Potential energy distribution function and its application to the problem of evaporation

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Abstract. Distribution function on potential energy in a strong correlated system can be calculated analytically. In an equilibrium system (for instance, in the bulk of the liquid) this distribution function depends only on temperature and mean potential energy, which can be found through the specific heat of vaporization. At the surface of the liquid this distribution function differs significantly, but its shape still satisfies analytical correlation. Distribution function on potential energy nearby the evaporation surface can be used instead of the work function of the atom of the liquid.

1. Introduction
In our previous work [1] we found that the atom velocity distribution function (DF) in the process of liquid evaporation can be written as

\[ f_z = \frac{mv_z}{T} \exp \left( -\frac{mv_z^2}{2T} \right), \] (1)

where \( v_z \) is the normal component of the velocity (along axis ‘z’) of the atom, \( m \) is the mass of the atom, and \( T \) is the temperature of the liquid.

Many interesting and useful results follow from Eq. 1 [2]: for instance, one can obtain the evaporation coefficient \( \alpha \approx 0.8 \), the temperature jump between the liquid phase [3–5] and the vapor one can be calculated analytically, etc.

To calculate the total flux from the evaporation surface the work function for the atom of the liquid would be found. There are some methods to obtain this value, but we choose another direction in this work. It is evidently that the binding energy of an atom in a liquid is not a certain value. There must be a distribution function on this parameter, i.e. there must be a distribution function on the potential energy for the particle in a correlated system.

The distribution function on kinetic energy – the Maxwellian one – can be obtained by various methods. In different correlated systems, with different type of inter-particle forces the Maxwellian DF is correct. Thus, we can expect that DF on potential energies of a particle has unique form, i.e. the probability of the value \( u \) for potential energy can be described by unique function \( g(u)du \).

In this work we will find the DF \( g(u) \).
2. Distribution on potential energy

2.1. An equilibrium system

Distribution on kinetic energy $\varepsilon$ is the well-known Maxwellian DF:

$$ f(\varepsilon) = \frac{2}{\sqrt{\pi}} \frac{1}{T^{3/2}} \sqrt{\varepsilon} \exp\left( -\frac{\varepsilon}{T} \right). $$

(2)

In this chapter we will obtain DF on potential energy $g(u)$ as follows. The evaluation of a mechanical system obeys the law

$$ \int l dt \rightarrow \text{m in.} $$

(3)

where $l = \varepsilon - u$ is the Lagrangian function. Thus, as the statistical equivalent of Eq. 3, we have a condition for the distribution function $F^L(l)$:

$$ \int l F^L(l) dl \rightarrow \text{m in,} $$

(4)

where limits, in many cases, can be chosen as $\pm \infty$.

From Eq. 5 we can see that $F^L(l)$ must be a symmetrical function of the argument $(l - l_m)$, where

$$ l_m = \int_{-\infty}^{+\infty} F^L(l) dl $$

(5)

coincides with the maximum of $F^L(l)$.

As it follows from Eq. 4 (or, in common, from the principle of least action), there must be a connection between $\varepsilon$ and $u$, that is, for functions $f(\varepsilon)$ and $g(u)$. We establish this connection in form

$$ g(u) = \int_0^\infty g_\varepsilon(\varepsilon, u) f(\varepsilon) d\varepsilon. $$

(6)

There are two conditions for function $g_\varepsilon(\varepsilon, u)$.

a) As function

$$ F^L(l) = \int_0^\infty f(\varepsilon) g(\varepsilon - l) d\varepsilon $$

(7)

must be symmetrical, so DF

$$ g_\varepsilon(\varepsilon, u) = g_\varepsilon(\varepsilon - u). $$

(8)
b) Potential energy $u$ is the sum of the energies of interactions with many other particles of the system. Thus, one can expect that the function $g_{e}(\varepsilon-u)$ for certain $\varepsilon$ (i.e. function on $u$) must be a stable DF with finite dispersion, that is

$$g_{e}(\varepsilon,u)=\frac{1}{\sqrt{2\pi}a^{2}}\exp\left\{-\frac{(\varepsilon-u-m_{2})^{2}}{2a^{2}}\right\}.$$  \hspace{1cm} (9)

Parameter $\theta$ defines additional fluctuations of $u$: different parts of the system at the same temperature $T$ may have different (local) mean potential energy $u$, then total fluctuations of $u$ consists of two parts – i) fluctuations of this mean potential energy (defined by $\theta$), ii) fluctuations connected with the fluctuations of kinetic energy of the given particle (defined by $T$). In equilibrium, evidently, there must be $\theta=T$. Further we will refer $\theta$ as fluctura, remembering B. Mandelbrot’s directions to avoid an overload of old definitions.

