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Statistical Mechanics in External Force Fields

G. H. Derrick
Department of Theoretical Physics, School of Physical Sciences,
University of St. Andrews, Fife, Scotland
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A theory is developed for the statistical mechanics of a system of interacting particles contained by an external potential instead of by a box. Most attention is paid to the special case of particles in a three-dimensional harmonic oscillator potential $V(r)=\beta^{-1}\pi r^2/L^2$, where the parameter L is a length of macroscopic dimensions which is ultimately allowed to increase indefinitely while keeping the density of particles at the origin finite. As an application of the formalism, an expression is obtained for the surface tension between a liquid and its vapor in equilibrium.

1. INTRODUCTION

In the grand canonical approach to statistical mechanics, the pressure $P(\beta,\mu)$ of a system of identical particles at temperature $1/k\beta$ and chemical potential μ is given by

$$P(\beta,\mu)=\lim_{V\to\infty}(V\beta)^{-1}\ln\Big(\sum_N \mathrm{Tr}_N\exp(-\beta H_N+\beta\mu N)\Big),\quad(1)$$

where H_N is the Hamiltonian for N particles and Tr_N denotes the trace over all N-particle states of appropriate symmetry. The volume V is normally taken to be that inside a cubical box with sides of length $L=V^{1/3}$, though in the limit of indefinitely large volume the exact shape should be irrelevant for physically sensible systems. The boundary conditions imposed on wave functions at the walls should also be irrelevant. For mathematical convenience one normally takes periodic boundary conditions, though if the walls be rigid and impenetrable the wave functions should strictly be required to vanish there.

While a containing box is usually necessary physically to stop the molecules flying apart, it can be a nuisance mathematically. This is especially so if we make a change of variables. For example, it is sometimes useful to replace the momentum variables $\vec{p}_1$, $\vec{p}_2$, $\vec{p}_3$, ... by the transformed set[1]

$$\vec{p}_1{}'=2^{-1/2}(\vec{p}_1-\vec{p}_2),$$

$$\vec{p}_2{}'=6^{-1/2}(\vec{p}_1+\vec{p}_2-2\vec{p}_3),$$

$$\vec{p}_3{}'=(12)^{-1/2}(\vec{p}_1+\vec{p}_2+\vec{p}_3-3\vec{p}_4),\ \ldots\ .$$

The corresponding orthogonal transformation of the position coordinates $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$, ... is, however, less fruitful because of the awkward domain over which the transformed position coordinates $\vec{r}_1{}'$, $\vec{r}_2{}'$, $\vec{r}_3{}'$, ... range as a consequence of the $\vec{r}_i$ being restricted to lie, say, within a cubical box. In contrast the $\vec{p}_i$ and $\vec{p}_i{}'$ extend over all real values. If we could only take the same infinite domain for our space coordinates, we would have at our disposal a much wider class of useful transformations.

In nature there are several examples of systems of particles which do *not* need a box to hold them together. To name two, stars contain themselves by gravitational attraction while nuclei are bound together by strong internucleon forces. In the shell model of the nucleus, each nucleon is taken to move independently in a common potential field representing the average effect of all interactions with other nucleons. This common potential has been taken by Mayer[2] and by Haxel, Jensen, and Suess[3] to be a central harmonic oscillator well modifed by a spin-orbit term, and it is this well rather than a box which prevents the particles flying off to infinity.

Blatt[4] has suggested that instead of using a box in statistical mechanics one could contain the particles by an external central harmonic oscillator well. We develop this idea in the present paper and consider each particle to be acted upon by an external force field, paying most attention to the special case of particles contained by a central harmonic oscillator potential $V(r)=\beta^{-1}\pi r^2/L^2$. The parameter L will ultimately be taken indefinitely large with the number of particles simultaneously approaching infinity in such a way as to keep the density of particles at the origin finite. This parameter will therefore play, in the present theory, a role similar to that of the side length of the cubical box in the conventional approach, though all position coordinates will here range between ± ∞.

In Sec. 4 an expression is obtained for the surface tension at the interface of a liquid and its vapor in equilibrium. The external force field plays an essential role in the derivation of this expression in effecting a spatial separation of the two phases.

