or (5.17).

The path of integration in (5.16) and (5.17) must be taken far away from the edges of the system. The deviation of p^T from its bulk value p results from the presence of the wall at $z = 0$ only. We ask the question what happens if the path of integration is chosen close to an edge and the influence of the edge on $\mathbf{p}$ is taken into account. Consider, as an example, the edge formed by the walls at $y = 0$ and $z = 0$. Define

$$\gamma_h^{yy}(y) = -\int_0^\infty dz(\Delta p_h^{yy}(z) + \Delta p_{hh}^{yy}(y, z)). \tag{5.18}$$

The integrand of (5.18) is

$$\Delta p_h^{yy}(z) + \Delta p_{hh}^{yy}(y, z) = p^{yy}(\infty, y, z) - p. \tag{5.19}$$

Identity (A1.2) in appendix 1 shows that

$$\gamma_h^{yy}(y) = \gamma_h \tag{5.20}$$

for all distances y. For large y, the term Δp_{hh}^{yy} vanishes and (5.18) reduces to (5.16). At the hard wall $y = 0$, p^{yy} is equal to $k_B T$ times the density at the wall, cf (2.11), and (5.18) becomes the density expression (4.13). Expression (5.18) is a generalization which contains both the pressure expression (5.17), at $y = \infty$, and the density expression (4.13), at $y = 0$.

We proceed with the term of order L in (5.9), $d\Omega_{hh}$ given by (5.12). Comparison with the term of order L in the thermodynamic expression for the change in grand potential, (4.3), gives the microscopic definition of τ_{hh}

$$\tau_{hh} = -\int_0^\infty dy \int_0^\infty dz(\Delta p_{hh}^{xx}(y, z) + \Delta p_{hh}^{yy}(y, z) + \Delta p_{hh}^{zz}(y, z)). \tag{5.21}$$

The second and third terms in the integral vanish (see (A1.2)) and the definition of τ_{hh} simplifies to

$$\tau_{hh} = -\int_0^\infty dy \int_0^\infty dz\, \Delta p_{hh}^{xx}(y, z) \tag{5.22}$$

which has precisely the same structure as the definition (5.16) of γ_h.

The plane of integration in (5.22) is taken far away from a corner: the integrand is determined by the presence of the edge alone. Analogous to the case of the surface tension, the plane of integration in (5.22) can be taken close to a corner. One can show this by defining

$$\gamma_{hh}^{xx}(x) = -\int_0^\infty dy \int_0^\infty dz(\Delta p_{hh}^{xx}(y, z) + \Delta p_{hhh}^{xx}(x, y, z)) \tag{5.23}$$

and demonstrating (see (A1.3)) that $\tau_{hh}^{xx}(x)$ is independent of x:

$$\tau_{hh}^{xx}(x) = \tau_{hh}. \tag{5.24}$$

In the limit that x is large, Δp_{hhh}^{xx} vanishes and (5.23) reduces to (5.22). At the wall $x = 0$, p^{xx} satisfies (2.11) and (5.23) reduces to density expression (4.14). τ_{hh}^{xx} plays the same role for the line tension as γ_h^{yy} played for the surface tension. It can be regarded as an expression that interpolates between the density expression (4.14), at $x = 0$, and the pressure expression (5.22), at $x = \infty$.

Finally, we consider the term of order L^0, $d\Omega_{hhh}$, in (5.9) which is defined in (5.12). Identity (A1.3) tells that the integral over each term in the integrand of (5.12) vanishes

$$d\Omega_{hhh} = 0 \tag{5.25}$$

in accordance with the fact that no terms of the order L^0 appears in the thermodynamic expression for the change in grand potential, (4.3). These terms are absent because the corners are not deformed by displacement field (4.1).

6. Surface tension of a structured wall

Up till now, we have restricted ourselves to hard walls. The case of a structured, soft wall will be treated in this section in which we focus on the pressure expressions. Density expressions also exist but are far less elegant than in the structureless case, as we discuss below. Moreover, the discussion will be restricted to the level of the surface tension alone since already at this level, the calculation is much more complicated than for the hard wall.

The box and displacement field are the same as in the previous sections with the wall at $z = 0$ replaced by a structured, soft wall. Such a wall is periodic and we denote the length of the period in the x direction by a_x, the length in the y direction is a_y. The change in grand potential upon the deformation equals

$$d\Omega = -p\, dV + \gamma_{st}(L)\, dA_{st} + \gamma_h\, dA_h + O(L) \tag{6.1}$$

$$\equiv d\Omega_B + d\Omega_{st} + d\Omega_h + O(L). \tag{6.2}$$

A_{st} denotes the surface of a structured wall, γ_{st} its surface tension (the subscript st stands for 'structured'). Terms of the order L are neglected since we restrict the discussion to the level of the surface tension. The increase dV is the same as previously, A_{st} and A_h change as

$$dA_{st} = 2\lambda\, L^2 \qquad dA_h = 10\lambda\, L^2. \tag{6.3}$$

Because of the structure of the wall, the change in grand potential under an infinitesimal shift of the boundary planes at $x, y = 0$ will depend on the location of these planes. The walls at $x = L$ and $y = L$ remain in place under displacement field (4.1). The shift defines a 'partial surface tension' $\gamma_{st}(L)$. To obtain the 'full' surface tension γ_{st} of the structured wall, one should consider an increase of A_{st} with an integer number of units of area $a_x \times a_y$. This increase is most easily visualized if $a_x = a_y = a$, in which case one can simply increase L with a periodic length a. For simplicity, we consider this case; the case $a_x \neq a_y$ presents no conceptual difficulties. From time to time, we will again distinguish in the notation between a_x and a_y to show what the result is for the general case.

