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A model for the thermodynamics of simple liquids

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ABSTRACT

The model liquids discussed herein are represented as correlated ensembles of particles, moving around and interacting with strong, short-range forces. A spectrum of local vibrations is introduced for the local, collective movements of particles in such model liquids. The resulting statistics is formally equivalent with that of an ideal gas of bosons in two dimensions, which in turn, as it is well known, leads to a thermodynamics which is equivalent to that of an ideal gas of fermions in two dimensions. The parameters used for describing the statistics of the model are the cohesion energy per particle, the spacing between the energy levels of local vibrations and a constraining volume. The corresponding thermodynamics is derived, with explicit emphasis on both low- and high-temperature regimes. The condensation occurring in the low-temperature limit is discussed.

The model liquids discussed in this paper are represented as ensembles of particles moving around and interacting strongly with short-range forces. The motion of the particles in such model liquids is highly correlated over short distances, in the sense that the movement of a particle entails appreciable movements of the neighbouring particles. The local character of the short-range, strong forces and the high correlations involved have special consequences on the particle motion. First the particle movements are collective, so they may imply comparatively small amounts of energy, in contrast with highly localized movements. Next, the correlated particle movements are local. In addition, the strong character of the interaction gives rise to a cohesion energy $-\varepsilon_0 < 0$, in the sense that one needs to spend such an amount of energy in order to take a particle out of the ensemble. The role played by the strong interactions and short-range correlations in such ensembles of particles has been previously emphasized [1–6].

The short-range correlations reduce the number of available spatial states of particles moving in volume V of the liquid. The motion of each particle is restricted by its neigbouring particles. These short-range correlated configurations of particles are identified by their distinct positions in space. It is convenient to associate a volume b to each of such local particle configurations, such that the total number of available spatial states is V/b and the corresponding density of states can be written as $\mathrm{d}V/b$. In view of the short-range character of these local correlations the constraining volume b is, typically, of the order of a^3, where a is the mean inter-particle distance.

The energy of an ensemble of interacting particles in equilibrium depends on this mean inter-particle distance a. An energy $\varepsilon(a)$ may therefore be assigned to each particle, such as the total energy can be written as $N\varepsilon(a)$, where N is the number of particles. This energy depends on the nature of the liquid, i.e. on the forces acting between the particles, on their mass, etc. In order to identify the possible movements of particles, one may allow small deviations δa of the mean inter-particle distance from its equilibrium value a and write down a series expansion of $\varepsilon(a)$ in powers of δa. Such a series expansion reads

$$\varepsilon = -\varepsilon_0 + A(\delta a)^2 + \cdots, \tag{1}$$

where A is an expansion coefficient. The first power in δa is missing from Eq. (1), as for an expansion about the equilibrium. Eq. (1) suggests that the local spectrum of energy in such a model liquid is a spectrum of vibrations with one degree of freedom. Higher-order terms may be included in the expansion (1), as corresponding to anharmonic vibrations. The local, short-range correlations make the vibration spectra given by Eq. (1) to be independent for each local particle configuration, in the sense that

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these vibrations are not coupled to each other for various particle configurations. At the same time, these vibrations do not correspond to individual particles, but to local particle configurations. Correspondingly they represent collective movements, extended over relatively short distances, and the expansion coefficient in Eq. (1) may correspond to vibration frequencies (and energies) much lower than the frequencies of a highly localized particle. The dynamics of the present model liquid is therefore represented by local particle configurations, labelled by distinct positions in space, moving around over a restricted number of spatial states and vibrating locally according to the vibration spectrum given by Eq. (1). These particle configurations can be viewed as elementary excitations of the model liquid.

The spectrum given by Eq. (1) corresponds to an isotropic liquid, where local vibrations do not depend on direction. More particular assumptions can be employed. Specifically, the range of the correlations may be extended, or the anisotropies may be taken into account, or anharmonicities may be included, etc. The discussion herein is limited to the most simple spectrum as the one described by Eq. (1), corresponding to a set of independent harmonic oscillators with one degree of freedom. The corresponding energy levels are therefore given by

$$\varepsilon = -\varepsilon_0 + \varepsilon_1(n + 1/2), \tag{2}$$

where $n = 0, 1, 2, \ldots$ is the quantum number of vibrations and ε_1 is the spacing between the energy levels. Both parameters ε_0 and ε_1 in Eq. (2) depend on a. For a continuum spectrum the dependence of ε_1 on a may be neglected.