2. SYSTEMS IN A CENTRAL HARMONIC OSCILLATOR POTENTIAL

2.1 Introduction

Let us consider a system of identical particles (in general interacting) described by an N-particle Hamiltonian H_N to be immersed in an external three-dimensional harmonic oscillator potential $V(r)=\beta^{-1}\pi r^2/L^2$ acting on all particles, where L is a length of macroscopic dimensions. The total Hamiltonian in an N-particle state is then

$$H_N{}'=H_N+\frac{\pi}{\beta L^2}\sum_{i=1}^{N}\vec{r}_i^{\,2} \ . \tag{2}$$

In analogy with (1) let us define

$$Q(\beta,\mu) = \lim_{L\to\infty}(L^3\beta)^{-1}\ln\Big(\sum_N \mathrm{Tr}_N\exp(-\beta H_N{}'+\beta\mu N)\Big) . \tag{3}$$

We stress that in evaluating (3) we allow the cartesian components of our position vectors to assume all values between ±∞. Thus the Hilbert space appropriate for the description of, say, N spinless bosons is the set of all wave functions $\psi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ square integrable over the domain of all real values of all $3N$ Cartesian coordinates.

The main results of this section are the relations between $Q(\beta,\mu)$ defined by (3) and $P(\beta,\mu)$ defined by (1):

$$Q(\beta,\mu)=\beta^{3/2}\int P(\beta,\mu-\pi r^2)d^3\vec{r} \ , \tag{4}$$

$$P(\beta,\mu)=\frac{\partial^3}{\partial\mu^3}\beta^{-3/2}\int Q(\beta,\mu-\pi r^2)d^3\vec{r} \ , \tag{5}$$

$$\equiv\frac{2\partial^2}{\partial\mu^2}\beta^{-3/2}\int_0^\infty Q(\beta,\mu-\pi r^2)dr \ . \tag{6}$$

The simple inverse expressions (5) and (6) enable us to bypass the conventional cubical box. Having obtained an approximation to $Q(\beta,\mu)$, say by variational evaluation of (3), we can then estimate the pressure $P(\beta,\mu)$ from (5) or (6), thus avoiding the use of (1).

2.2 Proof of (4)

We consider the parameter L so large that it is possible to divide space up into volumes δV which each contain a macroscopic number of particles, but such that $V(r)=\beta^{-1}\pi r^2/L^2$ varies insignificantly over the δV. We can then regard the material in a typical region δV, centered around position $\vec{r}$, as being in local thermodynamic equilibrium at an effective chemical potential $\mu(r)=\mu-\beta^{-1}\pi r^2/L^2$ (c.f. equilibrium in a gravitational field[5]). Thus the region δV contributes an amount $-P(\beta,\mu-\beta^{-1}\pi r^2/L^2)\delta V$ to the grand potential

$$\Omega=-\beta^{-1}\ln\{\textstyle\sum_N \mathrm{Tr}_N\exp(-\beta H_N{}'+\beta\mu N)\} ,$$

yielding on integration over all δV

$$\begin{aligned}\Omega&=-\int P(\beta,\mu-\beta^{-1}\pi r^2/L^2)d^3\vec{r}\\&=-L^3\beta^{3/2}\int P(\beta,\mu-\pi r^2)d^3\vec{r} \ ,\end{aligned}$$

on replacing the variable of integration by $\vec{r}/(\beta^{1/2}L)$. Inserting this expression into the definition (3) immediately yields (4).

2.3 Proof of (5) and (6)

If $P(\beta,\mu)$ possesses an expansion of form $\sum_n a_n(\beta)\exp(\beta\mu n)$, then the relations (5) and (6) follow quite trivially. A more general proof is as follows:

$$\begin{aligned}&\beta^{-3/2}\int Q(\beta,\mu-\pi r^2)d^3\vec{r}\\&=\int P(\beta,\mu-\pi r_1{}^2-\pi r_2{}^2)d^3\vec{r}_1 d^3\vec{r}_2\\&=16\pi^2\int_0^\infty\int_0^\infty P(\beta,\mu-\pi r_1{}^2-\pi r_2{}^2)r_1{}^2r_2{}^2dr_1dr_2\\&=\pi^3\int_0^\infty P(\beta,\mu-\pi R^2)R^5dR\\&=\tfrac{1}{2}\int_{-\infty}^{\mu}P(\beta,t)(\mu-t)^2dt \ ,\end{aligned}$$

on taking new variables R, θ defined by $r_1=R\cos\theta$, $r_2=R\sin\theta$, integrating over θ, then finally writing $t=\mu-\pi R^2$. Whence on differentiating three times with respect to μ, we obtain (5). The alternative form (6) follows from (5) by partial integration.