Considering an increase of L with one period, the increase of A_{st} equals

$$\Delta A_{st} = 2aL + O(L^0) \tag{6.4}$$

and the surface tension of the structured wall is

$$\gamma_{st} = \frac{1}{\Delta A_{st}} \int_L^{L+a} dL' \left(\frac{d\Omega_{st}}{dL'} \right) = \frac{1}{a} \int_L^{L+a} dL'\, \gamma_{st}(L') + O(L^{-1}) \tag{6.5}$$

using that $d\Omega_{st} = 2\lambda\, \gamma_{st}(L')L'^2$ and $dL' = \lambda L'$. The term of order L^{-1} vanishes in the thermodynamic limit.

If we try to obtain a density expression for the surface tension of a structured wall, we readily find that the density at the hard walls is related to $\gamma_{st}(L)$. Therefore, a density expression for γ_{st} also incorporates a shift of the walls over a complete periodic length. In other words, the density expression incorporates an average over all possible locations of the hard wall within a period a as in (6.5). This average makes the density expression far less elegant than the density expression (4.13) for a hard wall. This is the reason why we do not consider them further.

The microscopic expression (2.10) for the change in grand potential contains the extra term $nu \cdot \nabla \phi^{ext}$ as compared to (5.1). With displacement field (4.1) it takes the form

$$u(r) \cdot \nabla \phi^{ext}(r) = \lambda \left((x - L) \frac{\partial}{\partial x} \phi^{ext}(r) + (y - L) \frac{\partial}{\partial y} \phi^{ext}(r) + z \frac{\partial}{\partial z} \phi^{ext}(r) \right). \tag{6.6}$$

The pressure tensor is decomposed in the same fashion as in (5.4) but one has to distinguish between distortions of $\mathbf{p}$ near the hard walls and distortions near the soft wall. The distortions near the soft wall, far away from the corners and edges, are denoted $\Delta \mathbf{p}_s$. The distortions near an edge formed by the soft and a hard wall are denoted $\Delta \mathbf{p}_{sh}$. The distortions near a corner formed by two hard walls and the soft wall are denoted $\Delta \mathbf{p}_{shh}$. Decomposition (5.4) is replaced by

$$\mathbf{p}(x, y, z) = \mathbf{p}_B + \Delta \mathbf{p}_h(x) + \Delta \mathbf{p}_h(y) + \Delta \mathbf{p}_s(x, y, z) + \Delta \mathbf{p}_{hh}(x, y) + \Delta \mathbf{p}_{sh}^{(1)}(x, y, z)$$
$$+ \Delta \mathbf{p}_{sh}^{(2)}(x, y, z) + \Delta \mathbf{p}_{shh}(x, y, z). \tag{6.7}$$

Note that the correction terms $\Delta \mathbf{p}$ involving the soft wall are functions of all three coordinates x, y, z, due to the periodicity of the wall. Therefore, we have to distinguish between $\Delta \mathbf{p}_{sh}^{(1)}$ referring to the edge formed by the walls at $z = 0$ and $x = 0$ and $\Delta \mathbf{p}_{sh}^{(2)}$ referring to the edge formed by the walls at $z = 0$ and $y = 0$. The correction terms vanish far away from the walls, at positions $\zeta < x, y, z < \frac{1}{2}L$ which we denote as $(\tilde{x}, \tilde{y}, \infty)$. Taking, e.g., x and y far away from the hard walls, (6.7) gives the definition of $\Delta \mathbf{p}_s$

$$\Delta \mathbf{p}_s(\tilde{x}, \tilde{y}, z) = \mathbf{p}(\tilde{x}, \tilde{y}, z) - \mathbf{p}_B. \tag{6.8}$$

The periodicity of ϕ^{ext} is reflected in $\Delta \mathbf{p}_s$: it is a periodic function with, in the general case $a_x \neq a_y$, a period a_x in the x direction and a_y in the y direction.

Inserting the decomposition of $\mathbf{p}$ in (2.10), we obtain decomposition (6.2) of $d\Omega$ with $d\Omega_B$ given by (5.8) and

$$d\Omega_h = -5 \int_0^L dx \int_0^\infty dy \int_0^L dz \, \Delta \mathbf{p}_h : \nabla u \tag{6.9}$$

$$d\Omega_{st} = -\int_0^L dx \int_0^L dy \int_0^\infty dz (\Delta \mathbf{p}_s : \nabla u - nu \cdot \nabla \phi^{ext}). \tag{6.10}$$

Note that we did not decompose the density but included the term $nu \cdot \nabla \phi^{ext}$ in (2.10) completely in $d\Omega_{st}$. As it will turn out, we can do so as long as we restrict the discussion to the level of the surface tension. The correction terms $\Delta \mathbf{p}$ that involve edges or corners contribute to the order L just as in the previous section and are therefore not evaluated any further.

There are five terms $\Delta \mathbf{p}_h$, from the five hard walls. They contribute equally to $d\Omega$ and we took the plane $y = 0$ as an example to represent $d\Omega_h$. With (5.2), this contribution is

$$d\Omega_h = -\lambda 5L^2 \int_0^\infty dy (\Delta p_h^{xx}(y) + \Delta p_h^{yy}(y) + \Delta p_h^{zz}(y)). \tag{6.11}$$

From (5.14) we find

$$d\Omega_h = \lambda \gamma_h 10 L^2 \tag{6.12}$$

which shows that the definition (6.9) of $d\Omega_h$ is indeed equal to the original definition in (6.2). The remaining term of order L^2 in the thermodynamic expression (6.2), $d\Omega_{st}$, must therefore be equal to (6.10).