The next step is to set up the statistics for such a model, in order to establish its thermal properties. The vibration spectrum given by Eq. (2) corresponds to a Bose–Einstein type of statistics. It is associated with each local particle configuration, these configurations being labelled by distinct positions in space. Since these positions are different, and since the vibration spectrum given by Eq. (2) corresponds to a collective motion, it follows that the Bose–Einstein statistics, as defined by the energy spectrum (2) and by the motion of the vibrating configurations among distinct positions in space, does not depend on the particular fermionic or bosonic character of the constitutive particles of the liquid. It holds therefore for ensembles of particles, irrespective of the fermionic or bosonic character of the underlying particles in the ensemble. This is a consequence of the assumption of strong interaction and collective and correlated movements. As mentioned above, the quanta of the vibration spectrum given by Eq. (2) associated with the particle configurations moving around through the liquid may be viewed as the elementary excitations of such liquids.

Since the vibration spectrum given by Eq. (2) associates one degree of freedom to each particle, through the mean inter-particle spacing a, it follows that the mean occupation number of vibrations of each particle configuration is determined by the size of these configurations. Therefore, the Bose–Einstein statistics has a determined chemical potential μ and, for a continuum spectrum of energy with density $d\varepsilon/\varepsilon_1$, the number of particles can be written as

$$N = \frac{V}{b\varepsilon_1}\int_0^\infty d\varepsilon \frac{1}{z\exp(\beta\varepsilon) - 1}, \tag{3}$$

where $\beta = 1/T$ is the inverse of temperature T and $z = \exp[-\beta(\mu + \varepsilon_0)]$ is the inverse of the fugacity. The particle concentration is written as $c = N/V = 1/a^3$. The continuum-spectrum approximation is valid for $T \gg \varepsilon_1$. The degeneracy associated with the energy levels given by Eq. (2), as naturally arising from various particle movements in space, is incorporated in the spatial density of states dV/b.

The statistics given by Eq. (3) corresponds to an ideal gas of bosons in two dimensions. It is well known that it is equivalent with the statistics of an ideal gas of fermions in two dimensions [7–9], as expected from its applicability, irrespective of the fermionic or bosonic character of the constitutive particles, as noted above.

Eq. (3) requires $z > 1$, i.e. $\mu + \varepsilon_0 < 0$. With decreasing temperature the integral in Eq. (3) decreases, so that $\mu + \varepsilon_0$ increases, in order to satisfy this equation. For the limiting value $\mu + \varepsilon_0 = 0$ ($z = 1$) the integral in Eq. (3) has a logarithmic singularity at $\varepsilon = 0$, so it is divergent, in contrast with the three-dimensional case. Consequently, there is no critical temperature corresponding to a Bose–Einstein condensation in two dimensions, as it is well known. However, a continuous, gradual condensation on the zero-point vibration level occurs in the limit of the low temperatures, as it is shown below.

The integral in Eq. (3) can be performed straightforwardly. We get

$$b\varepsilon_1/a^3T = \sum_{n=1}(nz^n)^{-1} = \ln[z/(z-1)], \tag{4}$$

whence $z = (1 - e^{-C})^{-1}$ and the chemical potential

$$\mu = -\varepsilon_0 + T\ln(1 - e^{-C}), \tag{5}$$

where $C = b\varepsilon_1/a^3T = b\varepsilon_1 c/T$.