2.4 Behavior of $Q(\beta,\mu)$ at a First-Order Phase Transition

Suppose $P(\beta,\mu)$ is continuous in μ, but the number density $\rho(\beta,\mu)=\partial P(\beta,\mu)/\partial\mu$ has a number of finite discontinuities at isolated points $\mu=\mu_i$. Such a situation prevails at a solid-liquid or liquid-gas transition. The proofs of Secs. 2.2 and 2.3 are still valid in this case. It is interesting to enquire into the continuity of $Q(\beta,\mu)$ and its derivatives at the points μ_i of discontinuity of the density.

In the Appendix we prove the following: $Q(\beta,\mu)$, $\partial Q(\beta,\mu)/\partial\mu$, $\partial^2Q(\beta,\mu)/\partial\mu^2$ are continuous everywhere, and $\partial^3Q(\beta,\mu)/\partial\mu^3$ everywhere except at $\mu=\mu_i$. As $\mu\to\mu_i$ from below, $\partial^3Q(\beta,\mu)/\partial\mu^3\to$ a finite limit. As $\mu\to\mu_i$ from above, $\partial^3Q(\beta,\mu)/\partial\mu^3$ becomes singular like

$$\Delta\rho_i\beta^{3/2}[\pi(\mu-\mu_i)]^{-1/2} \ ,$$

where $\Delta\rho_i=\rho(\beta,\mu_i+0)-\rho(\beta,\mu_i-0)$ is the jump in density as μ passes through the value μ_i.

3. OTHER POTENTIALS

3.1 General Three-Dimensional Wells

We can readily generalize the results of Sec. 2 to the case of particles contained in a slowly varying external well of arbitrary shape. Suppose a particle at position $\vec{r}$ has a potential energy in this well of $\beta^{-1}w(\vec{r}/L)$, where the function w is arbitrary except for the normalizing condition $\int \exp[-w(\vec{r})]\,d^3\vec{r}=1$, and L is a parameter which is ultimately to be taken indefinitely large. The total N-particle Hamiltonian is now

$$H_N' = H_N + \beta^{-1}\sum_{i=1}^{N} w(\vec{r}_i/L) \quad . \tag{7}$$

We now define $Q(\beta, \mu)$ by (3) but use (7) for H_N' in place of (2). The arguments leading to (4) now yield in the general case

$$Q(\beta, \mu) = \int P(\beta, \mu - \beta^{-1}w(\vec{r}))\,d^3\vec{r} \quad . \tag{8}$$

The inverse relations to (8) for some particular well shapes are

(i) $w(\vec{r}) = 2\pi^{1/3}r$,

$$P(\beta, \mu) = \beta^{-3}\partial^3 Q(\beta, \mu)/\partial\mu^3 \quad ; \tag{9.1}$$

(ii) $w(\vec{r}) = (4\pi/3)r^3$,

$$P(\beta, \mu) = \beta^{-1}\partial Q(\beta, \mu)/\partial\mu \quad ; \tag{9.2}$$

(iii) $w(\vec{r}) = (4\pi n!\,r^3/3)^{1/n}$, $n = 1, 2, 3, \ldots$,

$$P(\beta, \mu) = \beta^{-n}(\partial/\partial\mu)^n Q(\beta, \mu) \quad ; \tag{9.3}$$

(iv) $w(\vec{r}) = (4\pi^3/9)r^6$,

$$P(\beta, \mu) = \beta^{-1/2}(\partial/\partial\mu)\int Q(\beta, \mu - 4\pi^3 r^6/9)\,d^3\vec{r} \quad . \tag{9.4}$$

Similar expressions can be found for any potential $w(\vec{r})$ which varies as a rational power of r, the relations being established by methods similar to those of Sec. 2.3.