The factor $u \cdot \nabla \phi^{ext}$ in $d\Omega_{st}$ consists of three terms: besides the term involving $z\partial_z$, the structured character of the wall has introduced a term involving $(x - L)\partial_x$ and $(y - L)\partial_y$ (see (6.6)). The integral over $nz\partial_z\phi^{ext}$ is easily evaluated. This integrand is periodic far away from the hard walls. Therefore, all units of area far away from the hard walls contribute equally to the integral, which is thus of order L^2. Similarly, all units of area far away from the hard walls contribute equally to the integral over $\Delta \mathbf{p}_s : \nabla u$, which is therefore also of order L^2.

The integrals over $n(x - L)\partial_x\phi^{ext}$ and $n(y - L)\partial_y\phi^{ext}$ are more difficult to evaluate. These integrands are not periodic and, moreover, they become of order L near the walls at $x = 0$ and $y = 0$, respectively. Therefore, it seems as if the integrals are of order L^3. This is, however, not the case: one can prove that although the integrands are not periodic, each unit of area far away from the hard walls still gives the same contribution to the integral. This follows immediately from the fact that the integrals of $n\partial_x\phi^{ext}$ and $n\partial_y\phi^{ext}$ over a unit of area in the middle of the soft wall vanish (see (A2.1)). As all units of area far away from the hard walls contribute equally to the integrals over $n(x - L)\partial_x\phi^{ext}$ and $n(y - L)\partial_y\phi^{ext}$, these integrals are of order L^2. The fact that the integrand becomes of order L gives these integrals a remarkable feature: the deviations of the density near the walls at $x = 0$ and $y = 0$ contribute to the order L^2. We therefore split $d\Omega_{st}$ into two terms

$$d\Omega_{st} = -L^2 \frac{1}{a_x a_y} \int_{cell} dx\, dy \int_0^\infty dz (\Delta \mathbf{p}_s(\mathbf{r}) : \nabla u - \lambda z n_s(\mathbf{r}) \frac{\partial}{\partial z} \phi^{ext}(\mathbf{r}))$$

$$+ \lambda \int_0^L dx \int_0^L dy \int_0^\infty dz\, n(\mathbf{r}) \left((x - L)\frac{\partial}{\partial x} + (y - L)\frac{\partial}{\partial y} \right) \phi^{ext}(\mathbf{r}) + O(L) \tag{6.13}$$

where a cell stands for an area $a_x \times a_y$ far away from the hard walls. n_s denotes the density at positions far away from the hard walls, such that the density is affected by the soft wall only. Dividing (6.13) by $2\lambda L^2$, we obtain from (6.1)

$$\gamma_{st}(L) = -\frac{1}{2a_x a_y} \int_{cell} dx\, dy \int_0^\infty dz \left(\Delta p_s^{xx} + \Delta p_s^{yy} + \Delta p_s^{zz} - z n_s \frac{\partial}{\partial z} \phi^{ext} \right)$$

$$+ \frac{1}{2L^2} \int_0^L dx \int_0^L dy \int_0^\infty dz\, n \left((x - L)\frac{\partial}{\partial x} + (y - L)\frac{\partial}{\partial y} \right) \phi^{ext} + O(L^{-1}). \tag{6.14}$$

To obtain γ_{st}, $\gamma_{st}(L')$ has to be averaged over all values of L' between L and $L + a$ as indicated in (6.5). The first integral in (6.14) does not depend on the location of the hard walls but is entirely given by the properties of the fluid in the middle of the soft wall. The average (6.5) of this integral over different locations of the wall is therefore trivial. The second integral, however, does depend on the location of the hard walls since the density in the edges, which contribute to order L^0, depends on it. Some knowledge about the density in the edges is necessary in order to be able to perform

the average. In appendix 3 we show, by using an expansion of the density in the activity, that the average (6.5) over the second term in (6.14) vanishes. Thus we find

$$\gamma_{st} = -\frac{1}{2a_x a_y} \int_{cell} dx\, dy \int_0^\infty dz \left(\Delta p_s^{xx} + \Delta p_s^{yy} + \Delta p_s^{zz} - z n_s \frac{\partial}{\partial z} \phi^{ext} \right). \tag{6.15}$$

The integral over Δp_s^{zz} cancels against the integral over $z n_s \partial_z \phi^{ext}$ (see (A2.2)) and the expression for γ_{st} simplifies to

$$\gamma_{st} = -\frac{1}{2a_x a_y} \int_{cell} dx\, dy \int_0^\infty dz (\Delta p_s^{xx}(x, y, z) + \Delta p_s^{yy}(x, y, z)). \tag{6.16}$$

Instead of displacement field (4.1) we could have used a displacement field that shifts the wall at $x = 0$ or $y = 0$ only. In that case, we would have obtained

$$\begin{aligned}
\gamma_{st} &= -\frac{1}{a_x a_y} \int_{cell} dx\, dy \int_0^\infty dz\, \Delta p_s^{xx}(x, y, z) \\
&= -\frac{1}{a_x a_y} \int_{cell} dx\, dy \int_0^\infty dz\, \Delta p_s^{yy}(x, y, z)
\end{aligned} \tag{6.17}$$

which shows that the integrals over a unit of area of Δp_s^{xx} and Δp_s^{yy} are equal.

We conclude this section with a consideration of the dependence of γ_s on the lower boundary $z = 0$ assigned to the system. This dependence was discussed in section 3, where it is made explicit in equation (3.12). The same dependence must appear in the microscopic definitions (6.16) and (6.17) of γ_s. The integrands that appears in (6.16) and (6.17) take the value $-p$ at $z = 0$, cf (6.8). If we shift the lower boundary by an amount δz, the integral changes by an amount

$$\delta\gamma_s = -p\,\delta z \tag{6.18}$$

which is equal to (3.12).

7. Summary and conclusions

We have derived microscopic expressions for the surface and line tension of solid–fluid interfaces. They were obtained from a careful analysis of the change in grand potential under a deformation of the fluid's vessel. These expressions fall into two classes: density expressions and pressure expressions. The density expressions relate thermodynamic quantities to the density at a hard wall, the pressure expressions relate them to the pressure tensor.