Similarly, the energy is given by

$$E = -N\varepsilon_0 + \frac{VT^2}{b\varepsilon_1}G(z), \tag{6}$$

where

$$G(z) = \sum_{n=1}(n^2z^n)^{-1} = \sum_{n=1}\frac{1}{n^2}(1 - e^{-C})^n. \tag{7}$$

In the low-temperature limit $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$ it amounts to

$$E = -N\varepsilon_0 + \pi^2VT^2/6b\varepsilon_1, \tag{8}$$

and for high temperature $T \gg b\varepsilon_1/a^3$

$$E = -N\varepsilon_0 + NT, \tag{9}$$

as for a classical ensemble. However, anharmonic corrections in the expansion (1) may be important in this limit, which modify the simple T-law given by Eq. (9).

The entropy for the Bose–Einstein distribution introduced here is given by

$$S = \frac{V}{b\varepsilon_1}\int_0^\infty d\varepsilon[(n+1)\ln(n+1) - n\ln n], \tag{10}$$

where $n = (ze^{\beta\varepsilon} - 1)^{-1}$ is the mean occupation number. It leads to

$$S = -N\ln(1 - e^{-C}) + \frac{2VT}{b\varepsilon_1}G(z), \tag{11}$$

the free energy

$$F = E - TS = -N\varepsilon_0 + NT\ln(1 - e^{-C}) - \frac{VT^2}{b\varepsilon_1}G(z) \tag{12}$$

and the thermodynamic potential

$$\Omega = F - \mu N = \frac{VT}{b\varepsilon_1}\int d\varepsilon \ln(1 - e^{-\beta\varepsilon}/z)$$
$$= -(E + N\varepsilon_0) = -\frac{VT^2}{b\varepsilon_1}G(z). \tag{13}$$

The pressure $p = -(\partial F/\partial V)_{T,N}$ is given by

$$p = -c^2\varepsilon_0' + \frac{T^2}{b\varepsilon_1}G(z), \tag{14}$$

where ε_0' is the derivative of the energy ε_0 with respect to concentration c. This is the equation of state of the present model liquid. The dependence of ε_1 on concentration is neglected. We note that for suitable values of $c^2\varepsilon_0'$ the equilibrium can be reached for low values of pressure.

In the low-temperature limit $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$, the pressure given by Eq. (14) reads $p = -c^2\varepsilon_0' + \pi^2T^2/6b\varepsilon_1$, whence the isothermal compressibility

$$\kappa_T = V^{-1}(\partial V/\partial p)_T = \frac{1}{c\partial(c^2\varepsilon_0')/\partial c} < 0. \tag{15}$$

It is worth noting that $c\partial(c^2\varepsilon_0')/\partial c$ must acquire large, negative values for the stability of the ensemble and for ensuring low values of the compressibility, in accordance with the behaviour of such liquids. Similarly, the thermal expansion coefficient at constant pressure is given by

$$\alpha = V^{-1}(\partial V/\partial T)_p = -\frac{\pi^2T}{3b\varepsilon_1}\kappa_T > 0. \tag{16}$$

The entropy (11) at low temperatures reads $S = \pi^2VT/3b\varepsilon_1$ and the heat capacity at constant volume is $c_V = T(\partial S/\partial T)_V = S$. The heat capacity at constant pressure is given by $c_p = c_V - V\alpha^2T/\kappa_T > c_V$. Similarly, the adiabatic compressibility is given by $\kappa_S = V^{-1}(\partial V/\partial p)_S = \kappa_T(1+\pi^2T^2\kappa_T/3b\varepsilon_1) > \kappa_T$. It is related to the sound velocity u by $u^2 = -1/\rho\kappa_S$, where ρ is the mass density. These quantities may give access to experimental determination of the parameters ε_0 and $b\varepsilon_1$.