3.2 One-Dimensional Wells

In this subsection we consider a compromise between containing our system in a cubical box and containing it in a three-dimensional potential well. We suppose the system to be restricted by a square box of side length L_1 in the X and Y directions with periodic boundary conditions at the walls, but allow the Z coordinates to range between $\pm\infty$, the particles being restrained from escaping by an external potential $\beta^{-1}w(z/L)$. In place of (3) we now define

$$Q(\beta, \mu) = \lim_{L\to\infty} L^{-1}\left(\lim_{L_1\to\infty} (L_1^{\,2}\beta)^{-1} \times \ln\Big[\sum_N \mathrm{Tr}_N \exp(-\beta H_N' + \beta\mu N)\Big]\right), \tag{10}$$

with $H_N' = H_N + \beta^{-1}\sum_{i=1}^{N} w(z_i/L)$. (11)

Then arguments similar to those leading to (4) yield

$$Q(\beta, \mu) = \int_{-\infty}^{\infty} P(\beta, \mu - \beta^{-1}w(z))\,dz \quad . \tag{12}$$

The inverse relations to (12) for some particular potentials are

(i) $w(z) = 2|z|$,

$$P(\beta, \mu) = \beta^{-1}\partial Q(\beta, \mu)/\partial\mu \quad ; \tag{13.1}$$

(ii) $w(z) = z$, $z > 0$

$$= \infty \ , \quad z < 0 \ , \tag{13.2}$$

$$P(\beta, \mu) = \beta^{-1}\partial Q(\beta, \mu)/\partial\mu \quad .$$

(iii) $w(z) = \pi z^2$, (13.3)

$$P(\beta, \mu) = \beta^{-1/2}(\partial/\partial\mu)\int_{-\infty}^{\infty} Q(\beta, \mu - \pi z^2)\,dz \quad ;$$

(iv) $w(z) = (2n!\,|z|)^{1/n}$, $n = 1, 2, 3, \ldots$,

$$P(\beta, \mu) = \beta^{-n}(\partial/\partial\mu)^n\, Q(\beta, \mu) \quad . \tag{13.4}$$

3.3 Prescribed Density

In the previous sections we have specified the external potential $\beta^{-1}w(\vec{r}/L)$, or equivalently, the local chemical potential $\mu(\vec{r}) = \mu - \beta^{-1}w(\vec{r}/L)$. An alternative approach is to prescribe the local number density of particles. The mathematical problem in this case is to minimize the free energy

$$F = \mathrm{Tr}\,U(\beta^{-1}\ln U + H)$$

over the set of positive definite Hermitian density matrices U for which

$$\mathrm{Tr}\,U = 1, \quad \mathrm{Tr}[U\psi^\dagger(\vec{r})\psi(\vec{r})] = \rho(\vec{r}/L) \quad .$$

Here $\psi^\dagger(\vec{r})\psi(\vec{r})$ is the number density operator in the formalism of second quantisation, and $\rho(\vec{r}/L)$ is an arbitrary given function which is everywhere positive and whose integral over all space converges. For sufficiently large L $\rho(\vec{r}/L)$ will be a slowly varying function of position, yielding for the total free energy

$$F = \int f(\beta, \rho(\vec{r}/L))\,d^3\vec{r}$$
$$= L^3\int f(\beta, \rho(\vec{r}))\,d^3\vec{r} \quad ,$$

where $f(\beta, \rho)$ is the free energy per unit volume of the system at density ρ in the absence of external fields. The total number of particles is

$$N = \int \rho(\vec{r}/L)\,d^3\vec{r} = L^3\int \rho(\vec{r})\,d^3 r \quad .$$

The optimum density matrix U is then

$$U = \exp\beta\Big[\Omega - H + \int \mu(\vec{r})\psi^\dagger(\vec{r})\psi(\vec{r})\,d^3\vec{r}\Big] \quad ,$$

where $\mu(\vec{r}) = [\partial f(\beta, \rho)/\partial\rho]_{\rho = \rho(\vec{r}/L)}$

is the local value of the chemical potential and Ω is the total grand potential given by

$$\begin{aligned}\Omega &= \int [f(\beta, \rho(\vec{r}/L)) - \mu(\vec{r})\rho(\vec{r}/L)]\, d^3\vec{r} \\ &= L^3 \int [(1 - \rho\partial/\partial\rho) f(\beta, \rho)]_{\rho=\rho(\vec{r})} d^3\vec{r} \ .\end{aligned}$$

To see how the above formalism could be used to calculate the free energy density $f(\beta, \rho)$, let us consider the special case

$$\rho(\vec{r}/L) = \rho_0 \exp(-\pi r^2/L^2) \ .$$

The total number of particles is then $N = \rho_0 L^3$. Defining $\mathfrak{F}(\beta, \rho_0) = \lim F/L^3$ as $L \to \infty$, we have

$$\mathfrak{F}(\beta, \rho_0) = \int f(\beta, \rho_0 e^{-\pi r^2}) d^3\vec{r} \ ,$$

with the inverse relation

$$f(\beta, \rho_0) = \left(\frac{\rho_0 \partial}{\partial \rho_0}\right)^3 \int \mathfrak{F}(\beta, \rho_0 e^{-\pi r^2}) d^3\vec{r} \ .$$

By choosing a suitable trial density matrix U, one could obtain a variational estimate of $\mathfrak{F}(\beta, \rho_0)$ and hence an estimate of the free energy density $f(\beta, \rho_0)$ at density ρ_0. However in what follows we shall not refer to this prescribed density method again, since it appears less useful than the external potential approach used elsewhere in this paper.