Density expression (1.1) for the pressure was already well known [3] and it is shown in this paper that it is the first in a hierarchy of three expressions, the second involving the surface tension, the third the line tension. Density expressions for the surface tension relate the density at a hard wall near an edge, to the surface tension of the wall which forms the edge with the hard wall. The second wall can be either a hard or a structureless soft wall, the density expression in both cases has the form

$$\gamma = -k_B T \int_0^\infty dz\, \Delta n(z) \tag{7.1}$$

cf (4.13). The second wall can also be a structured, soft wall, in which case $\Delta n(z)$ depends on the location of the hard wall in the elementary area which is defined by

the structured wall. If, e.g., the hard wall is placed in the yz plane, the RHS of (7.1) should be averaged over all locations of the hard wall within the periodic length in the x direction to obtain the density expression for the structured, soft wall.

Density expressions for the line tension have precisely the same form as (7.1). They relate the density at a hard wall near a corner to the line tension of the edge which stands tangential to the hard wall and terminates in the corner. The expression is

$$\tau = -k_B T \int_0^\infty dy \int_0^\infty dz \, \Delta n(y, z) \tag{7.2}$$

cf (4.14). The validity of (7.2) has been proven in the cases that the edge is formed by two hard walls. One can demonstrate that it also holds in the case of an edge between a hard and a structureless soft wall and for an edge between two structureless, soft walls. We did not consider edges which involve a structured wall. However, we have no reason to assume that anything else but the same averaging as in the case of the surface tension has to be applied to (7.2) in that case. In general, density expressions also exist near soft walls, as discussed at the end of section 4, but we did not pursue them in this paper.

The pressure equation for the surface tension is also well known [5]. It is

$$\gamma = - \int_0^\infty dz \, \Delta p^T(z) \tag{7.3}$$

which holds for both a hard and a structureless soft wall, see (5.16). The derivation of a pressure equation for the structured, soft wall is much more complicated, but the result is a straightforward extension of (7.3). In the case of a structured wall, Δp^T also depends on the position along the wall and we have shown that the RHS of (7.3) has to be averaged over a unit of area to obtain the pressure equation for the structured wall.

Pressure equations for the line tension have again the same form as the equation (7.3) for the surface tension. Whereas (7.3) expresses the surface tension of a wall in p^T, the component of $\mathbf{p}$ along the wall, the pressure equation for the line tension expresses this quantity in p^{xx}, the component of $\mathbf{p}$ along the edge. The expression is given by

$$\tau = - \int_0^\infty dy \int_0^\infty dz \, \Delta p^{xx}(y, z) \tag{7.4}$$

which is proven for an edge formed by two hard walls, cf (5.22). Again, one easily proves that it also holds for an edge formed by a hard and a structureless soft wall and in case of an edge formed by two structureless soft walls. We expect its validity, with the usual averaging procedure, for an edge which involves a structured soft wall, too. The latter assumption, however, is probably hard to prove rigorously.

Surprisingly, it turns out to be possible to generalize (7.3). One can evaluate p^T at an arbitrary distance from an edge formed with a hard wall and show that the influence of the edge on p^T does not alter the integral, cf (5.20). This generalized expression reduces to the density expression (7.1) if the distance to the wall is taken to vanish, since the diagonal components of the pressure tensor become equal to $k_B T$ times the density at a hard wall, cf (2.11). The same generalization is possible for (7.4), where it can be shown that the influence of a corner on p^{xx} leaves the integral unaltered. Reducing the distance to the corner, formed with a hard wall, transforms the generalized expressions to the density expression (7.2).

We have seen various expressions for the surface and line tension, all related to the routes (2.10) and (2.12) to the change in grand potential. The expressions are very symmetric: they are the same for all the models of a wall we have considered and, furthermore, each expression for the surface tension has its counterpart at the level of the line tension. The density expressions reveal that the density at a hard wall is related to thermodynamic quantities, a surprising fact. Probably of more practical use are the pressure equations since they are well suited to measuring surface and line tensions in a simulation. Especially the pressure equation for the structured soft wall is of immediate interest in view of the many investigations of the solid–fluid surface nowadays. If, however, simulations will ever deal with edges or contact lines, the expressions for the line tension will certainly prove to be equally useful.

Acknowledgments

Appendix 1

We prove the following properties of a pressure tensor near the hard wall in the plane $z = 0$

$$\Delta p_{\mathrm{h}}^{zz}(z) = 0 \tag{A1.1}$$

$$\int_0^\infty \mathrm{d}z \, \Delta p_{\mathrm{hh}}^{yy}(y, z) = 0 \tag{A1.2}$$

$$\int_0^\infty \mathrm{d}y \int_0^\infty \mathrm{d}z \, \Delta p_{\mathrm{hhh}}^{xx}(x, y, z) = 0. \tag{A1.3}$$

These properties all follow from the condition that the tensor is divergenceless near hard walls, (2.2) with $\phi^{\mathrm{ext}} = 0$.

First, we prove (A1.1). In terms of p^{zz} and p, $\Delta p_{\mathrm{h}}^{zz}$ has the form

$$\Delta p_{\mathrm{h}}^{zz}(z) = p^{zz}(\infty, \infty, z) - p. \tag{A1.4}$$

The off-diagonal components of $\mathbf{p}$ vanish near a hard wall, far away from edges and corners

$$p^{\alpha\beta}(\infty, \infty, z) = 0 \qquad \alpha \neq \beta \tag{A1.5}$$

in which case condition (2.2) on the divergence of $\mathbf{p}$ becomes

$$\frac{\partial}{\partial z} \Delta p_{\mathrm{h}}^{zz}(z) = 0. \tag{A1.6}$$

Since $\Delta p_{\mathrm{h}}^{zz}$ vanishes in the bulk fluid, at $z = \infty$, it has to vanish at any distance z as stated by (A1.1).