In the high-temperature limit $T \gg b\varepsilon_1/a^3$ the present model liquid behaves classically, with the entropy $S = N\ln(e^2a^3T/b\varepsilon_1)$ and pressure $p = -c^2\varepsilon_0' + NT/V$. The compressibilities are given by

$$\kappa_T = -\frac{1}{c}\cdot\frac{1}{T - \partial(c^2\varepsilon_0')/\partial c},$$
$$\kappa_S = -\frac{1}{2c}\cdot\frac{1}{T - (1/2)\partial(c^2\varepsilon_0')/\partial c}, \tag{17}$$

the coefficient of thermal expansion is

$$\alpha = \frac{1}{T - \partial(c^2\varepsilon_0')/\partial c}, \tag{18}$$

and the heat capacities are $c_V = N$ and

$$c_p = c_V - VT\alpha^2/\kappa_T = c_V + \frac{NT}{T - \partial(c^2\varepsilon_0')/\partial c}. \tag{19}$$

The validity of these expressions is restricted to a limited range of temperature and concentration characteristic for such liquids. Their experimental determination gives access only to the parameter ε_0. Likely, for high values of T anharmonic corrections have to be included.

For values of the temperature T comparable with the spacing ε_1 between the energy levels the quantum effects are important and the accuracy of replacing the summation over n in Eq. (2) by integral (3) must be checked, according to MacLaurin's formula

$$\sum_a^b f(x_n) = \int_{a-1/2}^{b+1/2} f(x)\,dx - (1/24)f'^{\,b+1/2}_{\,a-1/2} + \cdots . \tag{20}$$

Applying this formula to function $f = [ze^{-\beta\varepsilon_1(n+1/2)} - 1]^{-1}$ we get

$$\begin{aligned} b/a^3 &= \sum_{n=0}\frac{1}{z\exp[\beta\varepsilon_1(n+1/2)] - 1} \\ &= \int_0 dn\frac{1}{z\exp(\beta\varepsilon_1 n) - 1} - \frac{\beta\varepsilon_1}{24}\cdot\frac{z}{(z-1)^2} + \cdots \\ &= \frac{1}{\beta\varepsilon_1}\ln\frac{z}{z-1} - \frac{\beta\varepsilon_1}{24}\cdot\frac{z}{(z-1)^2} + \cdots, \end{aligned} \tag{21}$$

and we can see that the error made in approximating the summation by integral becomes comparable with the integral for large values of $\beta\varepsilon_1$ and $z \to 1$. This error arises from the fact that the integral gives little weight to the value of the function at $n = 0$. Consequently, we single out the term $n = 0$ in Eq. (21), and write

$$b/a^3 = \frac{1}{z'-1} + \frac{1}{\beta\varepsilon_1}\ln\frac{z'e^{\beta\varepsilon_1/2}}{z'e^{\beta\varepsilon_1/2} - 1} - \frac{\beta\varepsilon_1}{24}\cdot\frac{z'e^{\beta\varepsilon_1/2}}{(z'e^{\beta\varepsilon_1/2}-1)^2} + \cdots, \tag{22}$$

where $z' = ze^{\beta\varepsilon_1/2}$. In the low temperature limit $\beta\varepsilon_1 \to \infty$ it is the first term in Eq. (22) that brings the main contribution and we have

$$z = (1 + a^3/b)e^{-\beta\varepsilon_1/2}, \quad \beta\varepsilon_1 \to \infty. \tag{23}$$

In the high-temperature limit $\beta\varepsilon_1 \to 0$ the main contribution is brought by the ln-term in Eq. (22), and

$$z = \frac{a^3T}{b\varepsilon_1}e^{-\beta\varepsilon_1/2}, \quad \beta\varepsilon_1 \to 0. \tag{24}$$

A fair interpolation between Eqs. (23) and (24) gives

$$z = (1 + a^3/b + a^3T/b\varepsilon_1)e^{-\beta\varepsilon_1/2} \tag{25}$$

and the chemical potential

$$\mu = -\varepsilon_0 + \varepsilon_1/2 - T\ln(1 + a^3/b + a^3T/b\varepsilon_1). \tag{26}$$

As one can see, although there is a condensation on the lowest state of zero-point vibrations in the limit of low temperatures, there is no phase transition, i.e. no discontinuity, and z approaches gradually zero (not unity!) for $T \to 0$, in contrast to the Bose–Einstein condensation in the three-dimensional case [10]. The characteristic temperature of this continuous condensation is given by $\beta\varepsilon_1 \sim 1$. For such temperatures, the liquid may undergo, very likely, a phase transition, probably to a solid-like phase. Such a transition is characterized by the increase of the constraining volume b, which becomes of the order of the volume $V = Na^3$, such that the number of the available spatial states for each particle in the ensemble reduces to unity. The ensemble now becomes rigid and it can only move as a whole. At the same time, the vibration spectrum changes correspondingly, from one of local vibrations to global, collective oscillations.