4. SURFACE TENSION AT A LIQUID-VAPOR INTERFACE

4.1 Introduction

We shall make no pretense of mathematical rigor in this section, but shall adopt intuitive and plausibile arguments in the hope that the expressions so obtained can ultimately be justified by more powerful mathematical techniques.

Suppose we have a system which can undergo a gas to liquid phase transition. There will then exist a certain value of the chemical potential $\mu_0(\beta)$, a function of β defined for β greater than some critical value β_c, such that the density $\partial P(\beta, \mu)/\partial\mu$ is discontinuous at $\mu = \mu_0(\beta)$ though the pressure $P(\beta, \mu)$ be continuous. As we pass through $\mu_0(\beta)$, the density will jump from that of the gas for $\mu < \mu_0(\beta)$ to a higher value in the liquid phase for $\mu > \mu_0(\beta)$.

Now we know from observation that when we have a gas to liquid condensation in the earth's gravitational field, the denser liquid phase collects at the bottom of the vessel with the lower-density vapor above it. There is a continual interchange of particles between the two phases, but nevertheless a well defined surface of separation exists and contributes an energy proportional to its area. This surface energy is to good approximation independent of the local value of the acceleration due to gravity. However if gravity were not present to separate the phases the situation would be more complicated. In the absence of gravity the liquid would presumably collect into a number of nearly spherical drops executing Brownian motion about the vessel. What would happen when a drop approached a wall would depend critically on the forces acting between the walls and the molecules in the drop. A real drop in a real box would probably stick to the walls and assume a helmet shape, while a drop in a cubical box subject to periodic boundary conditions would merely disappear out one wall and reappear at another!

To remove such uncertainties let us immerse our system not in a box but in an external force field, which will play a role similar to that of the earth's gravity and lead to physical separation of the liquid and its vapor, the denser liquid phase collecting near the minimum of the well. We consider two particular potentials, firstly a three-dimensional harmonic oscillator, and secondly a constant one-dimensional "gravitational" field.

4.2 Gas-Liquid Transition in a Three-Dimensional Harmonic Oscillator Well

Let us consider the grand potential

$$\Omega = -\beta^{-1} \ln[\textstyle\sum_N \mathrm{Tr}_N \exp(-\beta H_N' + \beta\mu N)] \ , \quad (14)$$

with the Hamiltonian H_N' appropriate to the potential well $V(r) = \beta^{-1}\pi r^2/L^2$, i.e., (2). If $\mu < \mu_0(\beta)$ then the local chemical potential $\mu(r) = \mu - \beta^{-1}\pi r^2/L^2$ is everywhere less than $\mu_0(\beta)$ and the system is entirely gaseous. However if $\mu > \mu_0(\beta)$ then $\mu(r) > \mu_0(\beta)$ for all $\vec{r}$ inside a sphere of radius

$$R = L\pi^{-1/2}\beta^{-1/2}[\mu - \mu_0(\beta)]^{1/2} \ .$$

Thus there will be a sphere of liquid with this radius surrounded by gas. If the surface tension is $\alpha(\beta)$ (a function of the temperature) then the surface of separation should contribute an energy term[6]

$$4\pi R^2 \alpha(\beta) = 4\beta[\mu - \mu_0(\beta)]\, \alpha(\beta) L^2$$

to the grand potential Ω. Hence when L is large we expect the dominant terms in the grand potential to be

$$\begin{aligned}\Omega \approx &-Q(\beta, \mu) L^3 \\ &+ 4\beta[\mu - \mu_0(\beta)]\, \theta(\mu - \mu_0(\beta))\alpha(\beta) L^2 \qquad (15)\end{aligned}$$

where $Q(\beta, \mu)$ is given by (4) and θ is the step function.[7] Thus if we can evaluate the grand potential (14) correct to order L^2, we can immediately pick out the surface tension $\alpha(\beta)$ from (15). If the system admits other first-order phase transitions, such as liquid-solid, then as μ is increased we would expect additional surface terms to appear as each new interface is formed. Of course if we were to find L^2 terms which were not of the predicted dependence on μ, i.e.,

$$[\mu - \mu_0(\beta)]\theta(\mu - \mu_0(\beta)) \ ,$$

then this would be a sign that the intuitive arguments leading to (15) were inadequate.