Secondly, we prove (A1.2). In terms of p^{yy}, $\Delta p_{\mathrm{hh}}^{yy}$ has the form

$$\Delta p_{\mathrm{hh}}^{yy}(y, z) = p^{yy}(\infty, y, z) - p^{yy}(\infty, \infty, z) \tag{A1.7}$$

in this case (2.2) becomes

$$\frac{\partial}{\partial y} \Delta p_{\mathrm{hh}}^{yy}(y, z) = -\frac{\partial}{\partial z} p^{zy}(\infty, y, z). \tag{A1.8}$$

No derivative with respect to x appears since the tensor is translationally invariant in the x direction in the edge formed by the walls at $y = 0$ and $z = 0$, far away from the plane at $x = 0$. From (A1.8), we find

$$-\frac{\partial}{\partial y} \int_0^\infty \mathrm{d}z \, \Delta p_{\mathrm{hh}}^{yy}(y, z) = p^{zy}(\infty, y, \infty) - p^{zy}(\infty, y, 0) = 0. \tag{A1.9}$$

The term $p^{zy}(\infty, y, \infty)$ denotes an off-diagonal component of $\mathbf{p}$ near a hard wall, far away from the edges and vanishes due to (A1.5). The second term denotes an off-diagonal component at a hard wall which also vanishes, cf (2.11). Therefore, the derivative (A1.8) vanishes. Since the integral vanishes at $y = \infty$, where the integrand vanishes, the integral has to vanish at any distance y, which implies (A1.2).

Finally, we prove (A1.3). The derivative of $\Delta p_{\mathrm{hhh}}^{xx}$ with respect to x has the form

$$\frac{\partial}{\partial x} \Delta p_{\mathrm{hhh}}^{xx}(x, y, z) = \frac{\partial}{\partial x} (p^{xx}(x, y, z) - p^{xx}(x, y, \infty) - p^{xx}(x, \infty, z)). \tag{A1.10}$$

With (2.2), the derivative is rewritten as

$$\frac{\partial}{\partial x} \Delta p_{\mathrm{hhh}}^{xx}(x, y, z)$$

$$= -\frac{\partial}{\partial y} (p^{yx}(x, y, z) - p^{yx}(x, y, \infty))$$

$$- \frac{\partial}{\partial z} (p^{zx}(x, y, z) - p^{zx}(x, \infty, z)). \tag{A1.11}$$

This yields for the derivative of the integral (A1.3)

$$-\frac{\partial}{\partial x} \int_0^\infty \mathrm{d}y \int_0^\infty \mathrm{d}z \, \Delta p_{\mathrm{hhh}}^{xx}(x, y, z) = \int_0^\infty \mathrm{d}z \, [p^{yx}(x, y, z) - p^{yx}(x, y, \infty)]_{y=0}^\infty$$

$$+ \int_0^\infty \mathrm{d}y [p^{zx}(x, y, z) - p^{zx}(x, \infty, z)]_{z=0}^\infty. \tag{A1.12}$$

The off-diagonal components vanish at and near a hard wall due to (2.11) and (A1.5), respectively. The only remaining terms are the terms in the edges

$$-\frac{\partial}{\partial x} \int_0^\infty \mathrm{d}y \int_0^\infty \mathrm{d}z \, \Delta p_{\mathrm{hhh}}^{xx}(x, y, z) = \int_0^\infty \mathrm{d}z \, p^{yx}(x, \infty, z) + \int_0^\infty \mathrm{d}y \, p^{zx}(x, y, \infty). \tag{A1.13}$$

The arguments, based on the microscopic definition of $\mathbf{p}$, (2.1), and the symmetry in the pair correlation function, that lead to (A1.5) also show that these terms vanish. Thus, the derivative (A1.13) vanishes and since the integral vanishes at $x = \infty$, the integral vanishes at any distance x, yielding (A1.3).

Appendix 2

We prove the following properties of the density and pressure tensor near the structured,

soft wall in the plane $z = 0$

$$\int_{\text{cell}} dx\, dy \int_0^\infty dz\, n_s(\mathbf{r}) \frac{\partial}{\partial x} \phi^{\text{ext}}(\mathbf{r}) = 0 \tag{A2.1}$$

$$\int_{\text{cell}} dx\, dy \int_0^\infty dz\left(\Delta p_s^{zz}(\mathbf{r}) - z n_s(\mathbf{r}) \frac{\partial}{\partial z} \phi^{\text{ext}}(\mathbf{r}) \right) = 0 \tag{A2.2}$$

where a cell denotes a unit of area far away from the hard walls. Both identities follow from condition (2.2) on the divergence of $\mathbf{p}$.

First, we prove (A2.1). Condition (2.2) is

$$\frac{\partial}{\partial x} p^{xx} + \frac{\partial}{\partial y} p^{yx} + \frac{\partial}{\partial z} p^{zx} = -n_s \frac{\partial}{\partial x} \phi^{\text{ext}} \tag{A2.3}$$

since n equals n_s far away from the hard walls. Substituting the LHS into the integral in (A2.1), denoted by I_1, one obtains

$$-I_1 = \int_{a_y} dy \int_0^\infty dz [p^{xx}]_{x=x_0}^{x_0+a_x} + \int_{a_x} dx \int_0^\infty dz [p^{yx}]_{y=y_0}^{y_0+a_y} + \int_{\text{cell}} dx\, dy [p^{zx}]_{z=0}^\infty \tag{A2.4}$$

where x_0 and y_0 denote the lower boundaries of the cell. The periodicity of the tensor makes the first two terms vanish. The fact that the tensor vanishes completely at $z = 0$ and that its off-diagonal components vanish in the bulk fluid shows that the third term also vanishes, which proves (A2.1).