The low-temperature behaviour derived herein has long been introduced for the statistical model of the atomic nuclei [11–13]. Making use of Eqs. (8), (11) and (12), we get

$$Q = E + N\varepsilon_0 = -(F + N\varepsilon_0) = \pi^2VT^2/6b\varepsilon_1 \tag{27}$$

and

$$S = \pi^2VT/3b\varepsilon_1 = \sqrt{2\pi^2VQ/3b\varepsilon_1}, \tag{28}$$

where Q denotes the excitation energy of the nucleus. The density of states $\rho = d\mathcal{N}/dQ = e^S(dS/dQ)$ gives the spacing between the energy levels

$$\delta\varepsilon = \delta Q = \sqrt{6b\varepsilon_1 Q/\pi^2V}e^{-\sqrt{2\pi^2VQ/3b\varepsilon_1}}. \tag{29}$$

These equations are valid in the low-temperature limit corresponding to $\varepsilon_1 \ll T \ll b\varepsilon_1/a^3$, where $T = \sqrt{6b\varepsilon_1 Q/\pi^2Na^3}$. The distribution of the energy levels among states with different angular momenta changes to a somewhat extent the prefactor in Eq. (29), without material consequences for the estimations given here [12]. For heavy nuclei one may take approximately $\delta\varepsilon \sim 5$ eV for $Q \simeq 8$ MeV, as derived from experiments of neutron scattering, resonances, or radiative capture [12]. Eq. (29) gives then $b\varepsilon_1/a^3 \simeq 40$ MeV and temperature $T \simeq 1$ MeV for $N \sim 200$. If volume b is of the order of a^3, this temperature would be much lower than the energy ε_1 as derived from $b\varepsilon_1/a^3 \simeq 40$ MeV. It is likely, therefore, that a transition to a solid-like state is expected, i.e. the volume b becomes of the order of $b = Na^3$ (the volume of the nucleus is given by $V = Na^3$, where $a = 1.5 \times 10^{-15}$ m $= 1.5$ fm). The energy ε_1 acquires then the value $\varepsilon_1 \sim 40$ MeV$/N = 200$ keV for $N = 200$, and it may be viewed as an estimate of the mean separation of the energy levels in the nucleus.

A similar evaluation can be made for classical, common, liquids. A typical value for ε_1 for such liquids might be of the order of 1 meV. The mean inter-particle spacing is a few Å's and this is also the order of magnitude of the molecular size and short-range forces. It follows that each molecule has a number of spatial states of the order of N at its disposal, i.e. b is of the order of a^3.

In conclusion, a model liquid is introduced herein, described as a correlated ensemble of particles, moving around and interacting strongly with short-range forces. The correlations give rise to a constraining volume b, which is one of the parameters of the thermodynamics of such a model liquid. The local, collective movements are described as a set of independent harmonic oscillators with one degree of freedom, corresponding to vibrations of local particle configurations. The other two parameters are the distance ε_1 between the energy levels of these vibrations and the cohesion energy $-\varepsilon_0$ per particle. The statistics derived on this basis is formally equivalent with the statistics of an ideal gas of bosons in two dimensions, which, as it is known, leads to a thermodynamics which is equivalent with the one of an ideal gas of fermions. This thermodynamics is explicitly derived, both in the low- and the high-temperature limits. The limit of temperatures comparable with the distance ε_1 between the energy levels is also discussed, where a continuous, gradual condensation on the lowest energy level occurs, which may be the precursor of a transition toward a solid-like state. The transport properties of such a model, the thermoconductivity, fluctuations, diffusion and the response to external perturbations are worth investigating. Such investigations are underway, and will be reported in a forthcoming publication.

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