4.3 Gas-Liquid Transition in a Constant "Gravitational" Field

We consider here a system of the type discussed in Sec. 3.2, contained in the X and Y direction by a square box with sides L_1 and in the Z direction by a potential

$$\beta^{-1}w(z/L) = \beta^{-1}z/L, \quad z > 0 \ ,$$
$$= \infty, \quad z < 0 \ .$$

Particles are then restricted to the domain $0 < z < \infty$, wherein they experience a constant force in the negative Z direction. In this case we expect a liquid-vapor surface of area $L_1{}^2$ at a value of z given by $\mu - \beta^{-1}z/L = \mu_0(\beta)$, provided $\mu > \mu_0(\beta)$. Whence the relation corresponding to (14) and (15) is

$$\lim_{L_1 \to \infty} (L_1{}^2\beta)^{-1} \ln\Big(\sum_N \mathrm{Tr}_N \exp(-\beta H_N{}' + \beta\mu N)\Big)$$
$$\approx -Q(\beta, \mu)L + \theta(\mu - \mu_0(\beta))\,\alpha(\beta) \qquad (16)$$

with $H_N{}'$ now given by (11) and $Q(\beta, \mu)$ by (12).

4.4 Discussion

The arguments leading to (15) and (16) are not rigorous mathematical deductions of the form of Ω, but are rather plausible arguments based on our knowledge of the behavior of actual gas-liquid condensations in terrestrial laboratories subject to gravity. One could ask the question whether surface terms could arise in the grand potential Ω from sources other than the liquid-vapor interface energy. Might the fact that the local chemical potential is not constant but varies over distances of order L contribute extra terms proportional to L^2?

One piece of reassuring evidence in this regard comes from evaluating the grand potential (14) for a noninteracting Fermi-Dirac or Bose-Einstein gas contained in a three-dimensional harmonic oscillator. The result for a gas of molecules of mass M and spin s is

$$\Omega = -\frac{(2s+1)}{6\lambda^3\beta} L^3 \int_0^\infty \frac{dz}{e^{z-\beta\mu} \pm 1}\left(z^3 - \frac{3}{4}\frac{\lambda^2 z}{L^2} + \cdots\right),$$

where $\lambda = (2\pi\beta\hbar^2/M)^{1/2}$ and the upper and lower signs refer to the Fermi-Dirac and Bose-Einstein cases, respectively. There are no surface like contributions, which is consistent with the absence of first-order phase transitions for these systems. Indeed the leading correction term is a *linear* one, even for the Bose-Einstein case with $\mu = 0$.

Nevertheless we cannot have full confidence in (15) or (16) until it can be proved that the grand potential Ω is indeed of this form. Since such a proof would first have to show that a phase transition actually occurred for the assumed Hamiltonian, it seems beyond present mathematical techniques.

5. SUMMARY

The main point of this paper is to show how the conventional cubical box of statistical mechanics can be replaced by an external force field such as a central harmonic oscillator well. The motivation is primarily to enable one to work with space coordinates which extend over all values between $\pm\infty$ instead of over the inside of a finite box. Formulas (5), (6), (9), and (13) allow one to convert statistical quantities calculated in some particular external force fields back to the more conventional thermodynamical variables, in particular, to the pressure as a function of temperature and chemical potential.

Finally, in Sec. 4 the formulas (15) and (16) are derived relating the liquid-vapor surface tension to the coefficient of a surface contribution in the grand potential calculated in external force fields.

Note added in proof. Professor R. B. Dingle has kindly drawn the author's attention to the partial replacement of the containing box by a two-dimensional oscillator potential by C. W. Darwin [Proc. Cambridge Phil. Soc. 27, 86 (1930)] in his calculation of the diamagnetism of an electron gas.