The proof of (A2.2) goes similarly. Condition (2.2) is

$$\frac{\partial}{\partial x} p^{xz} + \frac{\partial}{\partial y} p^{yz} + \frac{\partial}{\partial z} \Delta p^{zz} = -n_s \frac{\partial}{\partial z} \phi^{\text{ext}}. \tag{A2.5}$$

Multiplying (A2.5) with z, integrating it over a unit of area and using the periodicity of $\mathbf{p}$, we obtain

$$\int_{\text{cell}} dx\, dy \int_0^\infty dz\, z \frac{\partial}{\partial z} \Delta p^{zz} = -\int_{\text{cell}} dx\, dy \int_0^\infty dz\, z n_s \frac{\partial}{\partial z} \phi^{\text{ext}} \tag{A2.6}$$

and thus the integral in (A2.2), denoted as I_2, can be written as

$$I_2 = \int_{\text{cell}} dx\, dy \int_0^\infty dz \frac{\partial}{\partial z} (z \Delta p^{zz}). \tag{A2.7}$$

Since Δp^{zz} vanishes in the bulk fluid at $z = \infty$, I_2 vanishes.

Appendix 3

We prove that the average (7.4) of the integrals

$$d\Omega_x \equiv \lambda \int_0^L dx \int_0^L dy \int_0^\infty dz\, n(\mathbf{r})(x - L) \frac{\partial}{\partial x} \phi^{\text{ext}}(\mathbf{r}) \tag{A3.1}$$

and

$$d\Omega_y \equiv \lambda \int_0^L dx \int_0^L dy \int_0^\infty dz\, n(\mathbf{r})(y - L) \frac{\partial}{\partial y} \phi^{\text{ext}}(\mathbf{r}) \tag{A3.2}$$

vanish. It will be proven explicitly for $d\Omega_x$ whereupon it follows for $d\Omega_y$ by symmetry.

At first, we find it more convenient to shift the origin $x, y = 0$ to $x, y = L$. Denoting the new coordinates as r', $d\Omega_x$ becomes

$$d\Omega_x \equiv \int_0^L dx' \int_0^L dy' \int_0^\infty dz' \, n(r')x' \frac{\partial}{\partial x'} \phi^{\text{ext}}(r'). \tag{A3.3}$$

To be strict, we should have replaced n by n' with $n'(r') = n(r)$ (and similarly for ϕ^{ext}) but since the properties of n' and n are essentially the same, we drop the prime. The density at a position r is evaluated in an expansion in the activity z, defined in (2.6) (the activity z should not be confused with the position z).

$$n(r_1) = \sum_{N=1}^\infty c_N(r_1)z^N \tag{A3.4}$$

where the coefficients are of the form [10]

$$c_N(r_1) = \frac{1}{\Lambda^{3N}} \int_V dr_2, \ldots, dr_N \{F_N^e(r_1, \ldots, r_N) + 1\}F_N(r_1, \ldots, r_N) \tag{A3.5}$$

with

$$F_N^e(r_1, \ldots, r_N) = \exp[-\beta(\phi^{\text{ext}}(r_1) + \ldots + \phi^{\text{ext}}(r_N))] - 1 \tag{A3.6}$$

and $F_N(r_1, \ldots, r_N)$ a function which depends only on the relative distances r_{ij} and is short ranged, i.e. vanishes when one of the r_{ij} becomes large, except for $N = 1$. Furthermore, F_N is symmetric under permutations of its arguments. For $N = 1, 2, 3$ we have

$$F_1 = 1 \tag{A3.7}$$

$$F_2(r_1, r_2) = f(r_{12}) \tag{A3.8}$$

$$F_3(r_1, r_2, r_3) = \tfrac{1}{2}(f(r_{12})f(r_{13})f(r_{23}) + f(r_{12})f(r_{13}) + f(r_{12})f(r_{23}) + f(r_{13})f(r_{23})) \tag{A3.9}$$

where $f(r_{ij})$ denotes the Mayer f function

$$f(r_{ij}) = \exp(-\beta\phi(r_{ij})) - 1 \tag{A3.10}$$

and ϕ stands for the interparticle potential. Inserting expansion (A3.5) into $d\Omega_x$ results in the expansion

$$d\Omega_x = \sum_{N=1}^\infty d\Omega_N z^N \tag{A3.11}$$

with, dropping the prime of the arguments,

$$-\beta \, d\Omega_N = \lambda \int_0^L dx_1 \, dy_1 \int_0^\infty dz_1 \int_V dr_2, \ldots, dr_N \, F_N(r_1, \ldots, r_N)x_1 \frac{\partial}{\partial x_1} F_N^e(r_1, \ldots, r_N). \tag{A3.12}$$

Due to the short ranged character of F_N and the fact that F_N^e vanishes if all the z_i are large, the integration over the z coordinates can just as well be taken from 0 to ∞

$$-\beta \, d\Omega_N = \lambda \int_0^L dx_1, \ldots, dy_N \int_0^\infty dz_1, \ldots, dz_N \, F_N(r_1, \ldots, r_N)x_1 \frac{\partial}{\partial x_1} F_N^e(r_1, \ldots, r_N). \tag{A3.13}$$

The average (7.4) has the form

$$\Delta\Omega_x \equiv \frac{1}{2aL} \int_L^{L+a} dL' \left(\frac{d\Omega_x}{dL'}\right). \tag{A3.14}$$

Expansion (A3.11) gives

$$\Delta\Omega_x = \sum_{N=1}^{\infty} \Delta\Omega_N z^N \tag{A3.15}$$

with

$$\Delta\Omega_N = \frac{1}{2aL} \int_L^{L+a} dL' \left(\frac{d\Omega_N}{dL'}\right). \tag{A3.16}$$

We will show that all terms $\Delta\Omega_N$ vanish.