The integral from Eq. 6 with Eq. 9 can be found as

$$\bar{g}(\bar{u})=1.05\bar{T}^{1/4}\sqrt{\frac{3\bar{e}_{0}}{2\pi\theta}}\left(1+\text{erf}(\sqrt{\bar{b}\bar{e}_{0}})\right)\exp\left\{-\bar{e}_{0}\bar{T}-\frac{1}{2}\frac{\left(\bar{e}_{0}-\bar{u}-\bar{m}_{2}\right)^{2}}{2}\right\},$$ \hspace{1cm} (10)

where factor $1.05\bar{T}^{1/4}$ must correct the norm of the DF, and

$$\bar{e} = \frac{\varepsilon}{\theta}, \quad \bar{u} = \frac{u}{\theta}, \quad \bar{m}_{2} = \frac{m_{2}}{\theta} = \frac{\varepsilon_{m}-u_{m}}{\theta}, \quad \bar{T} = \frac{\theta}{T};$$

$$\bar{e}_{0} = \frac{1}{2}\left[\bar{u} + \bar{m}_{2} - \bar{e}_{0} + \sqrt{2+\left(\bar{u} + \bar{m}_{2} - \bar{e}_{0}\right)^{2}}\right];$$

$$\bar{g}(\bar{u})=\theta g(\bar{u}); \quad b = \frac{1}{2} \left(1 + \frac{1}{2\bar{e}_{0}^{2}}\right); \quad \text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_{0}^{y} e^{-x^{2}} dx.$$ \hspace{1cm} (13)

The mean value $\bar{e}_{m} = 1.5\bar{T}^{-1}$. The mean value $\bar{u}_{m}$ can be found from reference data as a doubled specific heat of vaporization (with an opposite sign).

All distribution functions, including DF for the total energy $s = \varepsilon + u$

$$P_{s}(s) = \int f(s)g(s-s)ds,$$ \hspace{1cm} (14)

are presented on Fig. 1 in compare with results of MD-simulations for the bulk liquid Ar: $\theta = T$, $\bar{u}_{m} = -14.5$ from the NIST database [6]. Note the coincidence for DF (8): its symmetrical form was the key point of the theory presented above.

2.2. Distribution function for evaporating liquid

At the vicinity of the evaporation surface the liquid is in the nonequilibrium state. Temperature of the surface may be close to the bulk value, but the fluctura $\theta$ differs significantly from the equilibrium value (i.e. from $T$).
Figure 1. Distribution function: numerical calculation (dots) and theoretical results (lines).
1 – $D\bar{F}(\bar{u})$ (Eq. 6); 2 – $F^S(\bar{s})$ (Eq. 14); 3 – $f(\bar{e})$ (Eq. 2); 4 – $F^L(\bar{f})$ (Eq. 7).

Figure 2. Distribution functions on the binding energy of atom in a liquid Ar at various depths $D$.
Lines – theoretical curves for Eq. 7, dots – molecular dynamics simulation results.
1 – at the vicinity of evaporation surface ($D = 0$ nm); $\theta = 200K, \bar{u}_m = -3.2$.
2 – at $D = 1$ nm; $\theta = 115K, \bar{u}_m = -12.0$.
3 – at $D = 2$ nm; $\theta = 105K, \bar{u}_m = -13.7$.
4 – at $D = 3$ nm (corresponds to a bulk of a liquid); $\theta = 100K, \bar{u}_m = -14.5$. 
As it was mentioned above, $\theta$ describes additional fluctuations of potential energy. Since these fluctuations are stronger at the vicinity of the liquid surface, fluctura $\theta$ grows toward the direction of axis ‘z’.

On Fig. 2 one can see distribution functions on binding energy $\tilde{U} = -\tilde{u}$ at various distances from the evaporation surface of liquid argon at $T=100$ K.

3. Fluxes on evaporation surface

To calculate fluxes on evaporation surface we can use probability $w$ for atom with binding energy $U$ to leave the liquid surface at temperature $T$ in form of [1]:

$$w(U) = \begin{cases} \frac{1}{2\sqrt{\pi}} \Gamma\left(\frac{1}{2}\right) U, & U \geq 0; \\ \frac{1}{2}, & U < 0. \end{cases} \quad (15)$$

Combining previous results for the atom velocity DF from [1], we can find that the mass flux at the evaporation surface is

$$j = n^{surf} \sqrt{\frac{8m_0\omega_z}{\pi}} \int_{-\infty}^{\infty} w(U) g^{surf}(U) dU, \quad (16)$$

where indexes ‘surf’ denotes functions for the surface of the liquid and $\omega_z = 93$ K (parameter for DF on velocities, see [1]). Calculations with (16) give $j^{theory} = 680$ kg/m$^2$s while the numerical simulation result is $j^{numerical} = 630$ kg/m$^2$s.

Conclusion

The distribution function on binding energies of the near-surface atoms of the liquid can be used instead of the work function of the atom. This DF can be obtained in a common way, and the potential energy DF for the bulk liquid satisfies results numerical (molecular dynamics) simulations without any empirical parameters: the only parameter of the DF is the mean potential energy of the atom, which can be found in databases.

Using old representations for the fluxes on the evaporation surface [1] one can obtain full correlation for this value. Comparison of this correlation with results of numerical simulations shows rather good agreement.

References

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