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APPENDIX. BEHAVIOR OF $Q(\beta,\mu)$ AT A FIRST-ORDER PHASE TRANSITION

We prove here the results quoted in Sec. 2.4 concerning the continuity of $Q(\beta, \mu)$ and its derivatives with respect to μ at a first-order phase transition. For simplicity we suppose there is only one point $\mu = \mu_1$ where the density $\rho(\beta, \mu) = \partial P(\beta, \mu)/\partial\mu$ has a finite discontinuity, the proof for more than one such point being an obvious generalization. We shall assume that $\partial^2 P(\beta, \mu)\partial\mu^2$ is continuous except at $\mu = \mu_1$, and bounded as $\mu \to \mu_1$ from above or below.

On carrying out the angular integrations in (4), we obtain

$$Q(\beta, \mu) = 4\pi\beta^{3/2}\int_0^\infty P(\beta, \mu - \pi r^2)r^2 dr \ ,$$

whence

$$\frac{\partial Q}{\partial\mu}(\beta, \mu) = 4\pi\beta^{3/2}\int_0^\infty \rho(\beta, \mu - \pi r^2)r^2 dr$$

$$= 2\beta^{3/2}\int_0^\infty P(\beta, \mu - \pi r^2)dr \ ,$$

by partial integration. Differentiating again

$$\frac{\partial^2 Q}{\partial \mu^2}(\beta, \mu) = 2\beta^{3/2}\int_0^\infty \rho(\beta, \mu - \pi r^2)dr \ .$$

Clearly $Q(\beta, \mu)$ and its first two derivatives are continuous everywhere. A further differentiation is more troublesome because $\rho(\beta, \mu - \pi r^2)$ is discontinuous at

$$r = \pi^{-1/2}(\mu - \mu_1)^{1/2} \equiv r_1, \quad \text{if} \quad \mu > \mu_1 \ .$$

Hence we must consider the two cases $\mu \gtrless \mu_1$ separately. If $\mu < \mu_1$,

$$\frac{\partial^3 Q}{\partial \mu^3}(\beta, \mu) = 2\beta^{3/2}\int_0^\infty \frac{\partial \rho}{\partial \mu}(\beta, \mu - \pi r^2)dr \ ,$$

which approaches a finite limit as $\mu \to \mu_1$. If $\mu > \mu_1$ we must divide the range of integration into two regions $r \lessgtr r_1$. In this case

$$\frac{\partial^2 Q}{\partial \mu^2}(\beta, \mu) = 2\beta^{3/2} \lim_{\epsilon \to 0} \left(\int_0^{r_1 - \epsilon} dr + \int_{r_1 + \epsilon}^\infty dr\right) \times \rho(\beta, \mu - \pi r^2) \ ,$$

$$\frac{\partial^3 Q}{\partial \mu^3}(\beta, \mu) = 2\beta^{3/2} \lim_{\epsilon \to 0} \left(\int_0^{r_1 - \epsilon} dr + \int_{r_1 + \epsilon}^\infty dr\right) \times \frac{\partial \rho}{\partial \mu}(\beta, \mu - \pi r^2) + \Delta\rho\beta^{3/2}[\pi(\mu - \mu_1)]^{-1/2} \ ,$$

where $\Delta\rho = \rho(\beta, \mu_1 + 0) - \rho(\beta, \mu_1 - 0)$.

Hence as $\mu \to \mu_1$ from above

$$\frac{\partial^3 Q}{\partial \mu^3}(\beta, \mu) \to 2\beta^{3/2}\int_0^\infty dr \frac{\partial \rho}{\partial \mu}(\beta, \mu_1 - \pi r^2) + \Delta\rho\beta^{3/2}[\pi(\mu - \mu_1)]^{-1/2} \ .$$

The first term is merely the finite left derivative

$$[\partial^3 Q(\beta, \mu)/\partial \mu^3]_{\mu = \mu_1 - 0} \ ,$$

while the second term becomes singular in the limit.

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[1] A. Børs, Z. Physik 187, 221 (1965).

[2] M. G. Mayer, Phys. Rev. 75, 1969 (1949); 78, 16, 22 (1950).

[3] O. Haxel, J. H. D. Jensen, and H. E. Suess, Phys. Rev. 75, 1766 (1949); Z. Physik 128, 295 (1950).

[4] J. M. Blatt, private communication.

[5] L. D. Landau and E. M. Lifshitz, Statistical Physics (Addison-Wesley Publishing Company, Inc., Reading, Mass., 1958), p. 72.

[6] Reference 5, p. 459.

[7] $\theta(x) = 1$ if $x > 0$, $\theta(x) = 0$ if $x < 0$.