To do so, we have to calculate the derivative $d\Omega_N/dL$ and integrate it over the increase of L. The derivative is simply calculated by dividing $d\Omega_N$ by dL with $dL = \lambda L$. The integration is most easily performed if the dependence of the derivative on L can be brought from the integration boundary to the integrand. The first step to do this is partial integration

$$-\beta \frac{d\Omega_N}{dL} = \int_0^L dy_1 \int_0^L dx_2, \ldots, dy_N \int_0^{\infty} dz_1, \ldots, dz_N [F_N F_N^e]_{x_1=L}$$

$$- \frac{1}{L} \int_0^L dx_1, \ldots, dy_N \int_0^{\infty} dz_1, \ldots, dz_N F_N^e \left(F_N + x_1 \frac{\partial}{\partial x_1} F_N\right)$$

$$\equiv I_1 + I_2. \tag{A3.17}$$

The presence of L in the integration boundaries of I_1 can be removed. If one changes the integration variables x_i to x_{1i} ($i = 2, \ldots, N$, $x_{1i} = x_1 - x_i$), the x_{1i} can be taken to range from 0 to ∞ because of the short ranged character of F_N. The same substitution can be made for the y_i with y_{1i} ranging from $-\infty$ to ∞. This range neglects the presence of the corner: at positions $x_1 = L$ and $y_1, z_1 \geqslant 0$, the y_i should be restricted to $y_i > 0$. This restriction, however, only adds a correction of the order L^0 to the integral which itself is of the order L. We obtain

$$I_1 = \int_0^L dy_1 \int_0^{\infty} dx_{12}, \ldots, dx_{1N} \int_{-\infty}^{\infty} dy_{12}, \ldots, dy_{1N}$$

$$\times \int_0^{\infty} dz_1, \ldots, dz_N [F_N F_N^e]_{x_1=L} + O(L^0). \tag{A3.18}$$

Finally, we use the periodicity of F_N^e to remove the presence of L in the integration boundary of y_1

$$I_1 = \frac{L}{a_y} \int_{a_y} dy_1 \int_0^{\infty} dx_{12}, \ldots, dx_{1N} \int_{-\infty}^{\infty} dy_{12}, \ldots, dy_{1N}$$

$$\times \int_0^{\infty} dz_1, \ldots, dz_N [F_N F_N^e]_{x_1=L} + O(L^0). \tag{A3.19}$$

One would also like to remove the presence of L from the integration boundaries of I_2. If it were not for the factor x_1, the integrand of I_2 would be periodic in x_1 and y_1 and the presence of L could be removed by restricting the integral over x_1 and y_1

to one unit of area and changing the integration variables x_i and y_i to x_{1i} and y_{1i}. The restriction on the integration over x_1 and y_1 would be compensated for by multiplying the integral with a factor $L^2/(a_x a_y)$. The integration over the x_{1i} and y_{1i} would range from $-\infty$ to ∞. This range neglects the presence of edges but they only give a correction of order L^0.

The periodicity of the integrand in x_1 is restored if the absolute coordinate x_1 can be replaced by a relative coordinate such as x_{1i}. We show that such a substitution, namely

$$x_1 \frac{\partial}{\partial x_1} F_N \to \frac{1}{N} \sum_{i=2}^{N} x_{1i} \frac{\partial}{\partial x_1} F_N \tag{A3.20}$$

can indeed be made.

Under integral I_2, the term $x_1 \partial_{x_1} F_N$ can be replaced by

$$x_1 \frac{\partial}{\partial x_1} F_N \to \frac{1}{N} \sum_{i=1}^{N} x_i \frac{\partial}{\partial x_i} F_N. \tag{A3.21}$$

If F_N is taken to be a function of the relative coordinates r_{ij}, the RHS of (A3.21) can be written as

$$\sum_{i=1}^{N} x_i \frac{\partial}{\partial x_i} F_N = \sum_{i=1}^{N} x_i \sum_{j=1}^{N} \frac{\partial}{\partial x_{ij}} F_N = \sum_{i=1}^{N} \sum_{j=i+1}^{N} x_{ij} \frac{\partial}{\partial x_{ij}} F_N \tag{A3.22}$$

the RHS of (A3.20) is equal to

$$\sum_{i=2}^{N} x_{1i} \frac{\partial}{\partial x_1} F_N = \sum_{i=2}^{N} x_{1i} \sum_{j=2}^{N} \frac{\partial}{\partial x_{1j}} F_N. \tag{A3.23}$$

The difference between the RHS of (A3.22) and (A3.23) is

$$S \equiv \sum_{i=1}^{N} \sum_{j=i+1}^{N} x_{ij} \frac{\partial}{\partial x_{ij}} F_N - \sum_{i=2}^{N} x_{1i} \sum_{j=2}^{N} \frac{\partial}{\partial x_{1j}} F_N \tag{A3.24}$$

$$= \sum_{i=2}^{N} \sum_{j=i+1}^{N} x_{ij} \frac{\partial}{\partial x_{ij}} F_N - \sum_{i=2}^{N} \sum_{\substack{j=2 \\ j \neq i}}^{N} x_{1i} \frac{\partial}{\partial x_{1j}} F_N \tag{A3.25}$$

$$= \sum_{i=2}^{N} \sum_{j=i+1}^{N} x_{ij} \frac{\partial}{\partial x_{ij}} F_N - \sum_{i=2}^{N} \sum_{j=i+1}^{N} \left(x_{1i} \frac{\partial}{\partial x_{1j}} + x_{1j} \frac{\partial}{\partial x_{1i}} \right) F_N. \tag{A3.26}$$

Under the integral, the integration variables x_1 and x_i in the second term and x_1 and x_j in the third term can be interchanged

$$\left(x_{1i} \frac{\partial}{\partial x_{1j}} + x_{1j} \frac{\partial}{\partial x_{1i}} \right) F_N \to \left(x_{i1} \frac{\partial}{\partial x_{ij}} + x_{j1} \frac{\partial}{\partial x_{ji}} \right) F_N \tag{A3.27}$$

$$= x_{ij} \frac{\partial}{\partial x_{ij}} F_N. \tag{A3.28}$$

Therefore we find that S vanishes under the integral:

$$S = 0. \tag{A3.29}$$

This proves that the RHS of (A3.20) and (A3.21) are the same under integral I_2. Because (A3.21) is an allowed substitution, (A3.20) must be so. With this substitution, the integrand of I_2 becomes periodic in x_1 and I_2 can be written as

$$I_2 = \frac{L}{a_x a_y} \int_{\text{cell}} dx_1 \, dy_1 \int_{-\infty}^{\infty} dx_{12}, \ldots, dy_{1N} \int_0^{\infty} dz_1, \ldots, dz_N F_N^e$$

$$\times \left(F_N + \frac{1}{N} \sum_{i=2}^{N} x_{1i} \frac{\partial}{\partial x_1} F_N \right) + O(L^0). \tag{A3.30}$$

Note that apart from the prefactor L, I_2 is independent of L.

We have now brought the derivative $d\Omega_N/dL$ in such a form that we can perform the integration (A3.16). The derivative is the sum of I_1 and I_2, cf (A3.17). The integral over I_1 has the form

$$\Delta I_1 \equiv \frac{1}{2aL} \int_L^{L+a} dL' \, I_1(L') \tag{A3.31}$$

$$= -\frac{1}{2a_x a_y} \int_L^{L+a_x} dx_1 \int_{a_y} dy_1 \int_0^{\infty} dx_{12}, \ldots, dx_{1N} \int_{-\infty}^{\infty} dy_{12}, \ldots, dy_{1N}$$

$$\times \int_0^{\infty} dz_1, \ldots, dz_N F_N F_N^e + O(L^{-1}). \tag{A3.32}$$

Characteristic of the integral is the fact that all x positions x_i, $i = 2, \ldots, N$ should be below x_1. This restriction is easily removed

$$\Delta I_1 = -\frac{1}{N} \frac{1}{2a_x a_y} \int_{\text{cell}} dx_1 \, dy_1 \int_{-\infty}^{\infty} dx_{12}, \ldots, dy_{1N}$$

$$\times \int_0^{\infty} dz_1, \ldots, dz_N F_N F_N^e + O(L^{-1}) \tag{A3.33}$$

the factor $1/N$ compensates for the fact that each particle in the integral (A3.33) can have the largest x coordinate, whereas this is always particle 1 in (A3.32). Adding ΔI_1 and the similarly defined ΔI_2, $\Delta I_2 = I_2/2L$, we obtain

$$-\beta \Delta \Omega_N = \frac{1}{2a_x a_y} \int_{\text{cell}} dx_1 \, dy_1 \int_{-\infty}^{\infty} dx_{12}, \ldots, dy_{1N} \int_0^{\infty} dz_1, \ldots, dz_N F_N^e$$

$$\times \left(\frac{N-1}{N} F_N + \frac{1}{N} \sum_{i=2}^{N} x_{1i} \frac{\partial}{\partial x_1} F_N \right) + O(L^{-1}). \tag{A3.34}$$

The term of order L^{-1} vanishes in the thermodynamic limit. All the terms in the sum will give the same contribution to the integral. We can take the term with x_{12} as exemplary and write the integral as

$$-\beta \Delta \Omega_N = \frac{1}{2a_x a_y} \frac{N-1}{N} \int_{\text{cell}} dx_1 \, dy_1 \int_{-\infty}^{\infty} dx_{12}, \ldots, dy_{1N}$$

$$\times \int_0^{\infty} dz_1, \ldots, dz_N F_N^e \frac{\partial}{\partial x_1} (x_{12} F_N). \tag{A3.35}$$

One has to apply one more partial integration with respect to x_1 to see that this contribution vanishes

$$-\beta \Delta \Omega_N = \frac{1}{2a_x a_y} \frac{N-1}{N} \int_{a_y} dy_1 \int_{-\infty}^{\infty} dx_{12}, \ldots, dy_{1N} \int_0^{\infty} dz_1, \ldots, dz_N \, x_{12} F_N [F_N^e]_{x_1 = x_0}^{x_0 + a_x}$$

$$-\frac{1}{2a_x a_y} \frac{N-1}{N} \int_{\text{cell}} dx_1 \, dy_1 \int_{-\infty}^{\infty} dx_{12}, \ldots, dy_{1N}$$

$$\times \int_0^{\infty} dz_1, \ldots, dz_N \, x_{12} F_N \frac{\partial}{\partial x_1} F_N^e \qquad (A3.36)$$

where x_0 denotes the lower boundary of the unit cell. The first integral vanishes because of the periodicity of F_N^e. Changing the order of integration in the second integral gives

$$-\beta \Delta \Omega_N = -\frac{1}{2a_x a_y} \frac{N-1}{N} \int_{-\infty}^{\infty} dx_{12}, \ldots, dy_{1N} \int_0^{\infty} dz_1, \ldots, dz_N \, x_{12} F_N$$

$$\times \int_{\text{cell}} dx_1 \, dy_1 \frac{\partial}{\partial x_1} F_N^e \qquad (A3.37)$$

which shows that the periodicity of F_N^e also makes this integral vanish. Therefore, we have obtained the desired result

$$\Delta \Omega_N = 0. \qquad (A3.38)$$

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